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ENGINEERING INTRAPORE ENVIRONMENTS TO TUNE RATES AND SELECTIVITIES
FOR LIQUID PHASE CATALYSIS OVER ZEOLITES

BY

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DISSERTATION

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Chemical Engineering
in the Graduate College of the
University of Illinois Urbana-Champaign, 2024

Urbana, Illinois

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ABSTRACT

Covalent and non-covalent interactions among reactive species, solvent molecules, active sites, and intrapore functions influence the rates and selectivities of liquid-phase catalysis in zeolites by orders of magnitude. These effects carry consequences for many chemical processes, including reactions relevant to the conversion of renewable or recyclable feedstocks and the development of distributed chemical manufacturing. Prior literature demonstrates that the epoxidation of alkenes and the ensuing epoxide ring-opening reaction depend sensitively on covalent and non-covalent interactions at solid-liquid interfaces. However, the literature lacks a consensus on how to design more efficient catalysts and solvent systems for these important chemistries. Comparisons among rates and selectivities in previous reports are frequently convoluted by differences among synthesized catalysts, reaction conditions, kinetic regimes, and mass transfer artifacts. Here, we synthesize a suite of well-characterized zeolites with the *BEA framework, incorporated with various active metal atoms and possessing different silanol ((SiOH)_x) densities. We utilize a combination of kinetic, thermodynamic, and spectroscopic experimental methods to systematically probe how the solvent composition, reactant structure, and zeolite choice influence the rates and selectivities of alkene epoxidation and epoxide ring-opening. The analysis of these systems provides useful strategies for interpreting and controlling the intrapore interactions that govern liquid-phase catalysis in zeolites.

Chapter 1 discusses the importance of catalyst development in the design of next-generation sustainable chemical processes. We introduce a quantitative framework for understanding how interactions at solid-liquid interfaces influence heterogeneous catalysis, which carries relevance for both established and emerging chemistries. An overview of previous alkene epoxidation and epoxide ring-opening literature demonstrates the strong influence of interactions

among catalysts, solvents, and reactants on both chemistries, highlighting the utility of these reactions as probes to understand how to manipulate covalent and non-covalent interactions to promote the formation of desired products during catalysis.

The size and structure of alkenes significantly influence the rates and selectivities of the adsorption and catalytic transformation of these molecules; however, the physical origins of kinetic differences among substrates remain unclear. **Chapter 2** investigates the kinetics of alkene epoxidation with hydrogen peroxide (H_2O_2) and the thermodynamics of epoxide adsorption in hydrophilic (Ti-BEA-OH) and hydrophobic (Ti-BEA-F) zeolitic materials as a function of alkene and epoxide carbon number ($\text{C}_6\text{-C}_{18}$). We utilize a combination of experimental and computational methods to describe the significant effects of solvent displacement and confinement on epoxidation catalysis in zeolites. Epoxidation rates over hydrophilic, $(\text{SiOH})_x$ -rich Ti-BEA-OH exceed those over hydrophobic, $(\text{SiOH})_x$ -poor Ti-BEA-F by 40-450 times across the range of alkenes in acetonitrile (CH_3CN) solvent containing water (200 mM H_2O). Adsorption measurements with ^1H nuclear magnetic resonance (NMR) spectroscopy and grand canonical molecular dynamics simulations (GCMD) show that Ti-BEA-OH adsorbs 10-20 times more H_2O than Ti-BEA-F. While rates decrease for each catalyst under anhydrous conditions, rates decrease more significantly over Ti-BEA-OH (10-90 times) than Ti-BEA-F (< 3 times). The rate differences do not result from changes in reaction mechanism or mass transfer constraints, but rather changes in transition state stability described by activation enthalpies ($\Delta H^\ddagger$) and entropies ($\Delta S^\ddagger$). Values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ increase systematically with alkene carbon number over both zeolites because longer alkyl chains disrupt more solvent molecules. The disruption of H_2O in Ti-BEA-OH also yields greater changes in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ than for CH_3CN , which dominates the pores of Ti-BEA-F. Corresponding epoxide adsorption enthalpies, measured experimentally with isothermal titration

calorimetry and computed with GCMD, become more endothermic as chain lengths increase and correlate to $\Delta H^\ddagger$, providing evidence that the disruption of solvent molecules depends on adsorbate size. These findings show that the entropic gain for a given enthalpic cost of solvent disruption varies with alkene carbon number, $(\text{SiOH})_x$ density, and solvent composition within the pore. These manipulations of non-covalent interactions at zeolite surfaces offer opportunities to increase epoxidation turnover rates.

The fractional replacement of organic solvents with H_2O as a co-solvent reduces solvent waste but also impacts the kinetics of catalytic reactions. **Chapter 3** extends our understanding of solvation effects from the previous chapter by examining how replacing significant fractions of organic solvents with H_2O affects alkene epoxidation and the competing H_2O_2 decomposition pathway. Turnover rates for 1-hexene (C_6H_{12}) epoxidation over Ti-BEA-OH and Ti-BEA-F increase while rates for H_2O_2 decomposition decrease as the mole fraction of H_2O increases in CH_3CN , methanol (CH_3OH), and gamma-butyrolactone co-solvents, leading to significantly higher epoxidation selectivities at higher H_2O mole fractions. The mechanisms of epoxidation or H_2O_2 decomposition do not change across the range of H_2O mole fractions and organic co-solvents tested. Instead, differences among rates and selectivities stem from changes in the free energy of reactive species along each pathway, evidenced by $\Delta H^\ddagger$ and $\Delta S^\ddagger$ measurements, epoxide adsorption enthalpies, and rates normalized by reactant activities. Greater epoxidation rates at higher H_2O fractions appear to originate from the destabilization of liquid-phase C_6H_{12} and entropic stabilization of the epoxidation transition state through the disruption of hydrogen bonds between H_2O . In contrast, decreasing rates of H_2O_2 decomposition with increasing H_2O mole fraction likely result from disproportionate stabilization of reactive intermediates (Ti-OOH, liquid-phase H_2O_2) relative to the decomposition transition state. Overall, the findings from **Chapters 2**

and **3** show that creating a more polar reaction environment promotes catalytic pathways with predominantly hydrophobic reactive species while suppressing pathways involving hydrophilic species, providing further guidance for how to control non-covalent reactions to promote more efficient reactions at solid-liquid interfaces.

Chapters 4 and 5 demonstrate that the intrapore phenomena that influence alkene epoxidation also influence nucleophilic epoxide ring-opening reactions within both Lewis and Brønsted acidic zeolites, which appear as large differences in turnover rates and regioselectivities. While previous literature reported that active site and solvent environments affect rates and regioselectivities of epoxide ring-opening, a conceptual framework to explain these observations and the design principles necessary to improve these processes remains unestablished. **Chapter 4** develops a mechanistic understanding to explain how active metal (Al, Sn, Ti, Zr) in zeolite *BEA affects 1,2-epoxybutane (C_4H_8O) ring-opening with CH_3OH in CH_3CN co-solvent. Among Lewis acids, ring-opening rates increase with the Lewis acid strength of the transition metal ($r_{Ti} < r_{Zr} < r_{Sn}$), based upon reported Mulliken electronegativities and measured C_4H_8O adsorption enthalpy values. Rates depend on both $[CH_3OH]$ (where $[x]$ denotes the concentration of species x) and $[C_4H_8O]$. A single kinetic regime dominates at all conditions over Al-BEA, while each Lewis acid shows two kinetic regimes. These results suggest Lewis and Brønsted acidic materials catalyze ring-opening with distinct reactive intermediates or through different mechanisms. Regioselectivities towards the terminal ether product exceed 50% under most conditions but depend on metal identity and reagent concentrations. Values of regioselectivity to the terminal ether generally decrease with increasing $[CH_3OH]$ and increase with greater $[C_4H_8O]$ over each M-BEA. Al-BEA consistently gives the lowest regioselectivities to the terminal ether, while Ti- and Zr-BEA show greater regioselectivities than Sn-BEA among the Lewis acids. Values of $\Delta H^\ddagger$

suggest differences among regioselectivities arise from differences in the free energies of the transition states to form each product. CH₃OH uptake measurements support that differences in solvation between transition states contribute to regioselectivity changes. This work demonstrates that covalent (i.e., choice of active metal, acid type) and non-covalent (i.e., solvent environment) interactions in zeolite pores drive differences in regioselectivities for epoxide ring-opening.

Chapter 5 reveals that the (SiOH)_x density of Lewis (Zr-BEA) and Brønsted acid (Al-BEA) zeolites also carry significance for C₄H₈O ring-opening with CH₃OH in CH₃CN co-solvent. Ring-opening rates fall within a factor of two over a high density (SiOH)_x Al-BEA (Al-BEA-OH) and a low density (SiOH)_x material (Al-BEA-F) at all conditions. In contrast, Zr-BEA-OH provides ten times greater rates than Zr-BEA-F. These rate differences do not originate from differences in reaction mechanisms across materials. Zr-BEA-OH consistently yields more positive $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values than Zr-BEA-F, while Al-BEA-OH and Al-BEA-F show nearly identical activation parameters across the range of [CH₃OH]. Liquid and vapor intrapore solvent compositions, quantified by multiple methods, give evidence that Zr-BEA-OH adsorbs greater quantities of hydrogen-bonded solvent molecules than Zr-BEA-F. On the other hand, the pores of Al-BEA-OH and Al-BEA-F contain more similar solvent compositions. Examination of these measurements together with measured rates supports that the displacement of hydrogen-bonded solvent molecules leads to greater rates in Zr-BEA-OH through entropic gains that exceed the corresponding enthalpic penalties, as further corroborated by positive correlations between activation and C₄H₈O adsorption enthalpies. Product regioselectivities depend strongly on the solvent composition and zeolite acid type but weakly on (SiOH)_x density. This study further explains how the interplay between covalent and non-covalent interactions within zeolite pores influence epoxide ring-opening processes. Overall, **Chapters 4** and **5** demonstrate that both

synthetic control of the active metal, acid type, and zeolite (SiOH)_x density and selection of the solvent composition provide opportunities to increase epoxide ring-opening rates toward desired product isomers.

Chapter 6 summarizes the lessons learned from **Chapters 2 – 5** on manipulating covalent and non-covalent interactions to control rates and selectivities of liquid-phase catalysis in zeolites. **Chapter 6** also proposes future directions to develop a further understanding of the interactions that drive catalysis at solid-liquid interfaces. These directions include (1) utilizing batch kinetics and *in situ* ¹³C-NMR spectroscopy experiments to gain a deeper understanding of the mechanistic origins for rates and regioselectivities differences in ring-opening, using epichlorohydrin (C₃H₅ClO) as the epoxide reagent. We also propose to examine the effect of (2) organic co-solvent choice (CH₃CN, dioxane, dimethoxyethane) and (3) nucleophile choice (alcohol, amine, thiol) on C₄H₈O ring-opening. These future directions build on the lessons learned in this thesis and seek to establish further design principles for sustainable catalysis in the liquid-phase.

The studies outlined here utilize a combination of kinetic, spectroscopic, and thermodynamic techniques to demonstrate the strong role that covalent and non-covalent interactions play in zeolite catalysis and provide guidance on how to manipulate these effects to facilitate desired reaction pathways. While described here in the context of the industrially relevant alkene epoxidation and epoxide ring-opening processes, these principles apply to other relevant liquid and gas-phase chemistries and give a more general understanding of how to control rates and selectivities through catalyst and reaction design.

To my parents, my family, and my friends...
and to always being myself and finding my voice, no matter what stands in my way

ACKNOWLEDGMENTS

My time at the University of Illinois Urbana-Champaign (UIUC) has been extremely rewarding and transformative. I have met some of my very best friends, developed significantly as both a person and a scientist, and found a home away from home. After I visited campus in the spring of 2019, I was confident that UIUC was where I wanted to spend the next ~5 years and pursue my Ph.D. As I write this in the spring of 2024, I can say that I have not regretted my choice once. I am extremely grateful to my friends, family, and colleagues for their support and guidance during my time at UIUC.

I want to start by thanking my advisor, Professor David Flaherty (aka Dave). Despite coming to UIUC with zero experience in laboratory research, Dave put his trust in me and accepted me into his research group. I thank Dave for his patience and willingness to invest his time in me – he taught me to think critically and helped me become an effective graduate researcher. Despite all the effort required to set up the new lab at Georgia Tech, Dave has continued to provide me support and guidance while I remained at Illinois for the last year of my Ph.D., and I truly appreciate that effort. Dave has always been patient and supportive of me as a person who stutters, for which I am very grateful. I leave UIUC as a better scientist who is ready to take my next career step, and I have Dave to thank for that.

Thank you to those in the Chemical and Biomolecular Engineering department and the School of Chemical Sciences (SCS) at UIUC who have helped me during my time at Illinois. To my committee members, Professor Liviu M. Mirica, Associate Professor Damien S. Guironnet, and Assistant Professor Alexander V. Mironenko, thank you for your support, guidance, and feedback during the preliminary exam and defense process. Thank you to those in the SCS Electronics Shop, Machine Shop, and Microanalysis Lab for their assistance with many equipment

maintenance and experiment design questions over the years. Thank you to Jadii Rodgers, Connie Knight, Christy Bowser, Cindy Dodds, and everyone else on the ChBE administrative staff. Thank you to Jadii and Connie, in particular, who have been so helpful to me in many administrative matters over the last few years of my Ph.D.

I am very grateful to all my labmates that I have worked with over the last five years. Daniel, thank you for all your guidance and mentorship in my first year. You helped me craft a path to a successful and rewarding Ph.D., and I truly appreciate that. Pranjali, thank you for always being a friendly face in my early days in the lab. I appreciate your guidance and I admire your determination! Yao, thanks for being an excellent labmate and for providing me with a lot of laughs – whether it was something funny you said, or just noticing you taking a nap in the office. A special thank you to Abinaya, who became a great friend during the third year of my Ph.D. Thank you for your support as a labmate, and the great times that we shared together at friend’s dinners and the ski trip! Zeynep – thank you for being one of my closest friends from grad school. I am grateful for our many adventures: running two half marathons (!), friend’s dinners, movie nights, and more. Thanks for being a part of our epoxide ring with Ohsung and helping me expand my appreciation for Blair Waldorf. I learned a great deal as both a scientist and a person from you, and for that I am extremely grateful! Jason and Tom, I enjoyed working with both of you in the lab and hanging out outside of the lab as well. I really admire your work ethic and scientific curiosity! Danim and Yangsik, you were always friendly and supportive during our interactions in lab. I thank you both for your kindness and scientific insight! Chris – thank you for everything, whether it was taking the time to teach me one of many experimental techniques, providing helpful guidance with anything scientific or otherwise, or just sharing a laugh in or out of the lab. I admire your resolve to make STEM a more welcoming place for all! Ching-Tien, Yongwoo, and Lydia, thank you all

for your support and kindness. I admire your work ethic and wish you all the best moving forward! Matt, thanks for always providing a laugh and keeping things light around the lab. I have enjoyed working with you, and I admire your scientific knowledge and insight. Jieun, thank you for being a great labmate – you are also a great scientist and researcher, keep up the good work. Richa, thanks for all your support and your insight over the years! I admire your determination, and I look forward to seeing all the exciting and impactful things you will achieve in your career. I have always enjoyed our conversations in the lab, and the many fun times we have had outside the lab! I am grateful for the friendship we have built. Suchi, thank you for your being a good friend and colleague in and out of the lab – I have enjoyed our time together! Excited to see what you will accomplish for the rest of the Ph.D. and beyond. Huston, thank you for being an excellent mentee, co-worker, and friend. We have had great times in Atlanta and Urbana-Champaign, whether in the lab, playing poker, or other memorable adventures. I look forward to seeing the many great things you will achieve in your Ph.D! Minju, I wish we could have been labmates in person, but I am grateful that we have had the opportunity to hang out in Rhode Island, Tennessee, and Georgia! Thanks for being an excellent marathon buddy last year. I wish you the best of luck finishing up the postdoc, and I hope we will meet again in the future. To the new Georgia Tech lab members – Geoff, Adam, Eric, and Andy – we did not have an opportunity to spend much time together, but I am grateful for the interactions I have had with each of you. Best of luck as you move forward in your Ph.D. journey! I also need to mention a few special undergrads from the lab. First, Darshan – I am really glad we became friends (thanks to Zeynep for facilitating this). I have always enjoyed talking basketball and how we wish the Lakers would play better. I also think you are a very bright engineer, and enjoyed talking science with you as well. I look forward to keeping in touch with you in the future! And second, to Jess – my first, only, and very best undergrad mentee! I appreciate

your patience as I have (hopefully) learned to be a better mentor over these two years. It has been a pleasure and a privilege – your enthusiasm for research inspires me in my own work. I consider you not only a mentee but also a good friend. I am very excited to see all the amazing things you will achieve in your career! Thanks for all the laughs and good times in the lab.

Ohsung, thanks for the countless great times during grad school! We have been classmates, labmates, and roommates, and I consider you one of my best friends. I could not ask for a better person to start (and now finish) in the lab with. You have been extremely helpful and supportive to me both in and out of the lab. You are an excellent scientist and a more excellent person, and I look forward to more good times together in the future. And lastly, Claudia – thank you for being my rock in my last few years of grad school. I am so grateful for the times we have shared together, starting with me teaching you how to drive and evolving into so much more! You have been my biggest supporter in the lab and beyond, and it has meant everything to me. You positively impact so many people around you (including me), and your kindness and strength continue to amaze me. I love you, and I look forward to so many more adventures together!

Thank you to all those in the speech lab support group, operated by the Department of Speech & Hearing Science at UIUC. To my fellow stutterers who I participated with over the years – Reuven, Salil, Jeffrey, both Steve's, Heather, and Dhruv – thank you all for being a constant source of inspiration and laughs. I have learned a great deal from listening to you all speak about your perspectives and experiences. To all the graduate student speech pathologists who volunteered their time to work with us, thank you all very much for your time and your support. To the director of the speech lab, Clarion – thank you for allowing me to participate in this wonderful group. Your positivity is infectious, and I truly appreciate your effort to give us a safe

space to share our experiences. My time in the speech lab has had a profoundly positive impact on my outlook as a person who stutters. I will really miss seeing all of you each week!

To my friends from UIUC and Urbana-Champaign, thank you for the countless good memories during graduate school! To my great friends from my cohort and those who are cohort-adjacent – Azza, Frank, Eric, Tove, Paola, Edgard, Hyeonmin, Jemin, Christian, Jenny, Sam, Tsai-Wei, Kuan-Yu, Ohsung, Yash – thanks for SO many fun times at friend’s dinners, conferences, ski trips, and everything else. I will always cherish the friend group we have built and all those moments we shared – I hope we can organize some reunions in the future! Thanks to Christian, Emmanuel, Victor, Ohsung, Yash, and Jemin for being excellent roommates that I had at one point or another in grad school. Christian, you were my first friend at UIUC, and I still consider you one of my closest friends (but I am still sad you left in our second year). I remember laughing it up with you at the bar crawl on the recruiting weekend and feeling like I belonged at UIUC. Thanks to you and Jenny for many great memories in our time as roommates – looking forward to more in the future, including your bachelor party and wedding soon! Yash, thanks for being the most excellent friend and support system for me throughout grad school. I am very grateful for the times we shared – our walks during COVID, to late evenings in the office, to fun times at friends’ dinners and beyond. You are a true and lasting friend that I always knew was and will be there for me, and I am very grateful for that. We have not had our last adventure together; I am certain of that! Lastly, a sincere thank you to my UIUC friends outside of my lab and cohort, past and present – Drew, Alex Horn, Matt Wade, Cara, Briana, Haley, Lauren, Kyle, Michael, among many others – you all have positively impacted my life in one way or another. I wish you all the very best!

Thank you to my close friends from my time as an undergraduate at the University of Oklahoma. To my roommates Nic Tinney, Tyler Erickson, and Brandon Erickson – I cherish our

friendship and the many good times and laughs we shared at OU. I am so glad I was lucky enough to be suitemates with Nic and Tyler in my freshman year, as the three of you became my closest friends from undergrad because of that! I look forward to many more exciting reunion trips in the future. To Lars Ostervold, I am very grateful we have stayed friends through high school, undergrad, and now grad school. You are a true friend, and I am happy that we will both be working at Dow – hopefully, in the same place eventually! Until then, I will look forward to many future conversations about science, hockey, and OU football. To Josh, Beth, Kevin, Alé, and Vikas – thanks for being wonderful friends during our time at OU! I miss you all dearly and hope to reconnect very soon. To Profs. Steven Crossley and Daniel Resasco, thank you for all your support during my time as an undergraduate, my graduate school applications, and beyond. You both helped to spark my interest in catalysis! I look forward to staying in touch and hope to meet at future conferences.

A special thank you to my friends and mentors from my visit to Pacific Northwest National Laboratory (PNNL) in the spring of 2024. To Drs. Jian Zhi Hu and Sungmin Kim, thank you for being such supportive co-hosts! I really enjoyed working with you and learned a lot from you both. Thanks to my friends and colleagues, who welcomed me with open arms and helped Washington feel like home during my short stay: Alex, Marcus, Jose, Júlia, Pedro, Boda, Laura, Harrison, Yinjie, Maria, Dylan, Tatiana, Thuy, Xander, Niklas, Megan, Austin, Biva. Thank you all for your kindness and the good memories we shared – I cherish my time spent at PNNL because of you all!

I must also thank a long list of terrific colleagues that I have met through conferences – Alex, Sopuru, Chenfeng, Will, Sebastian, Abel, Tania, Ángel, Hansel, Matt Jacob, Rachel, Sam, Nikki, Conor, Deep, Anoop, Prince, Lukas, Mohammad, Kumari, Zhiyin, Fiji, and Yuanhui (Peter). I am very grateful to have kept in touch and formed lasting friendships with many of you

beyond the conferences. I look forward to keeping up with your careers and hope to get to work with some of you in the future! Thank you to Profs. Siddarth Krishna and Nick Brunelli as well, who were always friendly faces at conferences that gave me valuable career advice and with whom I shared great conversations.

Last but most certainly not least, thank you to my family, who have formed the foundation of my support system over the years. Thank you to my cousins, Christian, Jon, Mara, and Steven, for the many great memories and laughs we have shared and will continue to share. While I am an only child, I have rarely felt like it because you all feel like my brothers and sister! To Jake and all the Yount boys (Michael, William, Luke, Thomas), thanks for the good memories so far – I am looking forward to more as the boys grow up! Thank you to my Aunt Betty for her love and support – I miss you and hope to see you soon. To those who have passed on – Grandma Virginia, Grandma Doris, Grandpa Mike, Aunt Susie, and Uncle Sam – you all had such wonderfully positive impacts on my life. I miss you all so much, but I know you all are at peace. To my Aunt Leslie and Uncle Mike – you all are like my second parents. Thank you both for your love and constant encouragement and support. I am honored to carry on the UIUC legacy that you and my Mom started! To my Mom and Dad – thank you for all your sacrifices and support; I would not be where I am today without it. I am grateful for all we have shared together: many smiles and lots of laughter, tears for lost loved ones, and everything in between. We have made wonderful memories – from many exciting road trips, flying to fun locations, countless enjoyable sporting events, and simply playing board games, golf, or Mario Kart together. I look forward to many, many more! Love you both always.

2597 words later, it is abundantly clear how many people have positively impacted and helped me along my journey to getting a Ph.D. It takes a village, and I am very grateful for mine! To those I mentioned and anyone I missed, thank you from the bottom of my heart.

The research presented in this thesis was financially supported by the Department of Energy under grant number DE-SC0020224 and the National Science Foundation Graduate Research Fellowship Program under grant number DGE-1746047. I also acknowledge the Oak Ridge Institute for Science and Education for financial support in my PNNL visit through the DOE Office of Science Graduate Student Research program. This work was carried out in part in the Materials Research Laboratory at UIUC.

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CHAPTER 1

INTRODUCTIONⁱ

Heterogeneous catalysts hold a central role in energy production, the development of fine and commodity chemicals, pharmaceutical synthesis, and engine emissions control, among many other applications that benefit society.¹⁻² Catalyst development has significantly contributed to waste minimization efforts in these industries over recent decades,³⁻⁴ but significant progress remains in global efforts to combat climate change.⁵⁻⁶ Chemical and energy production contribute significantly to global waste production⁷⁻⁸ and CO₂ emissions⁹⁻¹⁰ today, underscoring the importance of designing more renewable and efficient industrial processes. In recent years, researchers have explored promising renewable energy sources¹¹ (e.g., biomass) and sustainable catalytic processes¹² (e.g., electrocatalysis and photocatalysis), along with continued efforts to make current industrial catalytic processes more sustainable.¹³ These research directions have great potential but face challenges relating to catalyst design and discovery, as outlined by the U.S. Department of Energy¹⁴ and the European Cluster on Catalysis.¹⁵ *The development of more active, selective, and stable heterogeneous catalysts is critical for the success of sustainability efforts in the chemical industry.*¹⁵⁻¹⁷ These efforts would benefit from a molecular-level understanding of the interactions between reactants, spectator molecules, and catalytic active sites at the interface of the catalyst and the reaction medium.

ⁱ Part of this chapter has been reprinted with permission from the following publication:
David S. Potts, Daniel T. Bregante, Jason S. Adams, Chris Torres, and David W. Flaherty, “Influence of solvent structure and hydrogen bonding on catalysis at solid-liquid interfaces”, *Chemical Society Reviews* **2021**, 50, 12308-12337. Copyright 2021 Royal Society of Chemistry.

1.1 Covalent and Non-Covalent Interactions Govern Catalysis at Solid-Liquid Interfaces

Catalysis science has progressed tremendously in understanding reactions over solid surfaces,¹⁸⁻²⁰ homogeneous molecular complexes,²¹⁻²³ and in complex phases (e.g., plasma,²⁴⁻²⁶ ionic liquids²⁷⁻²⁸). Since the earliest reports from Berzelius,²⁹ the majority of efforts in heterogeneous catalysis involved the investigation and design of active sites with a specific focus on covalent or ionic bonds formed with reactive species and their dependence on apparent properties of the solid catalyst (e.g., metal identity,³⁰⁻³¹ atomic coordination,³²⁻³³ oxidation state³⁴⁻³⁵). The reaction environment, however, also warrants consideration for liquid phase systems. Solvent molecules can influence reaction rates by directly participating in catalytic reactions (e.g., facilitating proton transfer, acting as reactants), influencing the stability of chemical species (e.g., solvating through hydrogen bonds), and reducing the number of active sites that bind reactants (e.g., through competitive adsorption).

Researchers first recognized that solvent molecules affect rates of organic reactions over a century ago. In 1890, Menshutkin found that rates for the quaternization of triethylamine with iodoethane depend strongly on solvent choice, as rates in benzyl alcohol are 700 times greater than in n-hexane, holding all other reaction conditions constant.³⁶ This rate increase occurs because protic benzyl alcohol molecules stabilize the separation of charges within the transition state for quaternization. Several publications have documented the effects of solvents on homogeneous chemical and catalytic reactions in recent years.³⁷⁻³⁸ Evidently, the field of catalysis recognizes the importance of solvent identity in chemical and catalytic reactions, which motivates the need to understand the variety of roles solvent molecules may hold for catalysis.

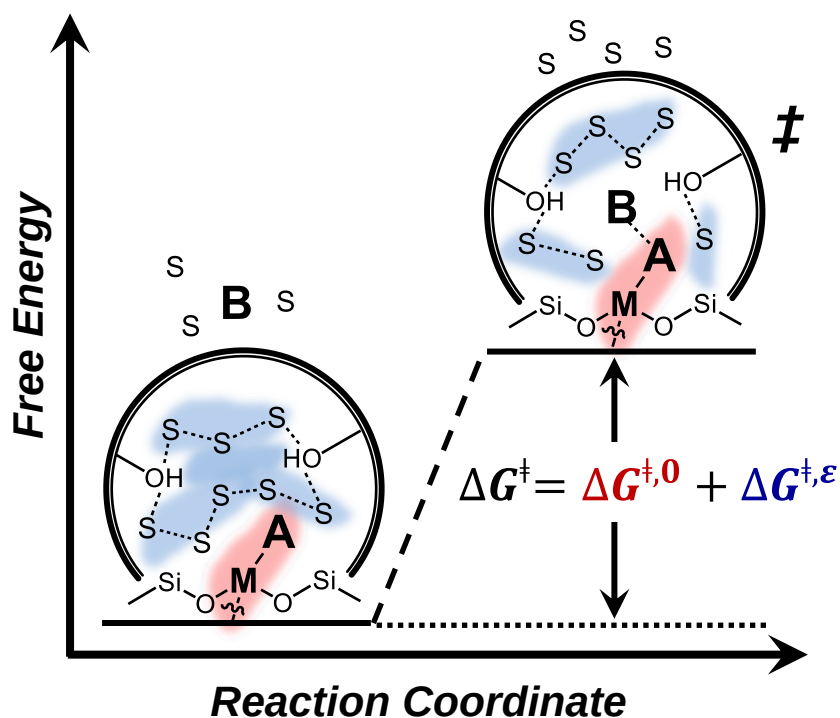
The non-covalent interactions between solvent molecules and reactants in the liquid phase and at active sites at solid-liquid interfaces introduce thermodynamic non-idealities to a catalytic

system.³⁹ The excess free energy (G^ε) quantifies the impact of these non-idealities on the free energy of reactive species. The activity coefficients of reactive species can be related to excess Gibbs free-energy contributions as follows:

$$\gamma_i = \exp\left(\frac{G_i^\varepsilon}{RT}\right) \quad (1)$$

While the excess free energies equal zero for ideal solutions and pure liquids, these terms are non-zero and may be significant within non-ideal solutions and at interfaces. The solvent can alter activation barriers and adsorption energies for a reaction when it affects G^ε values of reactants, intermediates, and transition states to different extents. These changes lead to differences in rates and selectivities, even in the absence of mass transfer limitations. The activation free energy ($\Delta G^\ddagger$) depends on both excess ($\Delta G^{\ddagger,\varepsilon}$) and standard state ($\Delta G^{\ddagger,0}$) contributions (**Scheme 1.1**):

$$\Delta G^\ddagger = \Delta G^{\ddagger,0} + \Delta G^{\ddagger,\varepsilon} \quad (2)$$



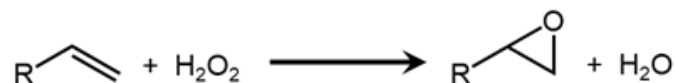
Scheme 1.1. Reaction coordinate for a generic reaction ($A + B \rightarrow C$) over a metal-incorporated zeolites, where $\Delta G^\ddagger$ depends on covalent ($\Delta G^{\ddagger,0}$) and non-covalent ($\Delta G^{\ddagger,\varepsilon}$) interactions within the zeolite pores.

$\Delta G^{\ddagger,0}$ encompasses the interactions of adsorbed species with pore walls (e.g., in zeolites⁴⁰⁻⁴²) through van der Waals interactions and with metal and metal-oxide surfaces⁴³⁻⁴⁵ or isolated metal atoms in zeolite frameworks through covalent bonding.^{30, 46-47} $\Delta G^{\ddagger,0}$ and $\Delta G^{\ddagger,\varepsilon}$ quantify the differences in the stabilities of the transition state and reference state species (adsorbed intermediates or liquid/gas phase reactants) during a catalytic reaction. When these covalent ($\Delta G^{\ddagger,0}$) and non-covalent ($\Delta G^{\ddagger,\varepsilon}$) interactions influence the stability of the transition state and intermediates to different degrees, they can lead to significant differences in reaction rates in the liquid phase. Evidently, these phenomena merit consideration in the design or investigation of processes that involve liquid phase chemical reactions (e.g., oxidation of hydrocarbons and oxygenates,⁴⁸ and alkylation or carbon coupling for pharmaceutical production^{38, 49}).

1.2 Strategies to Facilitate Alkene and Epoxide Transformations at Solid-Liquid Interfaces

Epoxides are produced on a massive scale as precursors for various fine and commodity chemicals, including plastics, pharmaceuticals, and fragrances.⁵⁰ The production of these industrially important materials commonly involves the epoxidation of alkenes with an oxidant (e.g., hydrogen peroxide (H_2O_2), oxygen (O_2)) and the subsequent ring-opening of the epoxide with a nucleophile (e.g., H_2O , amines, alcohols). The hydrogen peroxide to propylene oxide (HPPO) epoxidation process occurs in aqueous-organic solvents and utilizes microporous, crystalline silicates (i.e., zeolites) incorporated with titanium as catalysts.⁵¹⁻⁵⁶ The ring-opening of the propylene oxide product also predominantly occurs in aqueous-organic solvents over several classes of catalysts, including homogeneous complexes,⁵⁷⁻⁵⁹ ion-exchange resins,⁶⁰⁻⁶² and zeolites.⁶³⁻⁶⁵ The design of more sustainable alkene epoxidation processes requires high rates and H_2O_2 selectivities towards epoxidation over the undesired H_2O_2 decomposition pathway, while

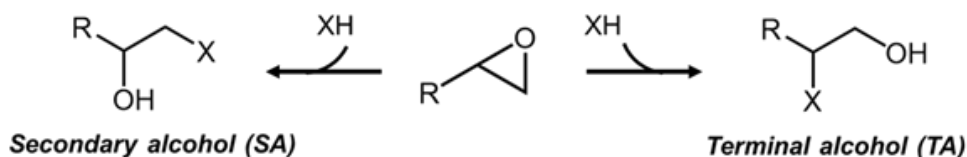
a) *Alkene Epoxidation with H₂O₂*



H₂O₂ Decomposition



b) *Epoxide Ring-Opening with Nucleophiles (XH)*



Scheme 1.2. Stoichiometric reactions relevant for a) alkene epoxidation with H₂O₂ and the competing H₂O₂ decomposition pathway, and b) epoxide ring-opening with a nucleophile, where either a secondary or terminal alcohol product may form.

epoxide ring-opening processes benefit from greater control of reaction rates and regioselectivities towards desired processes (**Scheme 1.2**). The terminal and secondary alcohol products from epoxide ring-opening serve as building blocks for unique classes of products, emphasizing the need to understand how to control reaction regioselectivity.⁶⁶⁻⁶⁸ The active site and surrounding solvent environment warrant consideration in both epoxidation and epoxide ring-opening processes, as they can strongly influence rates and selectivities through changes in $\Delta G^{\ddagger,0}$ and $\Delta G^{\ddagger,\varepsilon}$, respectively.

The identity of the active metal atom at tetrahedral positions within the zeolite framework strongly influences rates and selectivities for alkene epoxidation and epoxide ring-opening through changes in $\Delta G^{\ddagger,0}$. Previous studies demonstrate that Ti-incorporated zeolites yield the greatest rates among transition metals for the epoxidation of linear and cyclic alkenes with H₂O₂.^{30-32, 69-70} These rate differences partially originate from differences in the energy of unoccupied orbitals that accept

charge from reagents between metals, supported by density functional theory (DFT) calculations⁷⁰ and measured enthalpies of adsorption of acetonitrile in the vapor phase³¹ and epoxides in the liquid phase.³⁰ Similar energetic effects likely explain why Sn-incorporated zeolites provide greater rates for the ring-opening of linear and cyclic epoxides with CH₃OH⁶³ or H₂O⁶⁴ than Hf-, Zr-, and Ti-zeolites. The authors of these works argue that the tetrahedral Sn sites possess the greatest Lewis acid strength among these metals, based on ¹⁵N NMR chemical shifts^{63, 71} and desorption temperatures for pyridine.⁶⁴ In contrast, Zr-incorporated zeolites gave greater rates than Ti- and Sn-incorporated materials for the ring-opening of styrene oxide by reactions with amines, which the authors argue originates from the amines binding too strongly to Sn sites and preventing adsorption of styrene oxide.⁶⁵ These previous studies clearly show that differences in $\Delta G^{\ddagger,0}$ induced by changing the active metal within zeolites significantly influence rates, selectivities, and stabilities of solid catalysts for alkene epoxidation and epoxide ring-opening.

The environment introduced by surrounding solvent molecules and hydrogen-bonding species also influences the rates and selectivities of alkene and epoxide transformations by orders of magnitude through changes in $\Delta G^{\ddagger,\epsilon}$. Hydrophilic titanium-incorporated zeolites, which possess high densities of silanol ((SiOH)_x) groups, provide greater rates for alkene epoxidation with aqueous hydrogen peroxide (H₂O₂) than hydrophobic zeolites (i.e., low Si(OH)_x density) by up to two orders of magnitude in acetonitrile (CH₃CN)⁷²⁻⁷⁵ and methanol (CH₃OH)⁷⁶⁻⁷⁸ solvents. The hydrophilic pores stabilize clusters of H₂O molecules that provide entropy increases when disrupted by the formation of the hydrophobic epoxidation transition state. Previous studies also suggest that interactions between solvent molecules and reactive species affect product formation rates and regioselectivities for the subsequent epoxide ring-opening reaction. Over ion-exchanged FAU zeolites, polar solvents lead to greater selectivities but lower turnover rates to secondary

alcohol products compared to non-polar solvents for the ring-opening of 1,2-epoxyoctane with sodium azide (NaN_3),⁷⁹ although the reasons for this effect remains unclear. Furthermore, experimental and computational studies using a homogeneous tris(pentafluorophenyl)borane catalyst show that adding water increases terminal alcohol selectivity for the alcoholysis of 1,2-epoxyoctane.⁸⁰⁻⁸² The authors argue that water molecules form hydrogen bonding complexes with the catalyst, epoxide, and other hydrogen bond acceptors, which can facilitate the attack of the alcohol nucleophile at the more substituted epoxide carbon to form the terminal alcohol.⁸⁰⁻⁸² Evidently, manipulations to the catalyst structure, polarity, and reaction solvent can strongly influence rates and selectivities of liquid-phase catalysis through changes in $\Delta G^{\ddagger,\varepsilon}$.

The previous body of literature clearly demonstrates the significant effect of both covalent ($\Delta G^{\ddagger,0}$) and non-covalent ($\Delta G^{\ddagger,\varepsilon}$) interactions on alkene epoxidation and epoxide ring-opening catalysis. However, developing catalysts with greater performance for these important chemistries requires a better understanding of how several key variables influence the reactions. Prior findings show that the rates of epoxidation catalysis with H_2O_2 over zeolites depend strongly on both the size and structure of the alkene substrates. Previous work from our group found that alkene epoxidation rates increase from 1-hexene (C_6H_{12}) to 1-decene ($\text{C}_{10}\text{H}_{20}$) in hydrophilic Ti-BEA zeolite but decrease for hydrophobic Ti-BEA.⁷² These trends indicate that increases in excess entropy ($\Delta S^{\ddagger,\varepsilon}$) dominate over concomitant increases in excess enthalpy ($\Delta H^{\ddagger,\varepsilon}$) over the hydrophilic Ti-BEA but not in the hydrophobic analog. In contrast, earlier studies from other groups found that rates decreased from C_6H_{12} to $\text{C}_{10}\text{H}_{20}$ over Ti-BEA zeolites⁸³⁻⁸⁴ and attributed the trend to steric constraints for the adsorption of longer alkenes, but the $(\text{SiOH})_x$ density of the materials were not reported. Another study from our group showed that epoxidation rates decrease from C_6H_{12} to $\text{C}_{10}\text{H}_{20}$ in a hydrophilic, mesoporous material (Ti-SBA-15, 5 – 15 nm pore

diameter), credited to a weak enthalpic stabilization from adsorption into larger pores that does not compensate the loss in entropy.⁸⁵ The difference in rate trends between hydrophilic Ti-BEA (0.65 nm pores) and -SBA-15 materials demonstrates the complicated relationship between the stability of reactive species for epoxidation and the (SiOH)_x density and pore structure of the catalyst. A past study from Fan et al. reinforces this point, as they found Ti-MWW (0.5, 0.7 nm pores), -BEA (0.65 nm), and -MFI (0.55 nm) zeolites provide greater epoxidation rates for C₆H₁₂ than bulkier cyclohexene (C₆H₁₀).⁸⁶ Furthermore, they found that CH₃CN as solvent yields greater C₆H₁₂ epoxidation rates in Ti-MWW and Ti-BEA while CH₃OH gives greater rates over Ti-MFI, but the opposite solvent gives greater C₆H₁₀ epoxidation rates for each zeolite.⁸⁶ The authors credited the rate differences among catalysts and alkenes to differences in intrinsic hydrophilicity and active site locations between frameworks, but the (SiOH)_x density and band gaps of the materials appear very similar between each framework. To summarize, the previous body of literature reveals the strong impact of interactions between alkene substrates and surrounding solvent molecules or pore walls on epoxidation performance, but contradicting results and explanations among studies demonstrate the complexity of these systems and the need to develop further fundamental understanding of how intrapore interactions influence alkene epoxidation. **Chapter 2** seeks to advance understanding of these effects by examining the kinetics and thermodynamics of alkene epoxidation with H₂O₂ in hydrophilic (Ti-BEA-OH) and hydrophobic (Ti-BEA-F) zeolites as a function of alkene and epoxide carbon number (C₆-C₁₈), through a combination of experimental and computational methods. Spectroscopic techniques (infrared and ¹H NMR) and corresponding results from grand canonical molecular dynamics simulations (GCMD) show that Ti-BEA-OH absorbs greater quantities of both H₂O and CH₃CN than Ti-BEA-F. With 200 mM H₂O present in CH₃CN solvent, epoxidation rates are more than 40 times greater over Ti-BEA-OH than Ti-BEA-

F for all alkenes. The rate differences do not reflect changes in reaction mechanism, intrinsic alkene stability, or mass transfer limitations. Activation barrier measurements provide evidence that the disruption of these hydrogen-bonded solvent molecules within Ti-BEA-OH drives increases in rates through increases in $\Delta S^{\ddagger,\varepsilon}$ conferred to the transition state. Epoxide adsorption enthalpies ($\Delta H_{ads,epox}$, measured experimentally and computed with GCMD) correlate to activation enthalpies ($\Delta H^{\ddagger}$), providing evidence that longer alkyl chains disrupt more solvent molecules (H_2O or CH_3CN), which affects the stability of the transition state for $C_6 - C_{18}$ alkene epoxidations. These findings show that the stability of adsorbates is strongly affected by the number and type of solvent molecules displaced upon adsorption into zeolite pores, thereby providing opportunities to increase rate constants for desired over undesired reactions through changes in $\Delta G^{\ddagger,\varepsilon}$.

The mole fraction of H_2O (x_{H_2O}) within organic solvents also plays a key role in rate and selectivity trends for zeolite-catalyzed alkene epoxidation with H_2O_2 . Several past studies found that epoxidation rates vary negligibly at $x_{H_2O} < 0.25$ for propylene (C_3H_6),⁸⁷ $x_{H_2O} < 0.3$ for C_6H_{12} ,⁸⁸ and $x_{H_2O} < 0.01$ for 1-octene (C_8H_{16}),⁷⁴ attributed to either negligible adsorption of H_2O to Ti sites⁸⁷⁻⁸⁸ or negligible changes in the intrapore H_2O concentration in this regime of x_{H_2O} .⁷⁴ The C_3H_6 study showed a decrease in C_3H_6 epoxidation rates above $x_{H_2O} > 0.25$ and argued that competitive adsorption of H_2O to Ti sites suppresses rates at sufficiently high x_{H_2O} .⁸⁷ Other publications credit increases in epoxidation rates at all x_{H_2O} for C_3H_6 ⁸⁹ and C_6H_{12} ^{86, 90} to an increased stabilization of the titanium-hydroperoxo (Ti-OOH) reactive intermediate by H_2O . Rates for the undesired H_2O_2 decomposition side reaction also depend on the choice of organic solvent used in aqueous mixtures, with past studies showing complex dependences of decomposition rates on the protic or aprotic nature of the organic solvent that were not explained.⁹⁰⁻⁹¹ Furthermore,

studies on the effect of x_{H_2O} on H_2O_2 decomposition have not been reported. Overall, the previous body of epoxidation literature demonstrates that many phenomena may contribute to differences in epoxidation rates and selectivities with x_{H_2O} , but a lack of consistent catalyst synthesis and reaction conditions obscure the true effect of x_{H_2O} on epoxidation kinetics. **Chapter 3** describes how and why greater quantities of H_2O within organic solvents favor alkene epoxidations over the H_2O_2 decomposition pathway. As the mole fraction of H_2O increases from 0.002 to 0.8 in CH_3CN , gamma-butyrolactone (GBL), and methanol co-solvents, turnover rates for 1-hexene (C_6H_{12}) epoxidation increase while H_2O_2 decomposition rates decrease. The inverse trends lead to significantly higher epoxidation selectivities at higher H_2O fractions. Rates were normalized by reactant activities to show how changes in the stability of the Ti-OOH MARI and transition state contribute to rate differences. As H_2O fraction increases, activation enthalpies for epoxidation ($\Delta H_{epox}^\ddagger$) change monotonically over Ti-BEA-F but non-monotonically over Ti-BEA-OH for each co-solvent. Differences among $\Delta H_{epox}^\ddagger$ result from changes in the stability of reactive species within the pores of Ti-BEA-OH and Ti-BEA-F. Corresponding measurements of $\Delta H_{ads,epox}$ for 1,2-epoxyhexane with isothermal titration calorimetry correlate to $\Delta H_{epox}^\ddagger$ measurements, providing further evidence that $[H_2O]$ affects epoxidation transition state stability. Activation enthalpies for H_2O_2 decomposition ($\Delta H_{decomp}^\ddagger$) show that adding H_2O leads to enthalpic stabilization of the transition state (decreasing $H_{decomp}^{\ddagger,\varepsilon}$), but the corresponding stabilization of liquid-phase H_2O_2 suppresses decomposition. H_2O molecules stabilize the hydrophilic transition state for H_2O_2 decomposition through hydrogen bonding. In contrast, H_2O likely entropically stabilizes the hydrophobic epoxidation transition state, increasing $S_{epox}^{\ddagger,\varepsilon}$ through the disruption of hydrogen bonds between H_2O . Collectively, these findings show that adding H_2O to organic

solvents alters H^ε and S^ε for reactive species, thus providing opportunities to increase turnover rates and selectivities for desired reaction pathways.

Brønsted⁹²⁻⁹⁴ and Lewis^{59, 95-96} acidic materials both find use as catalysts for industrial epoxide ring-opening processes, but comparisons between these acid types are scarce. Not only do Brønsted and Lewis acids catalyze reactions through different charge transfer mechanisms,⁹⁷ these materials often respond differently to contact with a liquid; solvent molecules can solvate the protons at Brønsted acid sites in zeolites and form delocalized protonated clusters,⁹⁸⁻¹⁰⁰ while Lewis acidic metal sites do not detach from the framework. Brønsted and Lewis acid catalysts give different rates and selectivities for epoxide ring-opening with several nucleophiles, including water,^{64, 101} amines,^{65, 102} and alcohols.^{63, 103} The collection of previous studies highlights the importance of understanding how the characteristics of the acid site and the solvent environment in zeolites influence ring-opening catalysis. **Chapter 4** examines the consequences of varying the active metal and CH_3CN co-solvent fraction on rates and regioselectivities for 1,2-epoxybutane ($\text{C}_4\text{H}_8\text{O}$) ring-opening with CH_3OH over hydrophilic zeolite *BEA materials (M-BEA). Rates depend linearly on $[\text{CH}_3\text{OH}]$ and weakly on $[\text{C}_4\text{H}_8\text{O}]$ for all M-BEA at ratios of $[\text{CH}_3\text{OH}]$ to $[\text{C}_4\text{H}_8\text{O}]$ less than 40. At higher ratios, rates show similar dependence over Al-BEA but shift to a weak dependence on $[\text{CH}_3\text{OH}]$ and linear dependence on $[\text{C}_4\text{H}_8\text{O}]$ over the Lewis acids. These results suggest that the Lewis and Brønsted acidic materials may catalyze ring-opening through different mechanisms. Rates among Lewis acids correlated with reported Lewis acid strengths calculated from pyridine ^{15}N NMR chemical shifts^{63, 71} and desorption temperatures,⁶⁴ with the greatest rates over Sn-BEA and lowest over Ti-BEA. Regioselectivities toward the terminal ether product (equivalent to secondary alcohol in **Scheme 1.2**) exceed 50% under most conditions, in agreement with past interpretations of greater steric hindrance associated with terminal alcohol

formation.^{63, 104-106} Selectivity towards the terminal ether generally decreases with increasing [CH₃OH] and increases with [C₄H₈O] over each M-BEA. Al-BEA consistently gives the lowest regioselectivities to the terminal ether, with Ti- and Zr-BEA showing the greatest regioselectivities. $\Delta H^\ddagger$ values and reactant and product adsorption enthalpies give evidence that differences in regioselectivities stem from differences in the free energies of the transition states to form each product. CH₃CN-rich solvents show low $\Delta H^\ddagger$ values while CH₃OH-rich solvents show higher $\Delta H^\ddagger$ values, suggesting that entropic benefits drive high rates in a CH₃OH-rich solvent. The findings outlined here can guide the design of more selective catalytic reactions in the presence of solvents through the manipulation of both covalent and non-covalent interactions.

Altering the (SiOH)_x density of zeolites offers another strategy to manipulate the intrapore solvent structure and, consequently, the rates and regioselectivities of epoxide ring-opening through changes in $\Delta G^{\ddagger,\varepsilon}$. One study found that a Sn-BEA material with a low density of (SiOH)_x groups showed greater rates of epichlorohydrin ring-opening with CH₃OH by a factor of 2 compared to an (SiOH)_x-rich material.¹⁰⁷ Activation barrier measurements suggest that the presence of (SiOH)_x groups introduces entropic penalties for the reaction. In contrast, greater densities of (SiOH)_x groups increased rates of propylene oxide solvolysis with CH₃OH or H₂O over Ti-incorporated zeolites, which the authors attribute to direct participation of the (SiOH)_x groups in the reaction.¹⁰⁸ These studies show that the (SiOH)_x density influences epoxide ring-opening over Lewis acid zeolites; however, the exact nature of their influence and their impact in Brønsted acid zeolites is unestablished. **Chapter 5** uncovers the role of (SiOH)_x groups on rates and C₄H₈O ring-opening with CH₃OH in CH₃CN co-solvent over both Lewis (Zr-BEA) and Brønsted acidic (Al-BEA) zeolites. C₄H₈O-derived surface intermediates saturate active sites at most conditions over the Zr-BEA materials and nearly all conditions over the Al-BEA materials,

suggesting identical mechanisms regardless of $(\text{SiOH})_x$ density. Despite this similarity, turnover rates over $(\text{SiOH})_x$ -rich Zr-BEA (Zr-BEA-OH) exceed those over $(\text{SiOH})_x$ -poor Zr-BEA (Zr-BEA-F) by an order of magnitude. In contrast, turnover rates over Al-BEA-OH and Al-BEA-F materials vary by less than two times across reagent concentrations. Rate differences among materials appear to correspond to changes in intrapore solvent structure, originating from differences in $(\text{SiOH})_x$ density and active site identity (i.e., Zr atoms in Zr-BEA, H^+ in Al-BEA). Al-BEA-OH and Al-BEA-F show nearly identical $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for ring-opening and adsorption enthalpies for $\text{C}_4\text{H}_8\text{O}$, which leads to only slight rate differences between the catalysts and likely originates from similar measured solvent uptakes between the materials. In comparison, Zr-BEA-OH gives more positive values for the $\text{C}_4\text{H}_8\text{O}$ adsorption enthalpy, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ than Zr-BEA-F. The greater ring-opening rates in Zr-BEA-OH thus likely originate from greater densities of hydrogen-bonded solvent molecules, as demonstrated by solvent uptakes. The disruption of these networked molecules stabilized by $(\text{SiOH})_x$ groups provides entropy increases that exceed the corresponding enthalpy increases. Turnover rates and regioselectivities depend differently on the reaction system, as the regioselectivities vary with active metal and solvent composition but change marginally with $(\text{SiOH})_x$ density. This work reveals how the $(\text{SiOH})_x$ density and acid site (Lewis or Brønsted) control the solvent environment with zeolites to influence G^ε values for reactive species, thereby establishing design principles for manipulating the kinetics and thermodynamics of reactions in the presence of intrapore liquids.

Chapter 6 highlights our key insights on the consequences of the intrapore environment on the free energies of reactive species during liquid-phase catalysis. **Chapters 2 – 5** establish how covalent and non-covalent interactions among reactants, solvents, active sites, and zeolite pore functions drive differences in rates and selectivities of alkene epoxidation and epoxide ring-

opening. In **Chapter 2**, we examine alkenes of varying carbon numbers (C_6 - C_{18}) to establish the strong impact of solvent structure and displacement in zeolites on alkene epoxidation rates through a combination of experimental and computational methods. **Chapter 3** shows that adding greater fractions of H_2O to organic solvents increases selectivities to alkene epoxidation over unproductive H_2O_2 decomposition, demonstrating that changing the composition of aqueous solvents allows for the selective stabilization of hydrophobic or hydrophilic reactive species. **Chapter 4** utilizes synthesis, kinetic, and calorimetric techniques to build structure-function relationships for epoxide ring-opening over zeolites, which reveal that the intrapore interactions between reactants, active sites, and solvents allow for control of rates and regioselectivities. **Chapter 5** extends these structure-function relationships by studying epoxide ring-opening kinetics as a function of the $(SiOH)_x$ density of Lewis and Brønsted acidic zeolites, where modifications to the intrapore functions in zeolites provide further opportunities to modify rates and regioselectivities through changes in solvent structure.

Finally, **Chapter 6** presents future directions inspired by the findings from **Chapters 2 – 5**. First, employing a combination of kinetics and *in situ* ^{13}C -NMR spectroscopy provides valuable insight into the precise nature of the reaction mechanism for epichlorohydrin ring-opening over Lewis and Brønsted acidic zeolites, helping to explain the fundamental origins of the changes in regioselectivities described in this thesis. Second, changing the organic co-solvent presents another opportunity to alter turnover rates and tune selectivities towards the desired regioisomer for C_4H_8O ring-opening with CH_3OH , as demonstrated for comparisons of organic solvents of varying structure and polarity: CH_3CN , dimethoxyethane, and dioxane. Third, initial comparisons between butanol, butylamine, and butanethiol reveal significant differences in C_4H_8O ring-opening rates and selectivities for molecules with identical alkyl tails but different nucleophilic functions. This

study will reveal how the interactions of different nucleophiles with active sites, epoxides, and co-solvent molecules drive differences in ring-opening kinetics, providing insight into how to facilitate the formation of valuable epoxide-derived intermediates with a suite of relevant nucleophiles.

Overall, the design of catalytic processes for epoxide production and transformations frequently relies on guesswork and trial and error. A better understanding of how covalent and non-covalent interactions influence zeolite catalysis can help improve well-established processes, such as alkene epoxidation and epoxide ring-opening. However, this knowledge can also assist with process design for emerging green chemistries already shown to depend sensitively on these interactions, such as sugar isomerization,¹⁰⁹⁻¹¹⁰ dehydration,¹¹¹⁻¹¹² and hydrolysis.¹¹³⁻¹¹⁴ The combination of synthesis, kinetics, calorimetry, and spectroscopy highlighted in this thesis provides a helpful framework for designing more efficient and sustainable catalytic processes at solid-liquid interfaces.

CHAPTER 2

EFFECT OF INTERACTIONS BETWEEN ALKYL CHAINS AND SOLVENT STRUCTURES ON LEWIS ACID CATALYZED EPOXIDATIONSⁱⁱ

2.1 Introduction

Microporous silicates and zeolites provide useful properties for catalysis and separations,¹¹⁵⁻¹¹⁷ because the subnanometer pores intrinsic to these materials selectively admit and stabilize small molecules. During contact with gaseous species at elevated temperatures, micropores remain largely unoccupied such that interactions among molecules and siloxane pore walls stabilize adsorbates and reactive species primarily by van der Waals forces.¹¹⁸⁻¹²⁰ These non-specific interactions depend strongly upon distance, and therefore, the topology of the pores affects the stability of adsorbed species^{40, 42, 121} and warrants consideration during the selection of materials. In contrast, gases with higher relative pressures can condense spontaneously to create intrapore phases with molecular densities approaching liquids. These environments introduce additional complexities due to specific interactions (e.g., hydrogen bonds)¹²²⁻¹²⁶ among dissimilar molecules that give rise to thermodynamic non-idealities that change the enthalpies and entropies for adsorption and reaction of molecules in these environments.³⁹ Intuitively, the enthalpy and entropy of solutes in these processes depend upon the requisite displacement and reorganization of solvent molecules about species bound to catalytic active sites by covalent or ionic interactions.¹²⁷⁻¹³⁰ The importance of these effects is clear; however, recent investigations

ⁱⁱ This chapter has been reprinted with permission from the following publication:
David S. Potts, Vijaya Sundar Jeyaraj, Ohsung Kwon, Richa Ghosh, Alexander V. Mironenko, and David W. Flaherty, “Effect of Interactions between Alkyl Chains and Solvent Structures on Lewis Acid Catalyzed Epoxidations”, *ACS Catalysis* **2022**, 12, 21, 13372-13393. Copyright 2022 American Chemical Society.

demonstrate the molecular details of ostensibly simple processes (e.g., adsorption) exceed those for empty pores described in the majority of past investigations.^{124, 126} Confined solvent molecules in zeolite pores necessarily rearrange during catalytic reactions and alter activities and excess free energies (G^E) of adsorbed intermediates and transition states.

The numbers of Brønsted or Lewis acidic active sites and silanol ((SiOH)_x) functions and their spatial location within the pore network affect the solvent structure within zeolites. The structure of silanol groups (e.g., the value of x in (SiOH)_x, which may range from one to four) depends upon the mechanism by which these defects form. For example, removing Al atoms from tetrahedral positions in the framework generates (SiOH)₄ defects. Zhang et al. found that hydrophobic pores containing low densities of (SiOH)_x show 5 times greater selectivity than hydrophilic pores with high (SiOH)_x density for ethanol adsorption from ethanol and water mixtures.¹³¹ In a single component alcohol system, Vega-Vila and Gounder found that methanol molecules form extended hydrogen bonded networks stabilized by (SiOH)_x present in hydrophilic zeolites but pack at 2-5 times higher molecular densities within hydrophobic zeolites that do not contain appreciable amounts of (SiOH)_x groups.¹³² Di Iorio et al. found that turnover rates for cyclohexanone transfer hydrogenation with 2-butanol are 10 times greater in hydrophobic than hydrophilic Sn-BEA (0.65 nm pore size) and, with similar reasoning, attributed the difference to a denser and more ordered structure of 2-butanol in hydrophobic Sn-BEA that stabilizes the transition state more significantly.¹³³ In other instances, (SiOH)_x defects in hydrophilic pores of zeolites (e.g., MFI, *BEA) anchor hydrogen bonded networks of water (H₂O) that lead to greater densities of H₂O than within hydrophobic zeolites.^{74, 134-135} The presence of these H₂O networks affects rates for zeolite catalyzed reactions. Turnover rates for aqueous-phase glucose isomerization are 5-10 times lower in hydrophilic Ti- and Sn-BEA compared to hydrophobic

variants.^{132, 135-138} Reported activation enthalpy and entropy values indicate that hydrogen bond interactions between the isomerization transition state and extended networks of H₂O in hydrophilic pores provide enthalpic stabilization to the transition state, but more severe entropic destabilization ultimately leads to lower reaction rates.¹³⁶ In contrast, alkene epoxidations with aqueous hydrogen peroxide (H₂O₂) possess greater turnover rates over hydrophilic than hydrophobic Ti-BEA in acetonitrile (CH₃CN)⁷²⁻⁷⁵ and methanol (CH₃OH)⁷⁶⁻⁷⁸ solvents. These differences suggest that the alkyl group of the transition state for alkene epoxidation disrupts H₂O molecules in hydrophilic Ti-BEA and provide entropic gains that increase rates by orders of magnitude.⁷²⁻⁷⁴ The different dependences of glucose isomerization and alkene epoxidation turnover rates on (SiOH)_x densities in metal-incorporated *BEA zeolites originate from differences in the polarity of the transition state; the hydrophilic transition state for glucose isomerization shows enhanced reactivity in the absence of H₂O networks within hydrophobic pores, while more hydrophilic reaction environments lead to greater reactivity of the hydrophobic transition state for alkene epoxidation. For each reaction discussed here, solvent molecules alter reaction rates by affecting the excess free energy of the transition state ($G^{\ddagger,\varepsilon}$).

Our prior comparisons between rates and barriers for epoxidation of 1-hexene, 1-octene, and 1-decene among Ti-MFI, -BEA, and -FAU catalysts suggest that the magnitude of the G^ε contributions depends upon the size of the alkene reactant in ways that scale with the number of hydrogen bonded H₂O molecules disrupted.⁷² Rates increase from 1-hexene to 1-decene in hydrophilic Ti-BEA but decrease for hydrophobic Ti-BEA. The rate trends suggest that gains in the excess entropy of the transition state ($S^{\ddagger,\varepsilon}$) dominate over excess enthalpy ($H^{\ddagger,\varepsilon}$) increases in hydrophilic Ti-BEA but not in the hydrophobic analog.⁷² The reasoning for the decrease in rates in hydrophobic Ti-BEA as the number of methylene units in the alkene reactant increases is

unclear. Earlier studies from Van der Waal et al.⁸³ and Corma et al.⁸⁴ showed rates decreased from 1-hexene to 1-decene over Ti-BEA zeolites. These authors attributed the decreases to differences in intrinsic alkene reactivity and steric constraints of longer chain alkenes adsorbing into the pore but did not report characterization methods to probe the (SiOH)_x density or employ synthesis protocols intended to change the hydrophilicity of the zeolites used. Experimental^{120, 139} and computational¹⁴⁰ studies of C₂-C₈ alkane adsorption to Brønsted acid zeolites ranging in pore size from H-MFI (0.55 nm) to H-FAU (1.3 nm) concluded that zeolite pore walls enthalpically stabilize longer chain hydrocarbons through van der Waals interactions, which could contribute to rate differences for alkene epoxidation reactions. However, these studies took place in the absence of solvent at low coverages of adsorbates. Experimental studies showed that a liquid-phase influences the adsorption selectivity of C₇-C₉ alkanes¹⁴¹ and C₈ aromatics¹⁴² to FAU zeolites compared to gas-phase adsorption. The separation of C₆-C₁₆ alkenes from C₆-C₁₄ alkane solvents with FAU zeolites has also been shown experimentally to depend on adsorbate and solvent carbon number,¹⁴³⁻¹⁴⁶ but these previous reports conflict on the effect of carbon number on separation selectivity. Shetty et al. also demonstrated the effect of van der Waals and solvation interactions for dehydration of differently substituted alcohols, showing that secondary C₇ alcohols have greater rates over H-MFI (0.55 nm pore diameter) while tertiary C₇ alcohols react more rapidly over H-BEA (0.65 nm pore diameter).¹⁴⁷ The authors attribute the benefit of H-MFI for secondary alcohol dehydration to van der Waals stabilization with the pore walls. In contrast, they credit the greater rates for tertiary alcohols over H-BEA to enhanced alcohol uptake in H-BEA that leads to stabilization of the transition state by surrounding alcohol molecules. To summarize a significant body of prior findings, the physical reasons why rates and selectivities for hydrocarbon catalysis (e.g., alkene epoxidation, alcohol dehydration) and adsorption depend strongly on the size and

substitution of substrates in liquid-filled zeolite pores remain unknown. The leading hypotheses attribute molecular recognition exhibited in these processes to either van der Waals interactions between substrates and pore walls, diffusional limitations within networks of pores, solvating interactions between substrates and solvent molecules, or the requisite reorganization of solvent molecules to permit adsorption and catalysis.

Here, we reveal the effects of solvent displacement and confinement on reactions of alkenes in solvent-filled pores of zeolites by examining the kinetics of alkene epoxidations with H_2O_2 and thermodynamics of epoxide adsorption in hydrophilic (Ti-BEA-OH) and hydrophobic (Ti-BEA-F) pore environments as a function of alkene carbon number ($\text{C}_6\text{-C}_{18}$). Apparent activation enthalpies and entropies increase systematically with alkene carbon number over each zeolite, with a much weaker dependence on carbon number in Ti-BEA-F that likely results from the epoxidation transition state disrupting lesser quantities of H_2O molecules within Ti-BEA-F than Ti-BEA-OH pores. Enthalpies of epoxide adsorption measured with isothermal titration calorimetry (ITC) correlate to measured apparent activation barriers, indicating that the changes in apparent activation enthalpies result from the disruption of confined solvent structures within Ti-BEA zeolites. Epoxide adsorption requires similar solvent displacement as the formation of the epoxidation transition state, meaning that epoxide adsorption enthalpies support our prior interpretations of changes in transition state excess free energy⁷² in ways that other experiments cannot. Accordingly, the correlation between epoxide adsorption and activation enthalpies strengthens these interpretations. Computationally measured epoxide adsorption enthalpies and solvent uptakes correlate with experimental findings and show that solvent displacement strongly influences the stability of the adsorbed epoxide. Radial distribution functions (RDF) show that the solvent structure in the pores of Ti-BEA depends on silanol density and further demonstrate that

epoxide adsorbates interact with confined solvent molecules and influence the solvent structure. Collectively, these findings show that the stability of guest molecules depends intimately on the number of solvent molecules displaced when they adsorb into zeolite pores, thereby affecting the rates of catalytic reactions (i.e., alkene epoxidation with H_2O_2 in Ti-BEA).

2.2 Materials and Methods

2.2.1 Catalyst Synthesis

Ti-BEA-OH was prepared by post-synthetic modification of commercial Al-BEA, following previously published procedures.¹⁴⁸⁻¹⁴⁹ Al-BEA (TOSOH, lot no. 94HA6X02Y; Si:Al = 20) was treated in HNO_3 (Macron Chemicals, 68 – 70 wt%, $20 \text{ cm}^3 \text{ g}^{-1}$) at 433 K for ~ 24 h to remove Al-atoms from the *BEA framework by forming soluble $\text{Al}(\text{NO}_3)_3$. The dealuminated *BEA (Si-BEA-OH) was recovered by vacuum filtration of the warm mixture and then washed with deionized H_2O ($18.2 \text{ M}\Omega \text{ cm}$, Elga Purelab Flex 2, $50 \text{ cm}^3 \text{ g}_{\text{zeolite}}^{-1}$). This process was repeated three times to minimize the amount of residual Al atoms in the framework: the final Si:Al ratios of dealuminated *BEA equaled ~1200. Samples were then dried in an oven at 343 K for 12 h, then heated to 823 K (5 K min^{-1}) in flowing air ($200 \text{ cm}^3 \text{ min}^{-1}$; Airgas, Ultra Zero grade) and held at 823 K for 6 h to remove organic residues. Si-BEA-OH was heated in a round-bottom flask under vacuum ($<5 \text{ Pa}$, 473 K) to create a moisture-free environment, after which dichloromethane (CH_2Cl_2 , Fisher Chemicals, $20 \text{ cm}^3 \text{ g}_{\text{zeolite}}^{-1}$) solvent was added to the flask. Titanium atoms were then incorporated into the framework by adding TiCl_4 to the Si-BEA-OH and CH_2Cl_2 mixture under an inert atmosphere ($50 \text{ cm}^3 \text{ min}^{-1}$ Ar flow). The resulting material (Ti-BEA-OH) was recovered by rotary evaporation and then dried in an oven at 343 K for 12 h. Finally, the sample was heated to 823 K (5 K min^{-1}) in flowing air ($200 \text{ cm}^3 \text{ min}^{-1}$) and held at 823 K for 6 h, resulting in a white powder sample.

Ti-BEA-F was synthesized in fluoride media by following a previous hydrothermal procedure.^{136, 150} Tetraethylammonium fluoride hydrate (TEAF, Sigma-Aldrich, 98%) was dissolved in deionized H₂O (18.2 MΩ cm, Elga Purelab Flex 2) in a polypropylene container. Tetraethylorthosilicate (TEOS, Sigma-Aldrich, >98 wt%) was added to the mixture, and the solution was stirred for 30 min. Titanium (IV) isopropoxide (TIPO, Sigma-Aldrich, 99.999%) was then added to the mixture. The mixture was covered and stirred for an additional 16 h to produce an opaque white homogeneous solution. The cover was then removed, and the solution was stirred for 12 h to evaporate the alcohols that form from the hydrolysis of TEOS (ethanol) and TIPO (isopropanol). The mass of alcohols formed from the hydrolysis processes was calculated based on the masses of TEOS and TIPO added. The solution was allowed to evaporate until the total mass decreased by an amount equal to 115% of the calculated mass of the alcohol coproducts with the intent to remove the vast majority of these alcohols. The alcohols are assumed to evaporate preferentially based on their greater volatility relative to water. A mass of deionized H₂O equivalent to the difference between the total mass evaporated and the calculated mass of alcohols formed was added to account for the H₂O lost during evaporation. The mixture was then transferred to a Teflon liner (Parr Instruments, 125 cm³, Model 4748). The synthesis gel had an approximate molar composition of 1 Si:0.006 Ti:0.56 TEAF:8.89 H₂O. A small amount of Si-BEA-OH seeds (3% by mass relative to SiO₂) from a previous synthesis was added to promote crystallization.

The Teflon liner was loaded into a stainless-steel autoclave (Parr Instruments, 125 cm³, Model 4748) and heated to 413 K at dynamic conditions (60 rpm) in a convection oven for 20 days. The resulting material was recovered by centrifugation, washed with H₂O, and dried in an oven for 12 h at 343 K. The dried solid was heated to 823 K (5 K min⁻¹) in flowing air (200 cm³ min⁻¹) and held at 823 K for 6 h to produce a white powder Ti-BEA-F sample.

2.2.2 Catalyst Characterization

The crystallinities of the Ti-BEA samples were confirmed using an X-ray diffractometer (Bruker, D8 Advance) with Cu K α radiation under ambient conditions. The Ti-BEA were ground into a fine powder and gently pressed into a polypropylene sample holder for the measurements. **Figure A1** (appendix) shows the diffractograms of the Ti-BEA samples, which match previously reported powder diffraction patterns for zeolite BEA.¹⁵¹ These diffractograms confirm that all Ti-BEA samples possess the *BEA zeolite framework.

The titanium (Ti), silicon (Si), and aluminum (Al) contents of the Ti-BEA catalysts were determined with energy-dispersive X-ray fluorescence (EDXRF) and inductively coupled plasma – optical emission spectroscopy (ICP-OES). For EDXRF, finely ground samples of Ti-BEA (~70 mg) were loaded into a polypropylene sample cup (1 cm diameter) sealed with ultralene film. The sample cups were loaded into the He-purged spectrometer (Shimadzu, EDX-7000) chamber. The samples were scanned between 0 and 30 keV, and the intensities of the fluorescence features were used to calculate the mass of Ti, Si, and Al within the sample. The EDXRF measurements show that each Ti-BEA contains only trace quantities of Al (Si:Al ~ 1200). Compositions of the Ti-BEA samples were also assessed by ICP-OES, which confirmed each sample contained negligible quantities of Al (Si:Al > 2500) and possessed quantities of Ti consistent with the results from EDXRF. Titanium loadings for each zeolite are shown in **Table 2.1**.

The dispersity of the Ti-atoms in the Ti-BEA catalysts was measured with diffuse reflectance UV-vis (DRUV-vis) spectroscopy on a UV-vis spectrophotometer (Varian, Cary 5G). Magnesium oxide (MgO, Sigma-Aldrich, 99.9995%) was used as a background, and Ti-BEA samples were mixed and ground with magnesium oxide (MgO) at a MgO:Ti-BEA mass ratio of

Catalyst	Ti wt% ^a	Band Gap (eV) ^b	Φ_{IR} ^c	BET surface area (N ₂) (m ² g ⁻¹) ^d	BET surface area (Ar) (m ² g ⁻¹) ^d	Micropore volume (N ₂) (cm ³ g ⁻¹) ^e	Micropore volume (Ar) (cm ³ g ⁻¹) ^e
Ti-BEA-OH	0.355	4.27	2.25	653	628	0.184	0.172
Ti-BEA-F	0.261	4.32	0.27	528	543	0.166	0.173

Table 2.1. Ti Content, Band Gap, Relative Hydrophilicity, Surface Area, and Micropore Volume of Synthesized Ti-BEA.

^a Measured by EDXRF (ICP-OES yielded Ti loadings within 0.03% of EDXRF). ^b Determined from leading edge of TAUC plot from DRUV-vis. ^c Determined from FTIR spectra of dehydrated Ti-BEA samples. ^d Determined from N₂ and Ar physisorption. ^e Calculated using the *t*-plots from N₂ and Ar physisorption.

10:1 to measure sample spectra. The total reflectance spectra were measured under ambient conditions, and the band gap energies (**Table 2.1**) were determined by extrapolating the linear portion of the Tauc plots to the horizontal axis representing photon energy (eV) (**Figure A2**).

The relative density of silanol ((SiOH)_x) groups within the Ti-BEA catalysts was measured using infrared spectroscopy. Catalyst pellets (~50 mg) were loaded into a transmission cell configured with CaF₂ windows. The transmission cell was connected to a temperature controller and gas manifold, then loaded into a Fourier-transform infrared spectrometer (Bruker, Vertex 70) with a liquid N₂-cooled HgCdTe detector.¹⁵²⁻¹⁵³ The cell was first heated to 573 K at ~5 K min⁻¹ and held for 2 hours in flowing He (50 cm³ min⁻¹, 99.997%, Airgas) to desorb any water and volatile compounds. Infrared spectra (128 scans, 1 cm⁻¹) of the Ti-BEA samples were then taken at 573 K (**Figure A3**). Background spectra were obtained with the empty transmission cell at identical conditions. The vibrational modes on the dehydrated Ti-BEA spectra between 3300-3750 cm⁻¹ and 1800-2100 cm⁻¹ represent O-H and Si-O-Si features¹⁵⁴, respectively. The sharp feature at 3740 cm⁻¹ represents isolated SiOH groups that do not interact with other SiOH groups.¹⁵⁵⁻¹⁵⁶ The broader features from 3700 to 3350 cm⁻¹ represent defects containing multiple interacting (SiOH)_x groups.¹⁵⁵⁻¹⁵⁶ The ratio of the areas of the O-H stretch and Si-O-Si overtone stretches at 1865 and 2000 cm⁻¹ gives a relative measure of (SiOH)_x density in each Ti-BEA (Φ_{IR}):

$$\Phi_{IR} = \frac{A_{v(O-H)}}{A_{v(Si-O-Si)}} \quad (2.1)$$

The area of the isolated SiOH feature is excluded from the O-H area in Φ_{IR} calculations. The values of Φ_{IR} in **Table 2.1** show that Ti-BEA-OH contains a much greater density of (SiOH)_x groups than Ti-BEA-F. A full procedure for the calculation of Φ_{IR} is included in **Appendix Section A1.3**.⁷⁴

Ex situ Raman spectra of the Ti-BEA catalysts were measured with a Raman spectrometer (Renishaw, InVia) equipped with a 532 nm laser. The delivered power density was approximately 2 mW μm^{-2} as measured by a power meter (Gentec-EO, PRONTO-SI). The measurements were performed at ambient conditions on pressed catalyst pellets. The accumulation time was 20 s per scan, and each Raman spectra (**Figure A6**) was calculated by averaging 10 scans.

The surface area and micropore volumes of each Ti-BEA were determined using gas-phase adsorption isotherms of N₂ (77 K) and Ar (87 K), collected on a volumetric adsorption instrument (Micromeritics, 3Flex). The Ti-BEA samples were pelletized and sieved to retain particles from 100 – 250 μm in diameter. The samples were degassed by heating to 673 K under vacuum (<0.0007 kPa) for 3 h before the adsorption measurement. The surface area was calculated using the Rouquerol-modified Brunauer-Emmett-Teller (BET) method,¹⁵⁷ and the micropore volume was determined from the *t*-plot method.¹⁵⁸ The N₂ and Ar isotherms are shown in **Figure A7**, along with external surface areas and total pore volumes for each Ti-BEA in **Table A2**.

Collectively, the characterization results outlined here indicate that the Ti-BEA zeolites contain atomically dispersed Ti-atoms within a crystalline *BEA framework. From the measured atomic ratios of Si to Al in the original Al-BEA-20 material and the Si to Ti ratio in the final materials, both zeolites contain ~1 Ti-atom per 4 *BEA unit cells and Ti-BEA-OH contains an average of ~2.75 silanol nests ((SiOH)_x) per unit cell (see **Appendix Section A1.6**).

2.2.3 Epoxidation Turnover Rate Measurements

Turnover rates for 1-hexene (C_6H_{12} , Sigma-Aldrich, >99%), 1-octene (C_8H_{16} , Sigma-Aldrich, 98%), 1-decene ($C_{10}H_{20}$, TCI Chemicals, >95%), 1-dodecene ($C_{12}H_{24}$, Sigma-Aldrich, >99%), 1-tetradecene ($C_{14}H_{28}$, Sigma-Aldrich, >97%), 1-hexadecene ($C_{16}H_{32}$, TCI Chemicals, 99%), and 1-octadecene ($C_{18}H_{36}$, Sigma-Aldrich, >99.5%) epoxidation with aqueous hydrogen peroxide (H_2O_2 , Fisher Chemical, 30 mol% in H_2O) in acetonitrile (CH_3CN , Fisher Chemical, HPLC Grade) solvent were measured at low temperatures (308-338 K) in batch reactors stirred at 700 rpm. The alkene, benzene as an internal standard (Sigma-Aldrich, thiophene-free, >99%), H_2O_2 , and H_2O (18.2 M Ω cm, Elga Purelab Flex 2) were stirred in CH_3CN for 30 minutes before an initial aliquot (~500 μ L) was taken. Ti-BEA (~15-45 mg) was then added, and aliquots were taken as a function of time using a syringe equipped with a polypropylene filter (Tisch Scientific, 0.22 μ m) to separate the sample from the catalyst particles. The concentrations of alkene, benzene standard, and epoxide product were quantified with a gas chromatograph (Agilent, 6850) equipped with a flame ionization detector and liquid autosampler (CTC Analytics, GC Pal). All reported results were measured at differential conversion (<5%), and the uncertainty for the measurements is ~10%, as shown with replicated measurements. The conditions used for rate measurements in this study avoid issues with internal mass transfer constraints, as indicated by the linear dependence of turnover rates on alkene concentration (**Section 2.3.1**).¹⁵⁹ A mass-transfer limited material would likely show a sublinear dependence on alkene concentration at all concentrations because the average concentration of alkenes throughout the pores would be a non-linear function of the fluid-phase alkene concentration.

Reactions were carried out with either 200 mM or <3 mM H_2O present. For the experiments with <3 mM H_2O , CH_3CN and H_2O_2 were dried over combinations of $MgSO_4$ (Fisher Chemical,

>98%) and CaSO₄ (Alfa Aesar, 99%) prior to the reactions, yielding solutions with an estimated H₂O concentration below 3 mM. The drying procedure is detailed in **Appendix Section A5**.

2.2.4 Isothermal Titration Calorimetry

The heats released upon adsorption of 1,2-epoxyhexane (C₆H₁₂O, TCI Chemicals, >96%), 1,2-epoxydecane (C₁₀H₂₀O, TCI Chemicals, >97%), 1,2-epoxytetradecane (C₁₄H₂₈O, TCI Chemicals, >95%), and 1,2-epoxyoctadecane (C₁₈H₃₆O, TCI Chemicals, >85%) were measured with an isothermal titration calorimeter (ITC) (TA Instruments, NanoITC) equipped with sample and reference cells.

A multi-step cleaning procedure was performed to prepare the ITC cell for each experiment. A cleaning solution (75 volume percent 1 M NaOH, 20 volume percent methanol, 5 volume percent soap) was first injected into the sample cell and left for 5 minutes at room temperature. The sample cell was then rinsed with 500 cm³ of DI H₂O (18.2 MΩ cm, Elga Purelab Flex 2). Next, a 4 M NaOH (VWR, 10 N) solution was left in the cell for 2 hours at 353 K, followed by another rinse with 500 cm³ of DI H₂O. Finally, the cell was treated with a solution of 4 M HNO₃ (Macron Chemicals, 68 – 70 wt%) for 2 hours at 353 K, then a third rinse with 500 cm³ of DI H₂O. The sample cell, reference cell, and 50 μL ITC syringe were then filled with H₂O, and the syringe was loaded into the instrument. An electrical calibration was performed on the instrument after this, in which the instrument used sequential pulses to confirm a constant temperature was maintained when heat was added to the system. Finally, pure DI H₂O was injected into DI H₂O to ensure that the sample cell was clean enough to begin experiments. The cell was assumed to be clean when the H₂O to H₂O injections evolved between -3 μJ to +3 μJ for each injection of 1 μL. The entire cleaning procedure was repeated if the H₂O-H₂O injection did not give sufficiently low heat changes.

In a typical experiment, a slurry of ~20 mg of Ti-BEA in CH₃CN with one of three different H₂O concentrations (<3 mM, 39 mM, or 200 mM H₂O) was titrated by a solution of epoxide (1 – 5 mM) in CH₃CN with an equal concentration of H₂O (<3 mM, 39 mM, or 200 mM H₂O). The highest and lowest H₂O concentrations were chosen to match conditions for kinetic turnover rate and activation barrier measurements (**Sections 2.3.1** and **2.3.2**). The titrations were carried out at 313 K with a stirring rate of 250 rpm. The enthalpies of epoxide adsorption were calculated by averaging the integrated heats released upon adsorption of the epoxides to Ti-BEA sites from a 1 μ L injection of titrant at low coverages (<0.2 mol epoxide (mol Ti)⁻¹). The heats released in this low coverage regime remain approximately constant, suggesting that the calculated enthalpies represent the isosteric adsorption enthalpies for each epoxide.⁷³

2.2.5 ¹H NMR Spectroscopy

H₂O uptakes in Ti-BEA-OH and Ti-BEA-F were calculated from peak areas obtained with a ¹H NMR spectrometer (UNITY, INOVA 500 NB). For each data point, an aliquot (~250 μ L) of CH₃CN and H₂O was taken from a solvent solution (5 cm³) before and after 2 h contact with a Ti-BEA sample (~500 mg) at a stirring rate of 250 rpm to measure the change in the bulk liquid-phase concentration. The sample of CH₃CN and H₂O was then mixed with deuterated methanol as solvent and acetone as an internal standard to prepare the NMR sample. The final composition of the bulk liquid was determined using areas of ¹H-NMR features for H₂O (4.5 ppm), acetone (2.2 ppm), and CH₃CN (2.1 ppm). The H₂O uptakes were calculated experimentally (solid points) from the difference in bulk liquid-phase concentration before and after contacting the solvent with catalyst (see **Appendix Section A2**).

2.2.6 Transmission Infrared Spectroscopy

Transmission infrared spectroscopy of zeolite samples in contact with flowing streams of gas was conducted to determine the quantities of CH₃CN adsorbed within the catalyst pores. The H₂O uptakes from ¹H NMR were calculated by taking the relative differences between H₂O and CH₃CN bulk liquid concentrations (see **Appendix Section A2**), meaning that CH₃CN uptakes cannot be computed from the ¹H NMR measurements. Therefore, vapor phase CH₃CN adsorption experiments were performed to examine the quantities of CH₃CN that Ti-BEA-OH and Ti-BEA-F adsorb under anhydrous conditions. The extinction coefficient of CH₃CN was first measured with an empty transmission cell equipped with CaF₂ windows connected to a gas manifold (see **Section 2.2.2**). The cell was heated to 573 K at ~5 K min⁻¹ and held at 573 K for 0.5 h in flowing He (22.6 cm³ min⁻¹) to desorb water molecules and volatile species. The cell was cooled to 313 K, where a background spectrum was taken without flowing CH₃CN. Subsequently, spectra of gaseous CH₃CN were acquired at 313 K (4 cm⁻¹ resolution, 128 scans) with flowing CH₃CN in He (0.008 - 19.8 kPa CH₃CN, 23 ~ 226 cm³ min⁻¹). The procedure to calculate the extinction coefficient of the ν(C≡N) feature for gaseous CH₃CN and the calculations to determine the average number of CH₃CN contained per unit cell of *BEA are described in **Appendix Section A3**.

Ti-BEA (60 ~ 70 mg) was then pressed into a self-supporting disk and loaded into the cell. The cell was again heated and held at 573 K to desorb water and volatile species. Infrared spectra of the pellets were acquired at 573 K (4 cm⁻¹ resolution, 128 scans, 22.6 cm³ min⁻¹ He flow), which provided the intensity of the ν(Si-O-Si) features used to normalize CH₃CN uptake values. The cell was then cooled to 313 K, where a background spectrum was again taken without flowing CH₃CN. The peak areas of ν(C≡N) were measured at the same feed pressures of CH₃CN as with the empty

cell measurement above, and the areas were converted to CH₃CN uptakes per unit cell as described in **Appendix Section A3**.

The turnover rate, ITC, and ¹H NMR values reported in this text signify mean values, with the depicted error bars representing uncertainties corresponding to one standard deviation of the reported values. The uncertainties for the computational measurements, described in **Appendix Section A20**, are calculated in the same manner as experimental values.

2.2.7 Computational Details

Flexible-framework molecular dynamics simulations in a grand canonical (μ VT) ensemble¹⁶⁰⁻¹⁶¹ (i.e., Grand Canonical Molecular Dynamics, GCMD) were carried out using XSEDE resources¹⁶² to quantify solvent composition in Ti-BEA pores, compute the enthalpy of epoxide adsorption, and elucidate key factors explaining the trend. The Ti-BEA-F structure was built using the BEA crystallographic structure adopted from the IZA zeolite database.¹⁶³ Ti-BEA-F was modeled using a 2×2×1 supercell (containing 255 Si and 512 O-atoms with lattice parameters a=25.26, b=25.26, and c=26.17 Å) with a single Ti-atom substituted at an energetically favored T2 site¹⁶⁴⁻¹⁶⁵ exposed to the pore, as shown in **Figure 2.1**. The Ti-BEA-OH structures were generated from Ti-BEA-F by random insertion of 11 (SiOH)₄ sites into the supercell (the value of

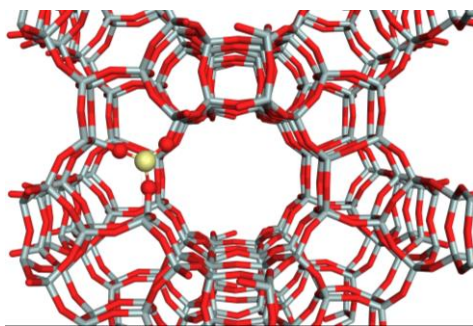


Figure 2.1. Ti-atom (yellow) is inserted at a T2 site and exposed to the pore to enable interaction with epoxide molecules. Oxygen and silicon atoms are represented by red and silver.

x is set as 4 for (SiOH)_x in the model). The density of (SiOH)₄ defects (2.75 defects or 11 OH groups per unit cell) closely resembles the experimental value. In addition, the Si:Ti ratio of the model structures (255) approximates that of the synthesized zeolites (223 for Ti-BEA-OH, 304 for Ti-BEA-F). We selected three Ti-BEA-OH structures out of 1000 randomly generated configurations as the most representative of synthesized zeolite samples using a procedure and selection criteria described in detail (**Appendix Section A12**).

Bonded interactions (bonds, angles, dihedrals) were described using CHARMM force field (FF) parameters developed for silica and silica/water interfaces.¹⁶⁶ We set Ti–O bonded parameters to be identical to Si–O parameters. Since the *BEA structure is rigid and local deformations are small, this assumption should have a negligible effect on simulation results. The non-bonded parameters for Si and framework O-atoms were taken from the P2 parameter set developed by Li et al.¹⁶⁷ This parameter set is accurate for describing non-bonded contributions to adsorption enthalpies of polar and nonpolar molecules in H-MFI and H-BEA zeolites and accurately reproduces experimental enthalpies of adsorption using quantum mechanics/molecular mechanics calculations.¹⁶⁷ The electrostatic and Lennard-Jones parameters for (SiOH)₄ groups were taken from Emami et al.¹⁶⁸ A universal force field (UFF)¹⁶⁹ was used to treat non-bonded interactions of the Ti-atom. Epoxides, water, and acetonitrile were described using the CHARMM General Force Field¹⁷⁰⁻¹⁷² (CGenFF). Standard Lorentz-Berthelot combining rules were employed. The charge imbalance due to multiple force fields was distributed evenly among all Si and O atoms in the framework, resulting in a very minor change in atomic charges (0.00245e). A cut-off of 10 Å was used for both electrostatic and van der Waals potentials. Electrostatic interactions were handled using the Ewald summation method.¹⁷³

The adsorption of epoxides ($C_6H_{12}O$, $C_{10}H_{20}O$, $C_{14}H_{28}O$, $C_{18}H_{36}O$) used in ITC measurements (**Section 2.2.4**) was examined. The epoxide molecules were formally treated as part of the flexible framework in simulations. The initial configuration of the epoxide was manually generated by placing the molecule parallel to the pore channel and the O-atom next to Ti. An artificial Lennard-Jones bond with a potential well depth (ϵ) of 125.52 kJ mol⁻¹ and a potential minimum (r_0) of 2.5 Å was used to represent the bonding between Ti and the O-atom of the epoxide. These values are based on earlier studies.^{120, 174} The artificial tether keeps an epoxide molecule near Ti, as the UFF model cannot describe the dative (donor-acceptor) interaction between O and Ti. Subsequently, the tether contribution to energy is removed from each trajectory when calculating the enthalpy of adsorption by re-computing the artificial LJ bond energy at each step and subtracting it from the total energy of the system before averaging.

GCMD simulations were carried out using RASPA¹⁷⁵ software at 313 K at 1 bar with a timestep of 0.5 fs. The simulated open system was equilibrated either with pure CH₃CN or 200 mM H₂O in CH₃CN. Fugacity coefficients (0.264 for CH₃CN and 1.37 for H₂O) were computed using the procedure described in **Appendix Section A14**. Additional details on GCMD simulations are given in **Appendix Section A24**.

Radial distribution functions (RDFs, $g(r)$) were computed to study the spatial distribution of solvent structure near (SiOH)₄ defects. VMD¹⁷⁶⁻¹⁷⁷ was used to generate RDF graphs with periodic boundary conditions. RDF at a distance r is defined as:

$$g(r) = \lim_{dr \rightarrow 0} \frac{\rho(r)}{4\pi(\frac{N_{pairs}}{V})r^2 dr} \quad (2.2)$$

where r is the distance between two particles in a pair, $\rho(r)$ is the average number of atom pairs found in a shell between r and $r + dr$, V is the volume of the system, and N_{pairs} is the number of

unique pairs of atoms. In a periodic simulation cell, $g(r) = 1$ corresponds to the average density of particles (such as molecules' centers of masses and geometric centers of defects) inside the cell in the absence of spatial correlations.

Energy decomposition analysis with the Born-Haber cycle was carried out to quantify contributions from solvent displacement, epoxide-solvent, and epoxide-zeolite interactions to adsorption enthalpy trends. Due to software limitations, μ VT enthalpy components were approximated with their NVT ensemble values. The approximation changed absolute adsorption enthalpy values but had minimal impact on the overall trends (**Figure A31**). Energy terms were computed using molecular dynamics for all epoxide systems. The 1 ns-long equilibration was followed by the 4 ns production run. Starting configurations were carefully selected from the previous GCMD production runs and contained integer numbers of adsorbed solvent molecules closest to the fractional GCMD uptake values. A detailed description of the enthalpy decomposition analysis is provided in **Section 2.3.6** and **Appendix Section A17**.

2.3 Results and Discussion

2.3.1 Epoxidation Kinetics over Ti-BEA Catalysts

Figure 2.2 demonstrates that turnover rates for alkene epoxidation depend strongly on the carbon number of the alkene (C_nH_{2n}), the concentration of H_2O ($[H_2O]$, where brackets denote the concentration of a species) in the CH_3CN solvent, and the $(SiOH)_x$ density of the Ti-BEA catalyst. Together these differences may imply that excess free energies (G^E) of reactive intermediates or transition states reflect these three properties. Ti-BEA-OH gives epoxidation rates 40–450 times greater than Ti-BEA-F across the full range of alkenes examined under aqueous conditions (0.5 mM C_nH_{2n} , 10 mM H_2O_2 , 200 mM H_2O , 313 K). Rates achieve a maximum with changes in carbon

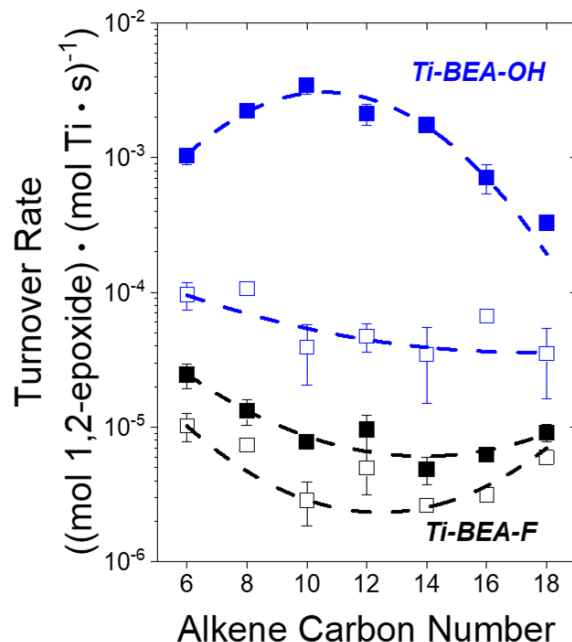


Figure 2.2. Turnover rates for epoxide formation as a function of alkene carbon number for C₆ to C₁₈ alkenes (0.5 mM alkene, 10 mM H₂O₂, < 3 mM (□, □) or 200 mM (■, ■) H₂O, CH₃CN solvent, 313 K) over Ti-BEA-OH (blue) and Ti-BEA-F (black).

number for C₁₀H₂₀ over Ti-BEA-OH and C₆H₁₂ over Ti-BEA-F at these conditions. Turnover rates for all alkenes and in both forms of Ti-BEA are significantly lower in nearly anhydrous conditions (0.5 mM C_nH_{2n}, 10 mM H₂O₂, <3 mM H₂O, 313 K). **Figure 2.2** shows that Ti-BEA-OH gives larger differences in turnover rates between aqueous and anhydrous conditions (10-90 times) than Ti-BEA-F (1.5-3 times). The water concentration in mixtures with organic co-solvents also affects rates of zeolite-catalyzed reactions by orders of magnitude in other systems, including alcohol dehydration¹¹² and hydrolysis¹¹⁴ over Brønsted acid zeolites and glucose isomerization¹⁷⁸ over Na-exchanged zeolites. The differences in rates caused by changes in alkene carbon number noticeably differ between Ti-BEA-OH in the presence of 200 mM H₂O and the other three sets of data, which reveals the impact of [H₂O] also depends on the (SiOH)_x density of the zeolite and the size of the alkene reagent. Overall, the different dependences of epoxidation rates on alkene carbon number, [H₂O], and zeolite (SiOH)_x density may result from a change in a kinetically relevant step,

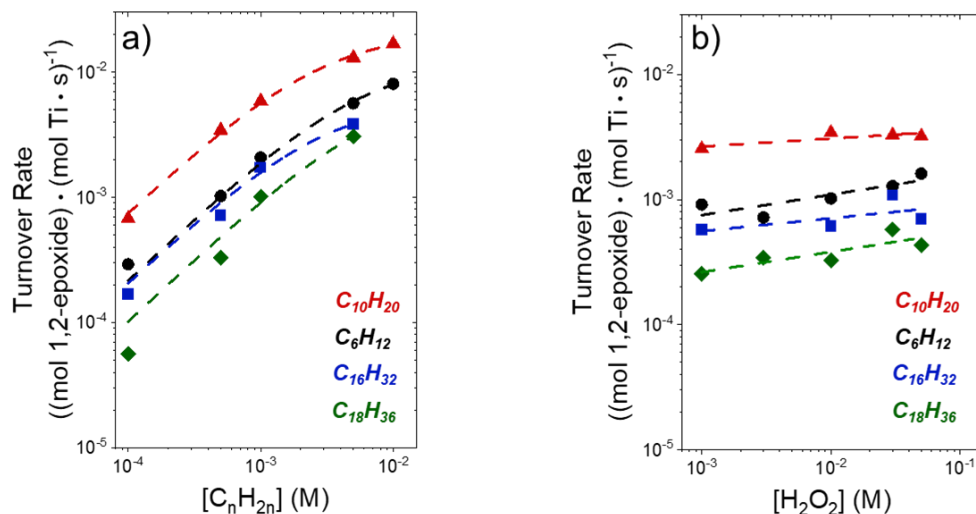
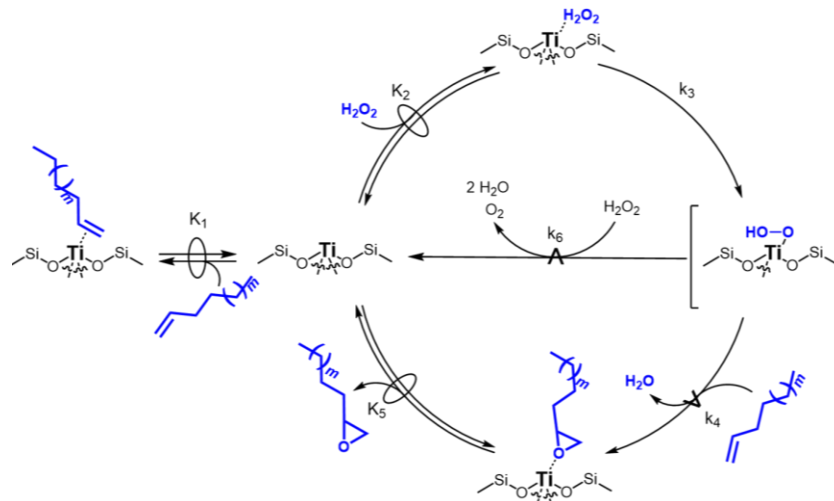


Figure 2.3. Turnover rates for epoxide formation as a function of a) C_nH_{2n} concentration (10 mM H_2O_2 , 200 mM H_2O) and b) H_2O_2 concentration (0.5 mM C_nH_{2n} , 200 mM H_2O) for primary n-alkenes (C_6H_{12} (●), $C_{10}H_{20}$ (▲), $C_{16}H_{32}$ (■), $C_{18}H_{36}$ (◆)) over Ti-BEA-OH in CH_3CN solvent at 313 K. Comparable measurements for Ti-BEA-F in **Appendix Section A6**.

coverages of reactive species, electronic structure differences in alkene or transition state stability caused by inductive effects, or excess contributions due to interactions between reactants and solvent molecules (*vide infra*).

Epoxidation turnover rates depend on the concentrations of the alkene, oxidant (H_2O_2), and epoxide product because these concentrations determine the coverage of surface species formed during catalysis. **Figure 2.3a** shows that turnover rates depend linearly on the concentration of the alkene ($r \sim [C_nH_{2n}]^1$) at low ratios of $[C_nH_{2n}]$ to $[H_2O_2]$ for all alkenes examined here. In comparison, rates at higher ratios of $[C_nH_{2n}]$ to $[H_2O_2]$ show a weak dependence on $[C_nH_{2n}]$. **Figure 2.3b** shows that turnover rates do not change with $[H_2O_2]$ ($r \sim [H_2O_2]^0$) at low ratios of $[C_nH_{2n}]$ to $[H_2O_2]$. Ti-BEA-F provides turnover rates that show similar rate dependencies as Ti-BEA-OH (**Appendix Section A6** presents data for Ti-BEA-F). Previous studies showed that turnover rates depend weakly on $[C_nH_{2n}]$, scale linearly with $[H_2O_2]$, and depend inversely on epoxide concentration ($[C_nH_{2n}O]$) at sufficiently high ratios of $[C_nH_{2n}]$ to $[H_2O_2]$ (i.e.,



Scheme 2.1. Proposed mechanism for alkene epoxidation with H_2O_2 and H_2O_2 decomposition on Ti-BEA catalysts in aqueous acetonitrile. $\rightleftharpoons$ denotes a quasi-equilibrated step, while $\xrightarrow{\text{A}}$ signifies kinetically relevant steps for formation of distinct products. Here, values of m equal $(n - 5)$, where n is equal to the total carbon number in the alkene. Solvent molecules are omitted for clarity.

$[\text{C}_n\text{H}_{2n}]:[\text{H}_2\text{O}_2] > 3$).³⁰⁻³¹ The dependence of turnover rates on reactant concentrations for C_6 - C_{18} alkenes over Ti-BEA materials (**Figure 2.3**) closely resembles that observed for epoxidation of C_6 to C_{10} linear alkenes over groups 4-6 metal-substituted *BEA,^{30, 74, 85, 179} Ti-MFI,⁷⁶ and Ti atoms supported on metal oxides.¹⁸⁰

Scheme 2.1 presents a system of elementary steps that lead to rate expressions that explain the distinct kinetic regimes in **Figure 2.3** and can account for turnover rates that depend upon the structure of alkenes, the $[\text{H}_2\text{O}]$, and $(\text{SiOH})_x$ densities. The epoxidation of alkenes involves the quasi-equilibrated adsorption of C_nH_{2n} (step 1) or H_2O_2 (step 2). Adsorbed H_2O_2 then activates irreversibly (in aprotic solvents) to form Ti-hydroperoxo (Ti-OOH)^{30, 181-186} and -peroxo ($\text{Ti-(}\eta^2\text{-O}_2\text{)}$)^{30, 32, 185-186} intermediates (step 3). For brevity, the combined pool of Ti-OOH and $\text{Ti-(}\eta^2\text{-O}_2\text{)}$ intermediates are described as Ti-OOH moving forward. Previous findings indicate that within these pools, Ti-OOH intermediates specifically react with alkenes for epoxidations over titanosilicate catalysts.^{30, 32, 185, 187-188} Ti-OOH intermediates react by kinetically relevant processes

that involve a C_nH_{2n} molecule to form an epoxide (step 4) or with a second equivalent of H_2O_2 to evolve H_2O and O_2 (step 6). The formed epoxide undergoes quasi-equilibrated desorption to form the 1,2-epoxide ($C_nH_{2n}O$) product (step 5) and complete the cycle. Each kinetic regime involves kinetically relevant O-atom transfer from Ti-OOH to C_nH_{2n} ; however, the identity of the most abundant reactive intermediates (MARI) distinguishes the two regimes. At low ratios of $[C_nH_{2n}]$ to $[H_2O_2]$, Ti-OOH intermediates saturate sites. While at high ratios of $[C_nH_{2n}]$ to $[H_2O_2]$, the epoxide products ($C_nH_{2n}O$) cover sites. The rate expression for the formation of the epoxide product may be derived by first describing the rate of the kinetically relevant step (r_4) :

$$r_{epox} = r_4 = k_4[Ti-OOH][C_nH_{2n}] \quad (2.3)$$

where k_4 is the rate constant for step 4 (**Scheme 2.1**), and $[Ti-OOH]$ is the number of Ti-OOH intermediates. A full derivation of the rate mechanism for epoxidation is included in **Appendix Section A7**. When Ti-OOH intermediates dominate sites (low ratios of $[C_nH_{2n}]$ to $[H_2O_2]$) and represent the MARI, $[Ti-OOH]$ equals the total number of active sites ($[L]$), and the rate expression simplifies to:

$$\frac{r_{epox}}{[L]} = k_4[C_nH_{2n}] \quad (2.4)$$

Equation 2.4 matches the observed first-order dependence of epoxidation turnover rates on $[C_nH_{2n}]$ (**Figure 2.3a**) and the independence of these rates on $[H_2O_2]$ (**Figure 2.3b**) when ratios of $[H_2O_2]$ to $[C_nH_{2n}]$ exceed 10. These similarities strongly suggest that epoxidation proceeds through the same reaction mechanism across the full range of alkenes and catalysts studied here. Therefore, the differences in turnover rates between alkenes, zeolites, and values of $[H_2O]$ likely do not result from changes in dominant surface intermediates, reaction pathways, or kinetically relevant steps. Yet, turnover rates differ by factors of 4–12 between $C_{10}H_{20}$ and $C_{18}H_{36}$ and across

the range of [H₂O]. Consequently, these differences likely stem from different values of the apparent rate constants that reflect changes in the stability of reactive species.

Previous studies showed that solvent networks within zeolite pores affect rates and apparent activation barriers for alkene epoxidation with H₂O₂,^{72, 74, 76} glucose isomerization,^{109, 132, 135-138, 178, 189-190} transfer hydrogenation,¹³³ and alcohol dehydration.^{99, 147, 191-193} The comparisons between epoxidation turnover rates between aqueous and anhydrous solutions of CH₃CN and over Ti-BEA-OH and Ti-BEA-F (**Figure 2.2**) show that the solvent composition affects this chemistry significantly. Having excluded mechanistic differences and mass transfer limitations, we postulate that the differences observed between turnover rates (**Figure 2.2, Figure 2.3**) result from solvent-mediated interactions between the epoxidation transition state and the surrounding void space. These interactions likely modify activation parameters for the epoxidation reaction.

2.3.2 Activation Barriers Depend on (SiOH)_x Density, [H₂O], and Alkene Carbon Number

Activation enthalpies ($\Delta H_{app}^\ddagger$) and entropies ($\Delta S_{app}^\ddagger$) increase as monotonic functions of alkene carbon number in both Ti-BEA-OH and Ti-BEA-F in aqueous solutions (0.5 mM C_nH_{2n}, 10 mM H₂O₂, 200 mM H₂O) (**Figure 2.4a**). These differences likely signify that longer alkyl chains disrupt more solvent molecules in Ti-BEA pores and increase enthalpy and entropy gains. **Figure 2.4a** also shows that Ti-BEA-OH gives more positive values of $\Delta H_{app}^\ddagger$ and $\Delta S_{app}^\ddagger$ than Ti-BEA-F for each alkene. Ti-BEA-OH gives apparent activation free energy ($\Delta G_{app}^\ddagger$) values 10 – 16 kJ mol⁻¹ less than Ti-BEA-F for any given alkene shown in **Figure 2.4a**, which demonstrates that gains in $\Delta S_{app}^\ddagger$ give rise to greater turnover rates over Ti-BEA-OH. Additionally, the values of $\Delta H_{app}^\ddagger$ and $\Delta S_{app}^\ddagger$ depend more strongly on carbon number in Ti-BEA-OH. These values show

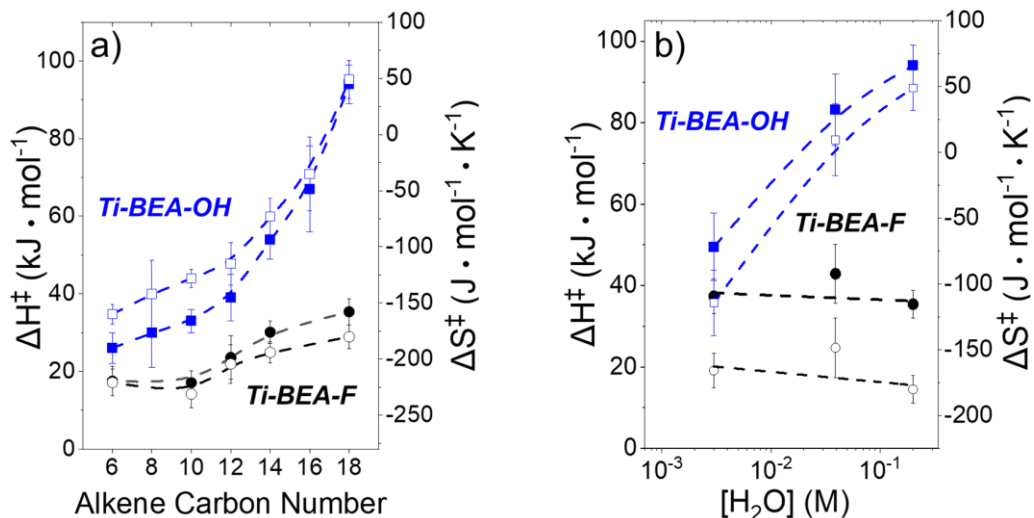


Figure 2.4. Apparent activation enthalpies ($\blacksquare, \bullet$) and entropies ($\square, \circ$) for C_nH_{2n} epoxidation as a function of a) C_nH_{2n} carbon number for C_6 to C_{18} alkenes (0.5 mM C_nH_{2n} , 10 mM H_2O_2 , 200 mM H_2O , CH_3CN solvent, 308–338 K) and b) $[H_2O]$ for $C_{18}H_{36}$ (0.5 mM $C_{18}H_{36}$, 10 mM H_2O_2 , CH_3CN solvent, 308–338 K) over Ti-BEA-OH (blue) and Ti-BEA-F (black).

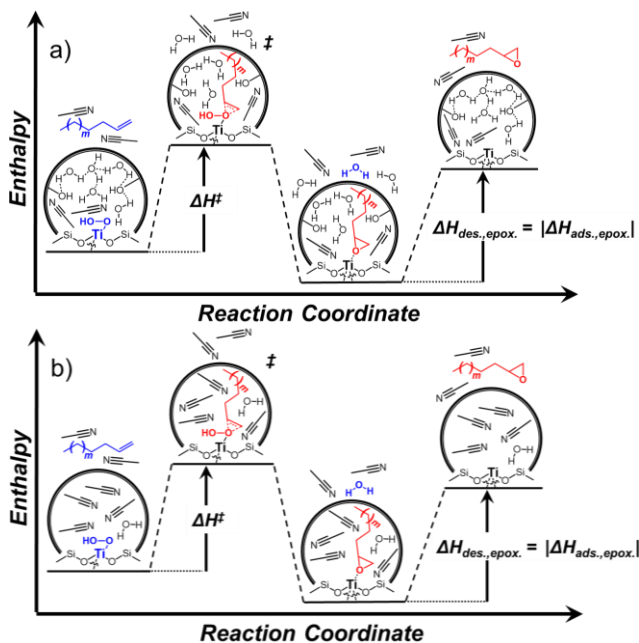
respective differences between C_6H_{12} and $C_{18}H_{36}$ of 68 $\text{kJ} \cdot \text{mol}^{-1}$ and 209 $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ in Ti-BEA-OH and 18 $\text{kJ} \cdot \text{mol}^{-1}$ and 41 $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ in Ti-BEA-F. The stronger dependences in Ti-BEA-OH may partially occur because hydrophilic zeolites adsorb greater quantities of H_2O than hydrophobic zeolites, as demonstrated from adsorption experiments from H_2O vapor.^{74, 134–136} This idea agrees with trends among $\Delta H_{app}^\ddagger$ and $\Delta S_{app}^\ddagger$ values as functions of $[H_2O]$ (Figure 2.4b). When the concentration of H_2O is reduced from 200 mM to < 3 mM H_2O , $\Delta H_{app}^\ddagger$ and $\Delta S_{app}^\ddagger$ for $C_{18}H_{36}$ epoxidation decrease by 45 $\text{kJ} \cdot \text{mol}^{-1}$ and 163 $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for Ti-BEA-OH but vary negligibly for Ti-BEA-F. Overall, the differences in $\Delta H_{app}^\ddagger$ and $\Delta S_{app}^\ddagger$ in Figure 2.4 may reflect changes in the stability of the liquid-phase alkenes, Ti-OOH intermediate, or epoxidation transition state.

Turnover rates for epoxidations follow a rate expression (Equation 2.3) that indicates that $\Delta H_{app}^\ddagger$, $\Delta S_{app}^\ddagger$, and $\Delta G_{app}^\ddagger$ values reflect the difference between the stability of the transition state complex and the combined stabilities of the fluid-phase alkene and the Ti-OOH that exists as

the MARI. **Scheme 2.2** depicts reaction coordinates that portray the anticipated changes in enthalpy as the alkene adsorbs to form the transition state with Ti-OOH, the epoxide product forms (step 4), and the epoxide desorbs from the pores (step 5). These processes intuitively require the reorganization of solvent molecules near active sites in response to the formation of the transition state and upon the desorption and departure of the epoxide product. The distinctions among (SiOH)_x densities of Ti-BEA-OH (**Scheme 2.2a**) and Ti-BEA-F (**Scheme 2.2b**) lead to differences between the density of H₂O molecules within the pores, which may contribute to excess free energies. Consequently, values of $\Delta G_{app}^\ddagger$ can be written as:

$$\Delta G_{app}^\ddagger = (G_i^{\ddagger,0} + G_i^{\ddagger,\varepsilon}) - (G_{alkene}^0 + G_{alkene}^\varepsilon) - (G_{Ti-OOH}^0 + G_{Ti-OOH}^\varepsilon) \quad (2.5)$$

where the free energy for each species *i* equals the sum of the standard state free energy (G_i^0) and excess (G_i^ε) contribution. G_i^0 and G_i^ε represent partial molar properties for a species *i*, not total molar properties for the system. Analogous expressions describe the corresponding apparent



Scheme 2.2. Reaction coordinate diagram for alkene epoxidation over a) Ti-BEA-OH, and b) Ti-BEA-F in acetonitrile + H₂O solvent. The alkene adsorbs into the pore and reacts with the Ti-OOH MARI to form the epoxide. The epoxide then desorbs to complete the cycle.

activation enthalpies and entropies ($\Delta H_{app}^{\ddagger}$, $\Delta S_{app}^{\ddagger}$). Values for G_i^{ε} relate to the activity coefficient of the same species (γ_i):

$$G_i^{\varepsilon} = RT * \ln (\gamma_i) \quad (2.6)$$

The excess free energies equal zero for ideal solutions (i.e., the activity coefficient equals one) but deviate significantly in non-ideal solutions and at solid-liquid interfaces, where intermolecular forces differ from pure components.³⁹

Equation 2.5 shows that differences in turnover rates and activation barriers must result from changes in standard state or excess free energies of the species involved. The standard state free energies of the reactive species (G_{alkene}^0 , G_{Ti-OOH}^0 , $G^{\ddagger,0}$) do not depend on the solvent environment or zeolite polarity; therefore, these terms cannot account for differences between epoxidation rates or barriers for Ti-BEA-OH and Ti-BEA-F. Moreover, the Ti-OOH intermediate remains the MARI for all alkenes studied, so the differences in kinetics among n-alkenes upon a single catalyst (**Figure 2.4**) cannot be attributed to values of G_{Ti-OOH}^0 . Values of G_{alkene}^0 correspond to the free energy of formation of the respective alkene. The formation free energy increases by $\sim 8 \text{ kJ mol}^{-1}$ for each $-\text{CH}_2$ unit added across the full range of alkenes (**Section A10**).¹⁹⁴ Assuming that the respective epoxide products show similar scaling (i.e., group additivity principles hold), the free energy of epoxidation remains nearly constant for all alkenes used here. This likely excludes the contributions of both G_{alkene}^0 and $G^{\ddagger,0}$ to differences in rates.

Such arguments suggest that the differences among values of $\Delta H_{app}^{\ddagger}$ and $\Delta S_{app}^{\ddagger}$ in **Figure 2.4** stem from differences in excess free energies (G_{alkene}^{ε} , G_{Ti-OOH}^{ε} , $G^{\ddagger,\varepsilon}$). Values of G_{alkene}^{ε} reflect the composition of the bulk liquid-phase and do not depend on the properties of the zeolite, and therefore, this quantity cannot cause differences between values of $\Delta H_{app}^{\ddagger}$ and $\Delta S_{app}^{\ddagger}$ for the

epoxidation of individual alkenes over Ti-BEA-OH and Ti-BEA-F. In addition, $G_{alkene}^{\ddagger,\epsilon}$ cannot lead to differences in the span of values for activation barriers among alkenes on each catalyst. The competing H_2O_2 decomposition pathway offers a way to examine $G_{Ti-OOH}^{\ddagger,\epsilon}$ without alkene present to remove the complicating presence of the epoxidation pathway. Ti-BEA-OH and Ti-BEA-F show similar H_2O_2 decomposition rates (within a factor of 2) and activation enthalpies and entropies (within 4 kJ mol⁻¹ and 15 J mol⁻¹ K⁻¹). Differences across $\Delta H_{app}^{\ddagger}$ and $\Delta S_{app}^{\ddagger}$ values for epoxidation for Ti-BEA-OH and Ti-BEA-F greatly exceed the differences in H_2O_2 decomposition barriers for all alkenes, which suggests that potentially small differences in $G_{Ti-OOH}^{\ddagger,\epsilon}$ between Ti-BEA-OH and Ti-BEA-F do not cause differences between $\Delta H_{app}^{\ddagger}$ and $\Delta S_{app}^{\ddagger}$ for epoxidation of a given alkene on the two catalysts (**Section A8**). With all other terms excluded, changes in $G^{\ddagger,\epsilon}$ appear to be responsible for the significant differences in $\Delta H_{app}^{\ddagger}$ and $\Delta S_{app}^{\ddagger}$ across alkenes and between Ti-BEA-OH and Ti-BEA-F.

The physical reason $G^{\ddagger,\epsilon}$ values sense (SiOH)_x densities and the bulk [H₂O] reflects the quantity and identity of solvent molecules disturbed near active sites by forming the transition state. The increases in $\Delta H_{app}^{\ddagger}$ and $\Delta S_{app}^{\ddagger}$ for longer chain alkenes in **Figure 2.4a** arise from the greater degree of solvent reorganization necessitated as longer alkyl chains adsorb to form the epoxidation transition state, which increases $H^{\ddagger,\epsilon}$ and $S^{\ddagger,\epsilon}$. The increases in $H^{\ddagger,\epsilon}$ and $S^{\ddagger,\epsilon}$ in Ti-BEA-F are less significant than in Ti-BEA-OH because epoxidation transition states in Ti-BEA primarily displace CH₃CN molecules under these conditions (**Figures 2.2** and **2.3**). In comparison, these same transition states must disrupt a combination of both CH₃CN and H₂O molecules in the pores of hydrophilic zeolites (e.g., Ti-BEA-OH) and to a greater extent at higher [H₂O] (*vide infra*).^{72-74, 134-135} The disruption of these hydrogen bonded mixtures incurs increases in both $H^{\ddagger,\epsilon}$ and $S^{\ddagger,\epsilon}$ that correlate with the enthalpy and entropy differences of hydrogen bonding pure H₂O in the pores of

zeolite catalysts.⁷² The greater excess entropy ($S^{\ddagger,\varepsilon}$) for the transition state in Ti-BEA-OH pores leads to a lower $G^{\ddagger,\varepsilon}$ and $\Delta G_{app}^{\ddagger}$ (**Equation 2.4**) that increases epoxidation rates relative to Ti-BEA-F with 200 mM H₂O present (**Figure 2.2**). This result also suggests that $H^{\ddagger,\varepsilon}$ and $S^{\ddagger,\varepsilon}$ decrease as [H₂O] decreases over Ti-BEA-OH (**Figure 2.4b**) because the transition state disrupts solely CH₃CN molecules and not H₂O networks. $H^{\ddagger,\varepsilon}$ and $S^{\ddagger,\varepsilon}$ likely increase with carbon number because longer alkyl chains must disrupt more solvent molecules within Ti-BEA pores. The compensation effect between enthalpy and entropy varies because longer chains disrupt larger numbers and different solvent molecules (i.e., H₂O, CH₃CN) and hydrogen bonds (between CH₃CN or H₂O and (SiOH)_x defects or between networked H₂O molecules). The differences in solvent structure between Ti-BEA-OH and Ti-BEA-F that cause the changes in activation barriers are confirmed in the following sections.

2.3.3 Zeolite Polarity Influences Solvent Uptake

The density of (SiOH)_x groups in zeolite pores affects the quantity of H₂O,^{74, 134-136} CH₃CN,⁷⁴ and alcohol¹³¹⁻¹³³ molecules adsorbed in the vapor phase. Here, the number of CH₃CN and H₂O per unit cell of Ti-BEA-OH and Ti-BEA-F was determined by a combination of liquid-phase CH₃CN-H₂O adsorption isotherms, vapor-phase CH₃CN adsorption isotherms, and comparable GCMD simulations.

Figure 2.5 shows the number of H₂O per unit cell of Ti-BEA materials increase as approximately linear functions of [H₂O] across the range of concentrations examined (0.005 – 4 M H₂O, CH₃CN, 313 K). Both experimental and computational methods indicate that Ti-BEA-OH adsorbs at least 10 times more H₂O molecules per unit cell than Ti-BEA-F under these

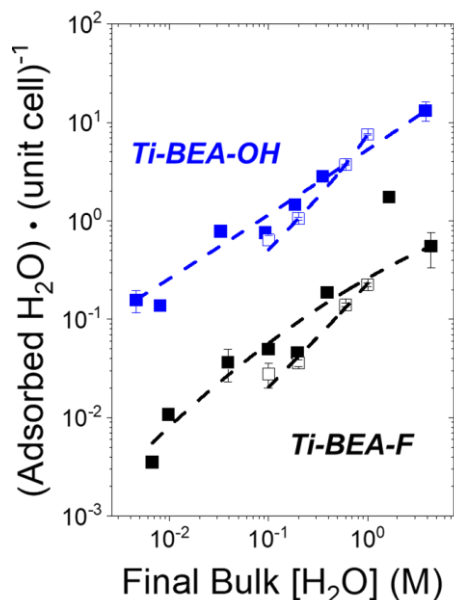


Figure 2.5. Molecules of H₂O per *BEA unit cell adsorbed into Ti-BEA-OH (blue) and Ti-BEA-F (black) obtained experimentally (■, ■) and computationally (□, □) as a function of the final water concentration in bulk solvent, calculated experimentally from CH₃CN and H₂O bulk concentrations (0.005 – 4 M H₂O, CH₃CN, 313 K).

conditions, due to the more negative H₂O adsorption enthalpy (from 0.2 M solution of H₂O in CH₃CN) in hydrogen-bond-forming Ti-BEA-OH pores (-47 kJ mol⁻¹) compared to hydrophobic Ti-BEA-F (-34 kJ mol⁻¹) (see **Section A17** for enthalpy calculation details). These uptake values (i.e., greater H₂O contents in Ti-BEA-OH and with increasing [H₂O]) agree with the physical interpretations for $H^{\ddagger,\varepsilon}$ and $S^{\ddagger,\varepsilon}$ values that increase with alkene carbon number, (SiOH)_x density, and [H₂O] (**Section 2.3.2**). In short, (SiOH)_x groups in Ti-BEA-OH stabilize networks of CH₃CN and H₂O molecules that reorganize to accommodate epoxidation transition states. Longer alkyl chains disrupt greater numbers of solvent molecules, and the enthalpy and entropy differences associated with this disruption become more positive as the mole fraction of H₂O within the vicinity of the active site increases.

Figure 2.6 shows that the presence of (SiOH)_x groups also influences the maximum uptake of CH₃CN (per unit cell) and the thermodynamics for adsorption from CH₃CN vapor because Ti-

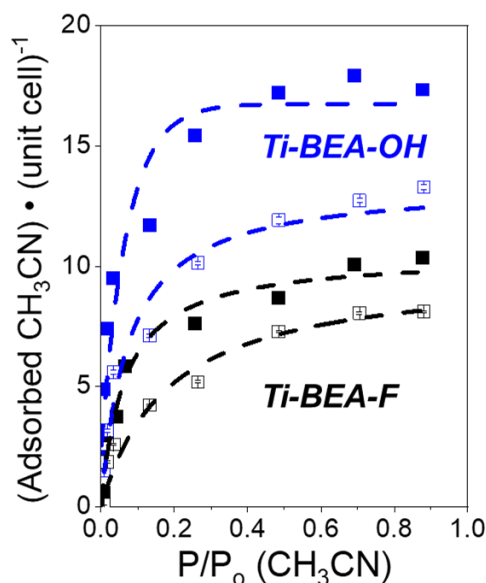


Figure 2.6. Molecules of CH₃CN per *BEA unit cell adsorbed into Ti-BEA-OH (blue) and Ti-BEA-F (black) as a function of relative CH₃CN pressure experimentally (■, ■) and computationally (□, □) (0.008 – 20 kPa CH₃CN, 313 K).

BEA-OH adsorbs greater quantities of CH₃CN than Ti-BEA-F at all CH₃CN pressures examined (0.008 – 20 kPa CH₃CN, 313 K). Both experimental and computational results show that the maximum CH₃CN uptake per unit cell in Ti-BEA-OH exceeds that in Ti-BEA-F by more than 1.5 times, likely because the (SiOH)_x groups stabilize adsorbing CH₃CN through electrostatic hydrogen-bonding interactions. The calculated micropore volume of Ti-BEA-OH from N₂ adsorption exceeds Ti-BEA-F by 1.1 times, while Ar adsorption yields nearly identical micropore volumes for each Ti-BEA (**Table 2.1**). Therefore, the micropore and total volume (see **Table A2**) differences obtained from each adsorbate likely cannot account for differences in CH₃CN or H₂O uptake between Ti-BEA-OH and Ti-BEA-F, supporting that (SiOH)_x density controls solvent adsorption. The proposal that (SiOH)_x stabilizes CH₃CN by direct interactions agrees with the computed adsorption enthalpy for CH₃CN from the liquid-phase that is more exothermic in Ti-BEA-OH (-42 kJ mol⁻¹) than in Ti-BEA-F (-36 kJ mol⁻¹). Similarly, greater computed CH₃CN uptakes from liquid-phase binary mixtures appear in Ti-BEA-OH (**Section A15**). These

differences between intrapore densities and the enthalpy of CH₃CN adsorption for Ti-BEA-OH and Ti-BEA-F correlate with the variations between $\Delta H_{app}^{\ddagger}$ (~ 12 kJ mol⁻¹) and $\Delta S_{app}^{\ddagger}$ (~ 50 J mol⁻¹ K⁻¹) for C₁₈H₃₆ epoxidation on these catalysts even at nearly anhydrous conditions (< 3 mM H₂O; **Figure 2.4b**). **Section A4** provides a comparison of the CH₃CN adsorption trends to those for alcohol molecules with infrared spectroscopy, as well as an outline of other information commonly gained from flowing gaseous species over zeolites (i.e., adsorption enthalpy, site quantification).

Taking **Figures 2.5** and **2.6** together, the greater uptakes of H₂O and CH₃CN in Ti-BEA-OH support the interpretation that disruption of greater numbers of solvent molecules increases $H^{\ddagger,\varepsilon}$ and $S^{\ddagger,\varepsilon}$ for epoxidation.

2.3.4 Structure of CH₃CN and H₂O Near Active Sites

While **Figures 2.5** and **2.6** demonstrate clear differences between the quantities of H₂O and CH₃CN present in pores, the molecular interpretation of these data should also consider the position of these molecules with respect to (SiOH)_x groups and framework Ti-atoms that form the active sites for epoxidations. Based on the strong agreement between computationally predicted uptakes and experimentally measured values, we calculated radial distribution functions from GCMD calculations to provide insight into the organization of solvent molecules (CH₃CN and H₂O) within pores and around active sites to rationalize observed trends in $\Delta H_{app}^{\ddagger}$ and $\Delta S_{app}^{\ddagger}$.

Figure 2.7 shows radial distribution functions (RDF) of the centers of mass for CH₃CN and H₂O molecules with respect to the geometric center of neighboring (SiOH)₄ groups (i.e., the silanol geometric center, SGC) in Ti-BEA-OH (**Figures 2.7a** and **2.7b**) and for the N-atoms within

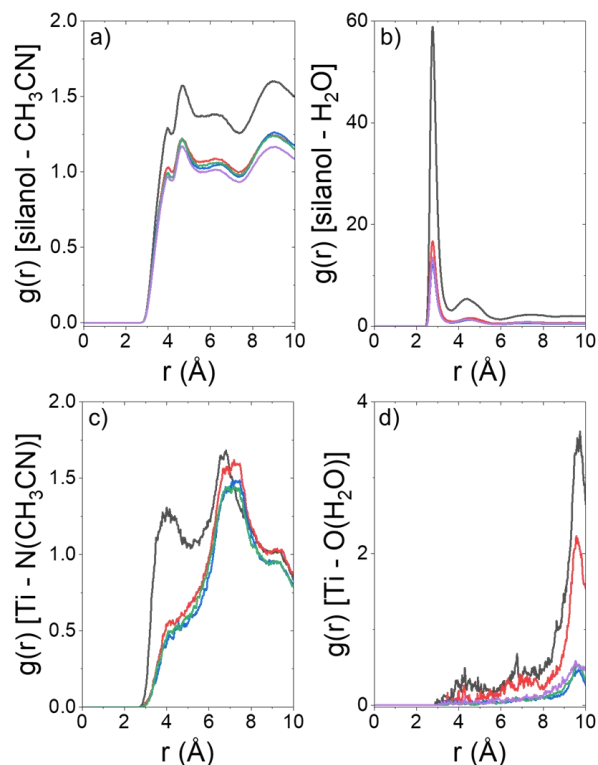


Figure 2.7. Radial distribution of a) CH₃CN and b) H₂O with respect to silanol defects and c) the N-atom of CH₃CN and d) O-atom of H₂O with respect to Ti in the absence of epoxides (black) and with C₆H₁₂O (red), C₁₀H₂₀O (blue), C₁₄H₂₈O (green), and C₁₈H₃₆O (purple) adsorbed to Ti-atoms in Ti-BEA-OH (200 mM H₂O, CH₃CN, 313 K).

CH₃CN and O-atoms within H₂O with respect to the framework Ti-atom that signifies the active site (**Figures 2.7c** and **2.7d**). Here, N- and O-atoms are considered in the RDF analysis as they form dative bonds with the Ti-atom. **Figure 2.8** visually captures the interactions quantified with the RDF, displaying the organization of H₂O near a (SiOH)₄ nest in Ti-BEA-OH (**Figure 2.8a**) and CH₃CN near Ti in Ti-BEA-F (**Figure 2.8b**) obtained from GCMD simulations. In **Figure 2.7**, individual curves represent the RDF either in the absence of an epoxide adsorbate or in the presence of an epoxide (C₆H₁₂O, C₁₀H₂₀O, C₁₄H₂₈O, or C₁₈H₃₆O) at standard conditions (200 mM H₂O, CH₃CN, 313 K). **Figure 2.7a** indicates that CH₃CN preferentially associates with the (SiOH)₄ groups by attractive electrostatics between nucleophilic N-atoms and electrophilic H-atoms, signified by a peak at ~4.5 Å with a shoulder at 4.0 Å that represents the first coordination

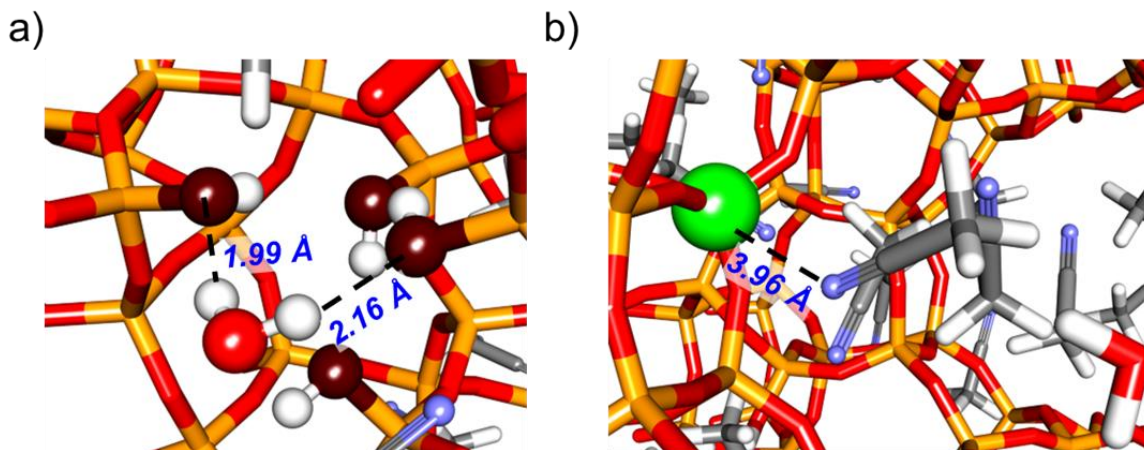


Figure 2.8. Snapshot of a) H_2O bound to a $(\text{SiOH})_4$ nest in Ti-BEA-OH (O-atom of H_2O in red, O-atoms of $(\text{SiOH})_4$ groups in dark red) and b) CH_3CN bound to Ti in Ti-BEA-F (Ti in green, N in blue). Bonding interactions between H and O-atoms in a) and Ti and N in b) shown by dashed lines, with bond length included. Represents the equilibrated solvent structure (200 mM H_2O , CH_3CN , 313 K).

shell. The broad feature at 9 Å likely represents CH_3CN in a neighboring pore. The RDF exceeds a value of 1.0 (i.e., the value in the absence of local correlations) for most distances between 3.2 Å – 10 Å, which signifies the increased local density of CH_3CN molecules due to stabilizing interactions with pore walls and $(\text{SiOH})_4$ groups.

Stabilizing interactions of $(\text{SiOH})_4$ influence the structure of H_2O within pores to an even greater extent. **Figure 2.7b** portrays the RDF for H_2O with respect to the SGC and exhibits a sharp peak at 2.9 Å with an intensity of ~ 60 due to hydrogen bond-driven association of H_2O with the $(\text{SiOH})_4$ groups (**Figure 2.8a**), consistent with previous reports.^{131, 195-197} The RDF intensity decreases significantly with distance and presents a second feature at ~ 4.4 Å, which signifies H_2O molecules that solvate silanol-bound H_2O . Together, these data (**Figures 2.7a** and **2.7b**) demonstrate that $(\text{SiOH})_4$ groups attract both CH_3CN and H_2O and stabilize clusters of these molecules with equilibrium densities that far exceed those in siloxane (i.e., hydrophobic) regions and the contacting liquid-phase. The adsorption of epoxides to framework Ti atoms lowers RDF peak intensities for CH_3CN and H_2O around the SGC (**Figures 2.7a** and **2.7b**), which represents

the displacement of solvent molecules associated with (SiOH)₄ groups to the bulk (**Section A15**). RDF peak intensities remain significant after epoxide adsorption, as most (SiOH)₄ sites are unblocked and free to interact with the solvent.

The adsorption of epoxides to framework Ti-atoms dramatically affects the organization of solvent molecules distributed about these catalytic sites. **Figures 2.7c** and **2.7d** show that the intensities of RDF between framework Ti-atoms and N-atoms of CH₃CN and O-atoms of H₂O decrease at length scales approaching 8 Å and 10 Å, respectively, upon adsorption of epoxides of different carbon numbers. Without an epoxide present, the RDF for CH₃CN shows peaks at 4 and ~6.5 Å (**Figure 2.7c**) that represent CH₃CN coordinated to Ti-atoms and uncoordinated CH₃CN near the Ti site (**Figure 2.8b**). **Figure 2.7c** demonstrates that epoxide adsorption decreases the peak intensity at 4 Å by a factor greater than two due to displacement of CH₃CN molecules coordinated to Ti-atoms. Decreases in the RDF intensity for CH₃CN (**Figure 2.7c**) depend weakly on epoxide carbon number, which agrees with gradual decreases in CH₃CN uptakes relative to H₂O with GCMD simulations (**Section A15**). Interestingly, **Figure 2.7d** shows that extremely small quantities of water molecules (~0.056 H₂O per Ti atom) reside within 4 Å of Ti sites in these aqueous CH₃CN solutions. In comparison, prior molecular dynamics (MD) simulations⁷² and EXAFS experiments¹⁵⁰ revealed that Ti-atoms in Ti-BEA zeolites coordinate 1–2 molecules of H₂O through non-covalent dative interactions in pure water. The scarcity of H₂O molecules near Ti-atoms even at 200 mM H₂O indicates that H₂O does not coordinate directly to Ti-atoms at these conditions, due to competitive adsorption of CH₃CN. The presence of H₂O weakly affects computed epoxide adsorption enthalpies in Ti-BEA-F (**Section 2.3.5**), which shows further that epoxides and H₂O do not compete for Ti sites at these conditions.

The findings outlined in **Section 2.3.3** and **Section 2.3.4** demonstrate that the (SiOH)_x density of Ti-BEA pores and carbon number of epoxide adsorbates strongly impact the structure of confined solvent molecules. The interactions between the epoxide and solvent molecules influence epoxide stability, as discussed in the next section.

2.3.5 Confined Solvent Molecules Influence Epoxide Adsorption Enthalpies

Principles of Brønsted-Evans-Polanyi relationships suggest that intrinsic activation barriers for a specific class of elementary steps scale linearly with the thermodynamics for that elementary step because the intervening transition state structurally resembles the stable intermediate (i.e., the reactant or product state) most similar in energy, as postulated by Hammond.^{97, 198} These concepts motivate measurements of molecular adsorption enthalpies for species that possess chemical functions or extended structures representative of epoxidation transition states. We demonstrated recently that $\Delta H_{app}^{\ddagger}$ values for liquid-phase epoxidation reactions correlate to gas-phase adsorption enthalpies for pyridine and deuterated acetonitrile (CD₃CN) over *BEA zeolites with varying group 4-5 metal heteroatoms (i.e., Ti, Nb, Ta, Zr, Hf).³¹⁻³² These linear correlations indicate that the covalent bonds between these Lewis base molecules and the Lewis acidic metal active sites (i.e., inner sphere interactions) mimic those between the epoxidation transition state and active metal site, which contribute to values for $\Delta H_{app}^{\ddagger}$. However, enthalpies of adsorption of small molecules into predominantly unoccupied zeolite pores (i.e., the state during gas-phase adsorption measurements) do not reveal the influence of non-covalent interactions introduced by solvent molecules and their impact on rates and barriers for epoxidation. In contrast, adsorption measurements of epoxides to active sites of zeolites suspended in the liquid-phase provide insight

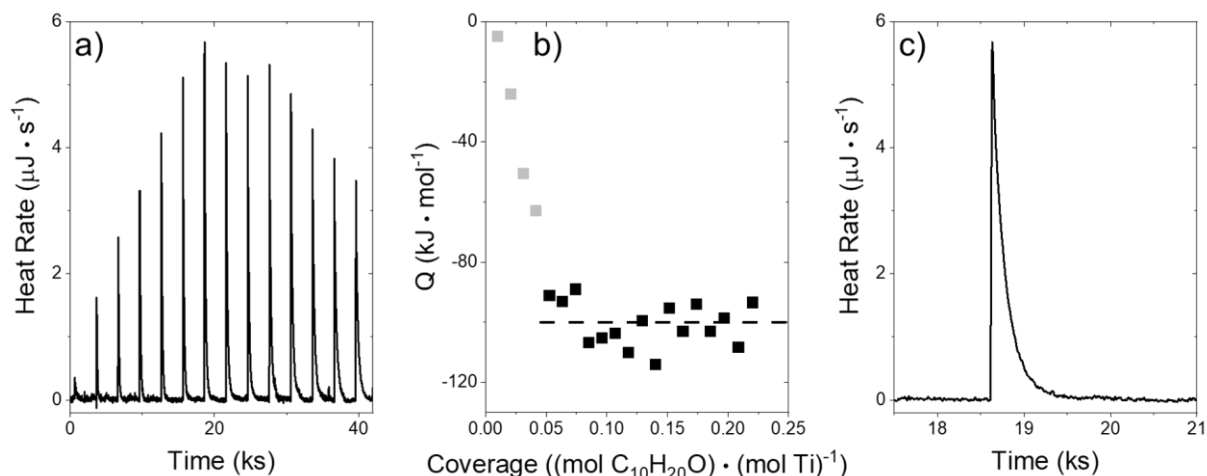


Figure 2.9. Isothermal titration calorimetry for adsorption of 1,2-epoxydecane onto Ti-BEA-OH (5 mM $\text{C}_{10}\text{H}_{20}\text{O}$, 200 mM H_2O , CH_3CN , 313 K, 1 μL per injection). a) Thermogram from the titration individual titrant injections, b) a representative injection peak from the thermogram to illustrate signal to noise ratio and baseline stability, and c) specific heats of 1,2-epoxydecane adsorption as a function of coverage (transparent points represent titrant doses omitted from calculations due to systematic errors typical for early injections).

into how intraporous solvent molecules influence the thermodynamics of adsorption, and by extension, the kinetics of catalytic reactions. The enthalpy of epoxide adsorption ($\Delta H_{ads,epox}$) and $\Delta H_{app}^\ddagger$ correlate linearly for C_8H_{16} epoxidation and $\text{C}_8\text{H}_{16}\text{O}$ adsorption with Ti-BEA catalysts of varying hydrophilicities⁷³ and C_6H_{12} and $\text{C}_6\text{H}_{12}\text{O}$ over *BEA zeolites with varying metal heteroatoms (i.e., Ti, Nb, W).³⁰ These correlations indicate that the adsorbed epoxide mimics the structure of the epoxidation transition state, as illustrated in **Scheme 2.2**. Moreover, the differences in $\Delta H_{app}^\ddagger$ observed in prior comparison between hydrophilic and hydrophobic forms of Ti-BEA⁷³ primarily reflect differences between the stability of transition states, and the organization of solvating molecules within the zeolite pores, rather than the reference state (Ti-OOH + liquid-phase alkene). The quantitative influence of excess interactions with solvent molecules upon values of alter $\Delta H_{ads,epox}$ follows a form similar to **Equation 2.4**:

$$\Delta H_{ads,epox} = (H_{ads,epox}^0 + H_{ads,epox}^\epsilon) - (H_{epox}^0 + H_{epox}^\epsilon) \quad (2.6)$$

where the terms H_i^0 and H_i^ε signify the standard state and excess enthalpic contributions for each species i , respectively. $\Delta H_{ads,epox}$ values were measured by ITC at solvent compositions that match those for kinetic measurements (<3 , 39, or 200 mM H_2O , CH_3CN , 313 K). **Figure 2.9a** shows a representative ITC thermogram in which the positive peaks represent the heat released due to exothermic adsorption of epoxide molecules with each subsequent injection. The integration of each peak yields the total heat evolved per mole of 1,2-epoxydecane ($C_{10}H_{20}O$) injected at low coverages of epoxide (**Figure 2.9b**). The average heat per mole at low coverages yields the value for $\Delta H_{ads,epox}$ assuming all injected epoxide molecules adsorb to unoccupied sites. These calculations omit the first few injections that exhibit less exothermic heats, which reflect smaller quantities of epoxide injected due to vapor within the syringe needle. **Figure 2.9c** presents a representative peak from the thermogram and demonstrates the high signal-to-noise ratio of these measurements. Thermograms for all epoxides and the integrated heats of adsorption appear in the appendix (**Section A11**).

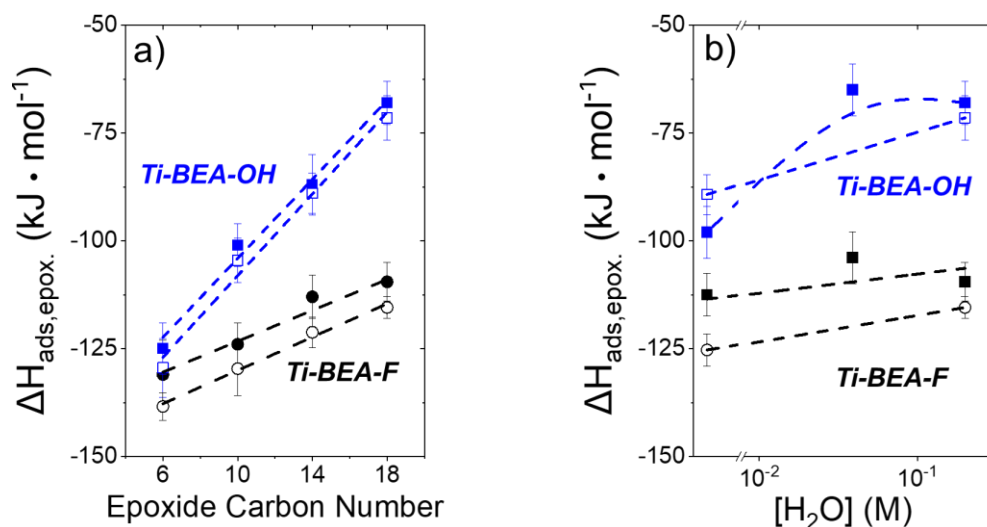


Figure 2.10. Enthalpies of adsorption for 1,2-epoxides obtained experimentally ($\blacksquare, \bullet$) and computationally ($\square, \circ$) as a) functions of the epoxide carbon number (200 mM H_2O , CH_3CN , 313 K), and b) functions of $[H_2O]$ for $C_{18}H_{36}O$ over Ti-BEA-OH (blue) and Ti-BEA-F (black) (CH_3CN , 313 K).

Figure 2.10 displays experimental measurements (ITC) and computational calculations (GCMD) for $\Delta H_{ads,epox}$ values as functions of 1,2-epoxide carbon number at 200 mM H₂O (**Figure 2.10a**) and as functions of water concentration for 1,2-epoxyoctadecane (C₁₈H₃₆O) (**Figure 2.10b**) on Ti-BEA-OH and Ti-BEA-F materials. In general, experimental and computational values provide consistent trends and offer nearly quantitative agreement in many cases. $\Delta H_{ads,epox}$ values become more endothermic with increasing epoxide carbon number over both Ti-BEA-OH and Ti-BEA-F with 200 mM H₂O present (**Figure 2.10a**). Ti-BEA-OH gives a greater span of $\Delta H_{ads,epox}$ values (57 kJ mol⁻¹) from 1,2-epoxyhexane (C₆H₁₂O) to C₁₈H₃₆O than Ti-BEA-F (22 kJ mol⁻¹). Ti-BEA-F provides more exothermic values of $\Delta H_{ads,epox}$ for all epoxides, which is consistent with $\Delta H_{app}^{\ddagger}$ trends from **Figure 2.4a**. These comparisons indicate that longer alkyl chains both in epoxidation transition states and in adsorbed epoxide molecules disrupt greater numbers of solvent molecules in zeolite pores, which introduces progressively larger enthalpic penalties that increase the enthalpy of these surface species. The more exothermic $\Delta H_{ads,epox}$ and smaller span of $\Delta H_{ads,epox}$ values over Ti-BEA-F suggest that epoxide molecules disrupt weakly bound CH₃CN molecules in Ti-BEA-F and solvent molecules strongly bound to (SiOH)_x groups in Ti-BEA-OH. The more exothermic $\Delta H_{ads,epox}$ in the less hydrophilic environment also agrees with reported trends for aqueous cyclohexanol adsorption in Brønsted acid MFI zeolites, where a greater density of hydrophilic hydronium ions (H₃O⁺) leads to a more endothermic adsorption enthalpy for cyclohexanol.¹⁹⁹

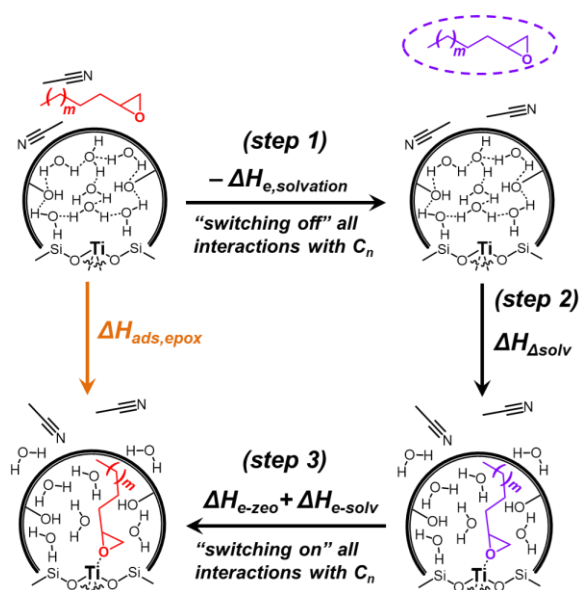
Figure 2.10b reveals that experimentally measured $\Delta H_{ads,epox}$ for C₁₈H₃₆O become more exothermic by 30 kJ mol⁻¹ as the [H₂O] decreases over Ti-BEA-OH but differs by only 10 kJ mol⁻¹ in Ti-BEA-F. These effects of [H₂O] agree well with computational predictions. Notably, Ti-BEA-OH gives more endothermic values for $\Delta H_{ads,epox}$ for C₁₈H₃₆O than Ti-BEA-F at all [H₂O],

but the difference between values on the two zeolites achieves a minimum at the lower $[\text{H}_2\text{O}]$ (i.e., $<3 \text{ mM H}_2\text{O}$). Together, these trends in $\Delta H_{ads,epox}$ indicate that the disruption of H_2O molecules associated with $(\text{SiOH})_x$ groups caused by epoxide adsorption contributes to greater enthalpy increases than given by CH_3CN alone. In addition, the $\Delta H_{ads,epox}$ values that are always more endothermic over Ti-BEA-OH (even at $<3 \text{ mM H}_2\text{O}$) suggests that $(\text{SiOH})_x$ groups stabilize CH_3CN molecules more effectively than siloxane regions of pores, which leads to sensible enthalpy penalties for adsorption (and reaction) in Ti-BEA-OH relative to Ti-BEA-F, even in nearly anhydrous conditions.

Computationally determined values for $\Delta H_{ads,epox}$ over Ti-BEA-F are systematically more exothermic than experimental results by $5\text{-}12 \text{ kJ mol}^{-1}$ (**Figure 2.10**). Part of this difference may stem from inaccuracies in the force field; however, the computational model possesses zero $(\text{SiOH})_x$ defects in contrast to the synthesized Ti-BEA-F, which contains a finite number of defects (Φ_{IR} , **Table 2.1**). Consequently, the small discrepancy between experimental and computational assessments for $\Delta H_{ads,epox}$ likely reflect the presence of hydrogen bonded H_2O and CH_3CN molecules in the experiments with Ti-BEA-F that are absent from the simulations. In contrast, experimental and computational values for $\Delta H_{ads,epox}$ on Ti-BEA-OH agree well across the range of carbon numbers and $[\text{H}_2\text{O}]$ examined without systematic differences (**Figure 2.10**). This further suggests that the offsets between experiment and simulation observed for Ti-BEA-F correspond to the small number of $(\text{SiOH})_x$ that appear in the synthesized material. Overall, the agreement between experimental and computational $\Delta H_{ads,epox}$ values provides compelling evidence that the identity and bonding configurations of solvent molecules influence the stability of adsorbed epoxide molecules in pores of Ti-BEA catalysts.

2.3.6 Deconvoluting Enthalpic Contributions of $\Delta H_{ads,epox}$

The stability of adsorbates in zeolite pores depends on both covalent (i.e., metal heteroatom to O atom or -OOH or transition states) and non-covalent interactions (i.e., van der Waals interactions with zeolite pore wall, intermolecular interactions with surrounding solvent molecules). Prior interpretation of rate measurements for 1-octene epoxidation⁷⁴ and measured $\Delta H_{ads,epox}$ for 1,2-epoxyoctane adsorption to framework Ti atoms⁷³ strongly suggest that the strength of the covalent bond between Ti and epoxidation transition states or epoxide products does not depend on the (SiOH)_x density. The (SiOH)_x density, however, does influence the organization of solvent molecules within pores (**Figure 2.7**) and the resulting non-covalent interactions between the reactive intermediates and solvent molecules. Having cross-validated computed $\Delta H_{ads,epox}$ values with experimental measurements (**Figure 2.10**), these values can be



Scheme 2.3. Thermodynamic cycle for decomposing the adsorption enthalpy into four physical components. Epoxide molecules shown in red interact with surrounding solvent, while those shown in purple do not. The four states represent: (1) interacting epoxide in bulk solvent, pre-adsorption, (2) non-interacting epoxide in bulk solvent, pre-adsorption, (3) non-interacting adsorbed epoxide, (4) interacting adsorbed epoxide.

deconvoluted to assess the contributions of the intrinsic epoxide energy, solvent displacement, and epoxide interactions with the zeolite and solvent using the following relationship:

$$\Delta H_{ads,epox (ED)} = -\Delta H_{e,solvation} + \Delta H_{\Delta solv} + \Delta H_{e-zeo} + \Delta H_{e-solv} \quad (2.7)$$

In **Equation 2.7**, $\Delta H_{e,solvation}$ represents the solvation enthalpy of an epoxide molecule, $\Delta H_{\Delta solv}$ signifies the difference between solvent enthalpy in the bulk solvent and in the zeolite, and ΔH_{e-zeo} and ΔH_{e-solv} equal the interaction energies between the adsorbed epoxide and zeolite pore walls and solvent molecules, respectively. Constraints in the computational methodologies cause the adsorption enthalpy from energy decomposition (ED) ($\Delta H_{ads,epox (ED)}$) in **Equation 2.7** to differ slightly from the $\Delta H_{ads,epox}$ computed in **Figure 2.10** (see **Section A17**).

Scheme 2.3 depicts a hypothetical Born-Haber thermochemical cycle that separates the individual terms in **Equation 2.7**. First, the epoxide decouples from the bulk solvent environment to form an ideal gas-phase molecule (step 1, $-\Delta H_{e,solvation}$). The value of $\Delta H_{e,solvation}$ does not depend on the zeolite, and hence, it does not contribute to differences between $\Delta H_{ads,epox}$ for Ti-BEA-OH and Ti-BEA-F. Second, the gaseous epoxide molecule enters the solvent-filled zeolite pore and displaces solvent molecules to the bulk phase (step 2), which produces an enthalpy change from disrupting the intermolecular forces involving solvent molecules ($\Delta H_{\Delta solv}$). Third, the system evolves in response to interactions between the epoxide and its surroundings (step 3), which yields enthalpy contributions represented by ΔH_{e-zeo} and ΔH_{e-solv} . These terms were individually examined computationally, as described in **Sections 2.2.7** and **A17**. Taken together, the sum of the energy contributions from these three steps equals $\Delta H_{ads,epox (ED)}$.

Figure 2.11 shows values for $\Delta H_{\Delta solv}$ become more endothermic as carbon number increases for both solvent compositions (200 mM H₂O + CH₃CN and pure CH₃CN): the values

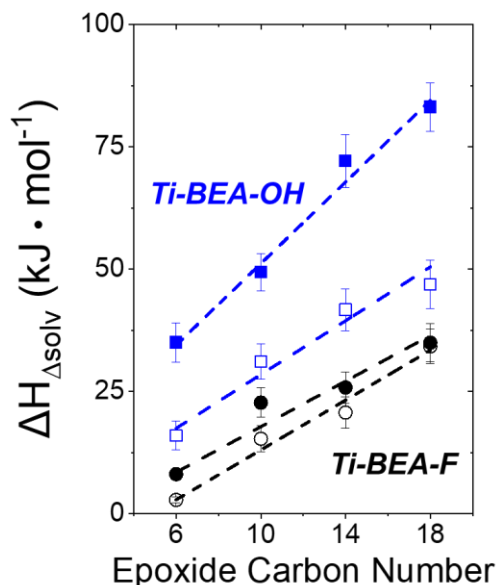


Figure 2.11. Computationally measured enthalpy changes due to solvent displacement to the bulk ($\Delta H_{\Delta solv}$) during 1,2-epoxide adsorption into Ti-BEA-OH (blue) and Ti-BEA-F (black) in CH₃CN with 200 mM H₂O (■,●) and pure CH₃CN (□,○) at 313 K.

increase by as much as ~ 45 kJ mol⁻¹ for a given combination of zeolite and solvent. This correlation illustrates a significant destabilizing enthalpy contribution that stems from the disruption of intrapore solvent molecules solvent and demonstrates that these penalties scale with the length of alkyl chains upon the epoxides. Ti-BEA-OH gives a larger enthalpic penalty than Ti-BEA-F for two reasons. First, greater solvent quantities desorb during epoxide adsorption in Ti-BEA-OH, according to computed solvent uptakes (**Section A15**). Second, the epoxide disrupts stronger attractive interactions between solvent molecules and (SiOH)₄ in Ti-BEA-OH (*vide supra*). $\Delta H_{\Delta solv}$ increases more strongly with the carbon number of the epoxide in aqueous solutions for Ti-BEA-OH than in Ti-BEA-F because H₂O interacts more strongly with (SiOH)₄ than CH₃CN (**Section 2.3.3**).

Figure 2.12 presents values for the enthalpy of interactions between the epoxide and the zeolite (ΔH_{e-zeo}), which become increasingly exothermic in both Ti-BEA-OH and Ti-BEA-F as

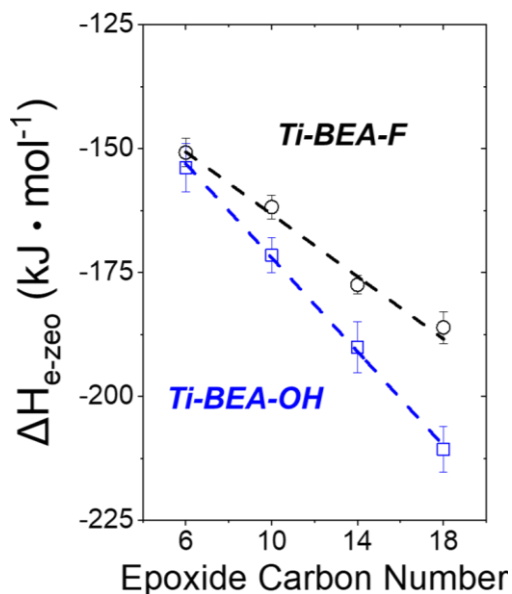


Figure 2.12. Computationally measured enthalpy changes due to epoxide interactions with the zeolite pore in Ti-BEA-OH (blue) and Ti-BEA-F (black) in CH₃CN with 200 mM H₂O, 313 K.

the carbon number of the epoxide increases (200 mM H₂O in CH₃CN). These data show these interactions stabilize molecules within pores via attractive van der Waals forces between the non-polar alkyl chains and pore walls of the *BEA structure. ΔH_{e-zeo} values in pure CH₃CN differ from those with 200 mM H₂O (**Figure 2.12**) by less than 0.1 kJ mol⁻¹ (**Tables A11 to A14**), which shows that the solvent does not significantly influence direct interactions between the epoxide and zeolite. The trends in **Figure 2.12** agree with prior studies of the adsorption of a series of homologous alkanes from the gas-phase into zeolite pores.¹⁴⁰ In particular, Li et al. showed that the adsorption enthalpy of gaseous linear chain alkanes becomes increasingly exothermic by 42 kJ mol⁻¹ per four additional methylene (-CH₂-) units in MFI zeolite.¹⁶⁷ In comparison, values of ΔH_{e-zeo} become more exothermic by 19 kJ mol⁻¹ and 12 kJ mol⁻¹ for Ti-BEA-OH and Ti-BEA-F, respectively, per four added -CH₂- units in both aqueous and pure CH₃CN. The less attractive adsorbate-zeolite interactions in *BEA may result from the greater pore diameter compared to MFI and to more effective solvation of alkyl chains by H₂O and CH₃CN, which reduces the average

distance between the $\text{-CH}_2\text{-}$ units and pore walls. Values of $\Delta H_{e-\text{zeo}}$ in Ti-BEA-OH depend more strongly on the length of the alkyl group, which shows that $(\text{SiOH})_4$ moieties provide more attractive van der Waals stabilization per $\text{-CH}_2\text{-}$ group of the epoxide than siloxane (Si-O-Si) units. The greater negative charge upon O atoms in $(\text{SiOH})_4$ groups (in comparison to Si-O-Si) likely increases the attraction between alkyl groups and framework O atoms.²⁰⁰

Figure 2.13 reveals that $\Delta H_{e-\text{solv}}$ becomes more endothermic as the carbon number of the epoxide increases, and once again, these values exhibit a stronger dependence on alkyl chain length in Ti-BEA-OH than in Ti-BEA-F. Values of $\Delta H_{e-\text{solv}}$ in Ti-BEA-OH are systematically $\sim 10 \text{ kJ mol}^{-1}$ more endothermic in pure CH_3CN than in aqueous CH_3CN . However, $\Delta H_{e-\text{solv}}$ values in Ti-BEA-F do not differ with or without H_2O . To examine the physical origins of these trends, we computed coordination numbers (CN) for CH_3CN to the C- and O-atoms of the epoxides to probe the local solvent environment (**Figure A37**, see **Section A22** for calculation details and further analysis). Similar to $\Delta H_{e-\text{solv}}$, CNs decrease monotonically with the epoxide carbon number

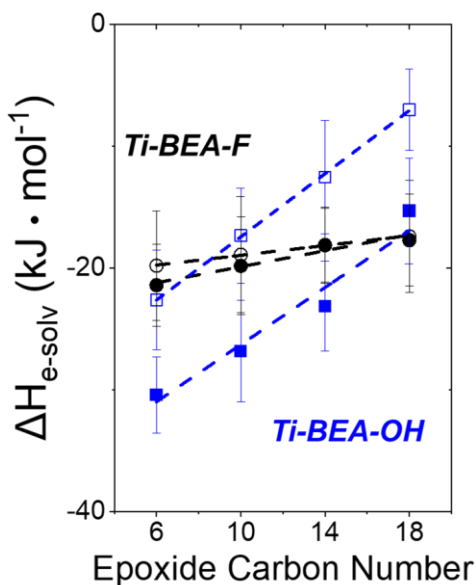


Figure 2.13. Computationally measured enthalpy changes due to epoxide interactions with the zeolite pore in Ti-BEA-OH (blue) and Ti-BEA-F (black) in CH_3CN with 200 mM H_2O (■,●) and pure CH_3CN (□,○) at 313 K.

because longer alkyl chains reduce the space available for solvent molecules within the pores. Additionally, alkyl groups of epoxides with greater carbon numbers spend more time near the pore walls rather than surrounded by solvent molecules due to favorable epoxide-zeolite interactions (ΔH_{e-zeo} , **Figure 2.12**). Lower CN values lead to weaker van der Waals interactions between the alkyl chain and CH₃CN (**Table A17**), which reduces the magnitude of ΔH_{e-solv} . Notably, Ti-BEA-OH shows a lower CN value than Ti-BEA-F for the C₆ epoxide adsorbed in pure CH₃CN, despite a much higher intraporous solvent density in Ti-BEA-OH (0.48 vs. 0.412 g cm⁻³, respectively; **Section A21**). Analysis of RDFs (**Figures A35 and A36; Section A22**) reveals that the (SiOH)₄ groups in Ti-BEA-OH attract solvent molecules. Consequently, solvation shells around the epoxides are depleted in the confined environment, and CNs decrease. Alkyl chains of epoxides with larger carbon numbers displace silanol-bound CH₃CN molecules, causing a significant reduction in the solvent uptake (**Figure A31**). As a result, the solvation shell is depopulated more in Ti-BEA-OH compared to Ti-BEA-F (**Figure A37**), which explains the steeper slope in the ΔH_{e-solv} trend with respect to the carbon number. Finally, the addition of H₂O displaces a fraction of CH₃CN in the proximity of (SiOH)₄ with the concurrent increase of the CN value around the alkyl chain by a nearly constant number of ~0.9. This causes a constant negative shift in ΔH_{e-solv} for all epoxides in Ti-BEA-OH. Collectively, variations of the local environment of Ti-coordinated epoxides and solvent density with the carbon number lead to differences in ΔH_{e-solv} (**Figure 2.13** and **Section A22**).

Notably, the changes in enthalpy quantities that correspond to interactions between the epoxide and either solvent molecules or the zeolite pore walls (i.e., ΔH_{e-solv} , ΔH_{e-zeo} , and $\Delta H_{e,solvation}$) exhibit dependencies upon alkyl chain length of similar magnitude (but with opposing signs) such that their sum (i.e., $-\Delta H_{e,solvation} + \Delta H_{e-zeo} + \Delta H_{e-solv}$) is nearly constant

across all epoxides examined here (**Figure A31**). In addition, $\Delta H_{\Delta solv}$ shows the strongest dependence on the epoxide carbon number among the three types of intermolecular interactions that depend upon the zeolite ($\Delta H_{\Delta solv}$, ΔH_{e-zeo} , ΔH_{e-solv}). Together, these comparisons show that the physical process of disrupting the solvent molecules organized near the Ti active sites dominates the observed trends in values for epoxide adsorption enthalpies ($\Delta H_{ads,epox}$, **Figure 2.10**). Consequently, the less exothermic adsorption of epoxides into Ti-BEA-OH, compared to Ti-BEA-F, signifies the greater enthalpic cost to displace solvent molecules from their preferred positions near (SiOH)_x groups within molecular distances from framework Ti sites.

2.3.7 Enthalpy Correlations Describe Solvent Interactions with Alkyl Chains

Figure 2.14 shows that $\Delta H_{app}^{\ddagger}$ and $\Delta H_{ads,epox}$ correlate across the range of alkene carbon numbers and [H₂O] for Ti-BEA-OH and Ti-BEA-F. The correlation suggests that both formation of the epoxide transition state and the adsorption of the epoxide to framework Ti atoms require similar reorganization of proximate CH₃CN and H₂O molecules (**Scheme 2.2**). $\Delta H_{app}^{\ddagger}$ and $\Delta H_{ads,epox}$ become more endothermic with increasing carbon number for both Ti-BEA-OH and Ti-BEA-F (**Figure 2.14a**), with Ti-BEA-OH yielding more endothermic enthalpies for each respective carbon number. From C₆ – C₁₈ alkenes and epoxides, $\Delta H_{app}^{\ddagger}$ and $\Delta H_{ads,epox}$ show respective spans of values of 68 and 57 kJ mol⁻¹ over Ti-BEA-OH and 18 and 21 kJ mol⁻¹ over Ti-BEA-F. **Figure 2.14b** reveals that $\Delta H_{app}^{\ddagger}$ and $\Delta H_{ads,epox}$ depend weakly on [H₂O] over Ti-BEA-F but become more endothermic at higher [H₂O] over Ti-BEA-OH. Here, $\Delta H_{app}^{\ddagger}$ and $\Delta H_{ads,epox}$ show respective spans of 46 and 30 kJ mol⁻¹ over Ti-BEA-OH and 7 and 8 kJ mol⁻¹ in Ti-BEA-F.

Epoxides with greater carbon numbers occupy greater volumes and, therefore, disturb larger numbers of solvent molecules and give more endothermic $\Delta H_{app}^{\ddagger}$ and $\Delta H_{ads,epox}$ values

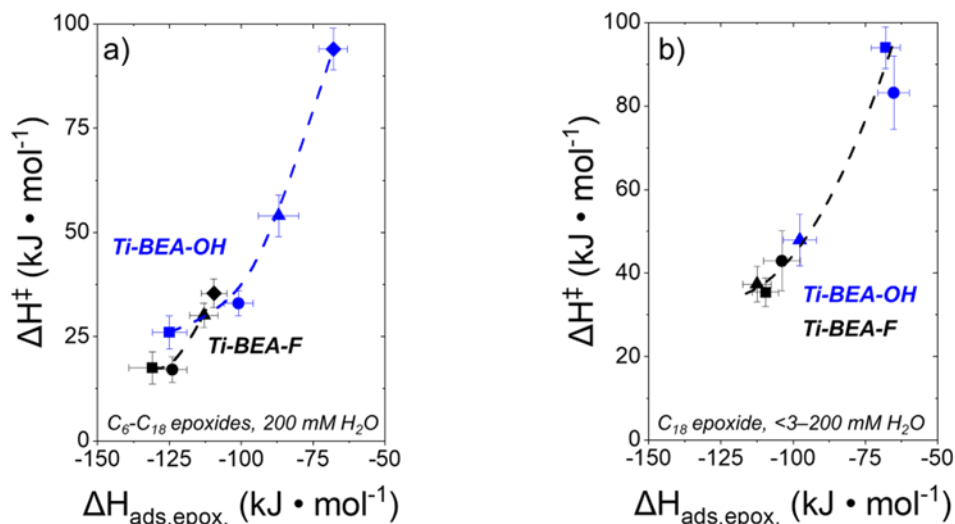


Figure 2.14. Apparent activation enthalpies for C_nH_{2n} epoxidation (0.5 mM C_nH_{2n} , 10 mM H_2O_2 , CH_3CN solvent, 308-333 K) as a function of 1,2-epoxide heat of adsorption (1-10 mM epoxide, CH_3CN solvent, 313 K) over Ti-BEA-OH (blue) and Ti-BEA-F (black) for a) C_6 (■, ■), C_{10} (●, ●), C_{14} (▲, ▲), and C_{18} (◆, ◆) alkenes/epoxides with 200 mM H_2O present and b) C_{18} alkene/epoxide with different $[H_2O]$ (200 mM H_2O (■, ■), 39 mM H_2O (●, ●), < 3 mM H_2O (▲, ▲)).

(Figure 2.14a). The more endothermic enthalpies and stronger enthalpy dependence on carbon number over Ti-BEA-OH in Figure 2.14a also reinforce that the disruption of H_2O yields greater enthalpic penalties than CH_3CN . This observation also aligns with the enthalpy trends as $[H_2O]$ changes over Ti-BEA-OH (Figure 2.14b), in which removing H_2O leads to more exothermic $\Delta H_{app}^\ddagger$ and $\Delta H_{ads,epox}$. The trends in Figure 2.14 indicate that $\Delta H_{app}^\ddagger$ and $\Delta H_{ads,epox}$ depend on the number and identity of the solvent molecules that reorganize to accommodate epoxidation transition states and adsorption of the product epoxide.

Interestingly, both Ti-BEA-OH and Ti-BEA-F show a positive and increasing derivative for the dependence of $\Delta H_{app}^\ddagger$ on $\Delta H_{ads,epox}$ in Figure 2.14. In other words, these correlations appear superlinear, and $\Delta H_{app}^\ddagger$ shows a stronger dependence on carbon number for longer chain epoxides. The difference suggests that the transition state structures become increasingly late (i.e., product-like) with increases in the alkyl carbon number. This trend matches the intuition that the

presence of the Ti-OOH MARI and the pendant -OH group in the transition state for epoxidation become less consequential as the alkyl chain increases in size and accounts for a greater fraction of the transition state interacts with solvent molecules. Moreover, alkyl groups with greater carbon numbers require the reorganization of greater numbers of solvent molecules, which make reactions more endothermic. In turn, this difference lead to later transition states with larger transfer coefficients, as described by Bell-Evans-Polanyi principles and Hammond.²⁰¹⁻²⁰²

These comparisons give strong evidence that solvent restructuring alters the excess enthalpies of the adsorbed epoxide ($H_{ads,epox}^{\epsilon}$) and epoxidation transition state ($H^{\ddagger,\epsilon}$) in ways that demonstrate the structure of the covalently bound species and the organization of surrounding solvent molecules are similar in both cases. The number of solvent molecules displaced increases with the carbon number of the reactive intermediate, which confers enthalpic penalties for the reaction of Ti-OOH with alkenes. These concomitant differences lead to later epoxidation transition states and the non-linear correlations evident in **Figure 2.14**. Overall, these findings indicate that interactions between solvent molecules and adsorbed reactive species affect the stability of reactive species at solid-liquid interfaces. While demonstrated here for alkene epoxidations, this concept can be applied to optimize the rates and selectivities of other zeolite-catalyzed reactions in the liquid-phase.

2.4 Conclusions

Kinetics of catalytic epoxidation reactions, thermodynamics of epoxide adsorption, and spatial distributions of solvent molecules about Ti active sites within *BEA depend sensitively on interactions among confined solvent molecules and with covalently bound reactive species. The stability of surface intermediates and transition states at these sites differ with the identity of the

surrounding molecules and functional groups, which lead to excess contributions (e.g., G^ε) that reflect the need to reorganize solvents in pores to accommodate reactive species. The origins, magnitude, and significance of these excess contributions (i.e., thermodynamic non-idealities) were determined by examining experimental rate measurements and adsorption enthalpies together with cross-validated findings from grand canonical molecular dynamics (GCMD) simulations. While rates and barriers for the epoxidation of linear alkenes (C₆-C₁₈) with H₂O₂ in either hydrophobic or hydrophilic variants of Ti-BEA differ substantially, the mechanism of these reactions, the dominant surface intermediate (Ti-OOH), and the kinetic relevance of the intervening elementary steps remain constant for all combinations of reactants and catalysts. The interpretation of turnover rates and apparent barriers ($\Delta H_{app}^\ddagger$, $\Delta S_{app}^\ddagger$) for epoxidation in Ti-BEA materials show increases in the carbon number of the reactant alkene lead to proportional gains in thermodynamic excess enthalpies and entropies for epoxidation transition states ($H^{\ddagger,\varepsilon}$, $S^{\ddagger,\varepsilon}$). These changes give rise to values for $\Delta H_{app}^\ddagger$ and $\Delta S_{app}^\ddagger$ that span more than ~ 70 kJ mol⁻¹ and ~ 200 J mol⁻¹ K⁻¹, respectively. Moreover, these quantities become more positive with increasing intrapore hydrogen bonding functions such as (SiOH)_x groups and CH₃CN and H₂O molecules, which increase epoxidation rates under typical conditions. Adsorption enthalpies for epoxides ($\Delta H_{ads,epox}$) show trends with similar direction and magnitude as $\Delta H_{app}^\ddagger$. Comparisons of radial distribution functions of solvent molecules and Born-Haber analysis of individual enthalpic contributions for adsorption from GCMD show that these trends predominantly reflect the enthalpy difference caused by the displacement of hydrogen bonded solvent molecules (i.e., H₂O and CH₃CN) from the pores of Ti-BEA to the liquid-phase to form voids that accommodate epoxides and epoxide-like transition states at framework Ti-atoms ($\Delta H_{\Delta solv}$). In comparison, the combined enthalpic contributions from intermolecular forces between the bound intermediates and

the solvent molecules or the pore walls are less significant. These conclusions agree with strong correlations between $\Delta H_{app}^{\ddagger}$ and $\Delta H_{ads,epox}$ values and provide strong evidence that the enthalpy (and free energy) costs to displace solvent molecules from active sites give rise to large differences in rates and selectivities for catalysis and adsorption processes in solvent-filled zeolite pores.

These findings carry implications for adsorption, transport, and catalysis within microporous materials immersed within liquids that can permeate pores, but also in contact with gases when spontaneous pore condensation may fill voids with liquid-like densities of molecules. The physical processes described here demonstrate that the reorganization and displacement of molecules within microporous materials contribute to free energy changes for adsorption, desorption, diffusion, and reactions.¹²⁴ These contributions reflect attributes of the solid material, such as the functionalization and topology of the pores,⁷² but also the functional groups constituting the solvating molecules within pores and the structure of the substrate (i.e., the organic adsorbate or reactant). While these principles pertain to broad classes of materials, including zeolites, metal-organic-frameworks, mesoporous silicas, microporous carbons, and cross-linked polymers, each class of these materials finds use in unique applications and offer distinct synthetic control over aspects of the resulting solid-liquid interfaces. Knowledge of these interactions and their magnitude for sets of substrates, solvents, and solids provide opportunities to improve rates and selectivities for molecular separations and catalytic transformations.

CHAPTER 3

ENGINEERING INTRAPOROUS SOLVENT ENVIRONMENTS: EFFECTS OF AQUEOUS-ORGANIC SOLVENT MIXTURES ON COMPETITION BETWEEN ZEOLITE-CATALYZED EPOXIDATION AND H₂O₂ DECOMPOSITION PATHWAYSⁱⁱⁱ

3.1 Introduction

Epoxides are used as intermediates to manufacture fragrances, plastics, and biologically active ingredients and are produced and consumed on a massive scale.⁵⁰ The primary methods to produce epoxides industrially include the chlorohydrin process, organic-hydroperoxide (Halcon) process, and hydrogen peroxide (H₂O₂) to propylene oxide (HPPO) process.⁵⁰ Industrial HPPO processes involve one of two combinations of a microporous titanosilicate catalyst and an aqueous organic solvent: Ti-MFI (i.e., titanosilicate-1) with aqueous methanol (CH₃OH)⁵¹⁻⁵² or Ti-MWW with aqueous acetonitrile (CH₃CN).⁵²⁻⁵⁶ The reactant streams for these processes often include aqueous H₂O₂, which introduces a mole fraction of water (x_{H_2O}) reported in the range of 0.05 to 0.3;^{51-52, 54-55} however, patented processes add water (H₂O) to the reaction mixture even when producing H₂O₂ in situ from H₂ and O₂.^{52-53, 56} These reports imply that H₂O may improve epoxidation performance, but the reasons for these differences and the magnitude of the effects are not reported.⁵¹⁻⁵⁶

The quantity of H₂O combined with organic solvents in binary, ternary, or more complex solvents affects rates of catalytic reactions. For example, turnover rates for homogeneous Brønsted

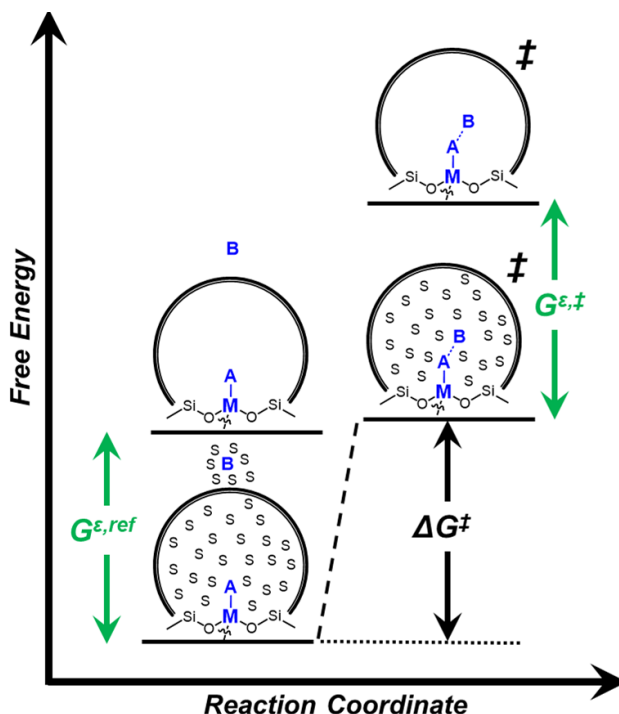
ⁱⁱⁱ This chapter has been reprinted with permission from the following publication: David S. Potts, Chris Torres, Ohsung Kwon, and David W. Flaherty, “Engineering intraporous solvent environments: effects of aqueous-organic solvent mixtures on competition between zeolite-catalyzed epoxidation and H₂O₂ decomposition pathways”, *Chemical Science* **2023**, 14, 3160-3181. Copyright 2023 Royal Society of Chemistry.

acid-catalyzed alcohol dehydrations increase by two to three orders of magnitude when changing the solvent from neat H₂O to mixtures of H₂O and organic solvents (i.e., > 0.3 molar fraction of dimethyl sulfoxide, dioxane, tetrahydrofuran (THF), CH₃CN, or gamma-valerolactone).^{112, 203-204} A separate work revealed that furfuryl acid hydrolysis yields over Brønsted acidic zeolite H-MFI increased from less than 10% in neat H₂O to nearly 70% in an equimolar THF-H₂O mixture.¹¹⁴ Authors of these studies attribute rate changes to differences in the solvent environment around the reactant in the fluid phase or within the zeolite pores as the solvent composition varies. Solvent molecules interact with and alter the stability of reactive species, which can influence rates of homogeneous and heterogeneous catalytic reactions.¹²²⁻¹²⁶

Within the field of organocatalysis, recent studies sought to manipulate the rates and selectivities achieved by catalytic complexes by tailoring outer-sphere interactions, also known as second coordination sphere effects.²⁰⁵⁻²⁰⁶ Outer-sphere interactions encompass hydrogen bonding, electrostatic, and hydrophobic interactions, among others. These interactions may be manipulated through alterations to the ligand structure and ion pairs but also by changes to the composition of the solvent.³⁷ Researchers have long appreciated that solvents influence enzymatic²⁰⁷ and organocatalytic³⁸ reactions, with publications dating to 1890 showing that the solvent choice altered rates for the quaternization of triethylamine with iodoethane by nearly 3 orders of magnitude.³⁶ Classical theories (e.g., Kirkwood,²⁰⁸ Debye and Hückel,²⁰⁹ and Kamlet and Taft²¹⁰) provide frameworks to understand the influence of solvents on reaction rates by correlating bulk solvent properties to the thermodynamic activity of reactive intermediates (i.e., solutes). These descriptions rely on mean-field descriptions and do not describe phenomena at a molecular level. For these reasons, they cannot account for outer-sphere or solvent-mediated interactions at solid-liquid interfaces. Recently, we described a conceptual framework¹²⁴ for quantifying these effects

within rate expressions for chemical reactions that captures the impact of solvent mediated interactions on the stability of reactive species through excess free energy contributions (G^E) (**Scheme 3.1**). These contributions arise from thermodynamic non-idealities that alter the activity coefficients of reactive species.³⁹ The non-idealities brought about by solvent molecules are functionally identical to second coordination sphere effects considered for homogeneous, enzymatic, and electrochemical catalytic processes.

Interactions between solvents and reactants at solid-liquid interfaces provide energetic contributions that strongly influence zeolite-catalyzed epoxidation reactions,^{72-78, 211} among other chemistries. For example, the identity of the organic solvent affects alkene epoxidation turnover rates. Previous work from our group and others showed that CH₃OH solvent gives greater epoxidation turnover rates for C₆ – C₁₈ linear and cyclic alkenes than CH₃CN over Ti-MFI,^{76, 86, 88, 212} but lower rates than CH₃CN over Ti-BEA^{76, 86, 90, 213} and Ti-MWW.^{86, 89, 214} These differences reflect either direct effects of the zeolite topology or inadvertent or unrecognized effects that may include differences related to the densities of silanol defects ((SiOH)_x, where x ranges from 1 to 4 and depends upon the mechanism of defect formation), variations in the crystal habit, particle dimensions, and associated intraparticle transport effects caused by variations in the synthesis protocol. Notably, the density of (SiOH)_x impacts the hydrophilicity of the pores and the kinetics of liquid phase alkene epoxidations. Turnover rates for epoxidations of C₆ – C₁₈ linear alkenes in CH₃CN with aqueous H₂O₂ in hydrophilic Ti-BEA surpass rates in hydrophobic Ti-BEA by factors of 40 to 450.^{72, 74, 211} The most hydrophilic zeolites possess multiple (SiOH)_x nests per unit cell that stabilize hydrogen bonded networks of H₂O molecules within their pores, while the most hydrophobic zeolites contain far less than one (SiOH)_x per unit cell and contain less H₂O.¹³⁴⁻¹³⁵ During epoxidation turnovers, the formation of the alkene epoxidation transition state (or the



Scheme 3.1. Reaction coordinate depicting the influence of solvent molecules on a generic reaction over a metal (M)-incorporated zeolite between A and B through changes in the excess free energy of the reference state ($G^{\epsilon, ref}$) and transition state ($G^{\epsilon, \ddagger}$).

adsorption of an epoxide) disrupts and displaces hydrogen bonded H_2O and CH_3CN molecules from pores and brings entropic gains that stabilize the transition state to increase rates.^{74, 211} In general, solvent molecules alter rates and activation free energies for catalytic reactions through changes in G^{ϵ} (**Scheme 3.1**).

Recent literature indicates that the presence of H_2O influences rates of alkene epoxidation; however, discrepancies among reports regarding the magnitude of these effects, the values of $x_{\text{H}_2\text{O}}$ needed, differences between organic solvents, and disagreement over the physical origins motivate closer examination of these phenomena across common aqueous organic solvent mixtures. A fraction of studies showed that increasing $x_{\text{H}_2\text{O}}$ does not affect rates for alkene epoxidations. Ramachandran et al. reported that 1-hexene (C_6H_{12})⁸⁸ epoxidation rates do not depend on $x_{\text{H}_2\text{O}}$ ($0.03 \leq x_{\text{H}_2\text{O}} \leq 0.3$) and argued that H_2O does not enter pores or reside near Ti active sites. Bregante

et al. showed that 1-octene (C_8H_{16}) epoxidation rates did not change with x_{H_2O} ($0.0002 \leq x_{H_2O} \leq 0.008$) and reasoned that the intrapore H_2O concentration remains constant in this dilute limit.⁷⁴ Other reports found that adding H_2O increases epoxidation rates of propylene (C_3H_6)⁸⁹ and C_6H_{12} .^{86, 90} The rate increases for each C_6H_{12} epoxidation study were attributed to the stabilization of titanium-hydroperoxo (Ti-OOH) reactive intermediates by the formation of a 5-membered ring with an H_2O molecule.^{86, 90} The ratio of the organic solvent (CH_3CN) to H_2O was proposed to affect rates by changing the hydrophilicity of the environment around Ti sites, which affected the access of C_3H_6 and H_2O_2 to Ti sites.⁸⁹ Rates and barriers for H_2O_2 decomposition (an undesirable side reaction) also depend on the choice of organic solvent used in aqueous mixtures,⁹⁰⁻⁹¹ however, the dependence upon x_{H_2O} has not been reported. Notably, these prior studies utilized different combinations of organic solvents (e.g., CH_3OH , CH_3CN , acetone), Ti-zeolites (i.e., *BEA, MFI, MWW frameworks), and reaction conditions (i.e., temperature, reactant, and H_2O concentrations). Furthermore, reactant concentrations varied in ways that apparently yielded distinct kinetic regimes. Finally, speculative interpretations were rarely corroborated by complementary experimental methods to confirm the influence of x_{H_2O} on rates. Consequently, intentional pairing of solvents with surfaces for new systems of reactants, solvents, and catalysts relies on guesswork and experimentation. Solvent composition clearly influences the kinetics and possibly the mechanism for alkene epoxidation and H_2O_2 decomposition reactions at solid-liquid interfaces, underscoring the importance of understanding how x_{H_2O} influences epoxidation and H_2O_2 decomposition pathways.

Here, the interpretations of differences between the intrinsic kinetics for C_6H_{12} epoxidation and H_2O_2 decomposition reactions in aqueous-organic solvent environments within Ti-BEA zeolites show that solvation effects primarily govern rates and barriers. These comparisons control

for potential variations in zeolite framework and reaction conditions that differed among previous studies, strengthening conclusions that solvent structures interact with adsorbed and liquid phase reactive species to influence catalysis. Turnover rates for C₆H₁₂ epoxidation with aqueous H₂O₂ increase with x_{H_2O} ($0.002 \leq x_{H_2O} \leq 0.8$) while turnover rates for H₂O₂ decomposition decrease over hydrophilic (Ti-BEA-OH) and hydrophobic (Ti-BEA-F) zeolites in aqueous mixtures of three organic solvents (CH₃CN, CH₃OH, and γ -butyrolactone (GBL, C₄H₆O₂)). These trends result in greater epoxide formation rates and H₂O₂ selectivities at higher x_{H_2O} , regardless of the identity of the organic component of the solvent. Comparisons among turnover rates normalized by the solvent-dependent activity coefficients of the fluid phase reactants demonstrate that the solvent composition strongly influences the stability of intermediates and transition states within the pores of Ti-BEA. The interpretation of measured activation enthalpies and entropies for epoxidation and H₂O₂ decomposition shows that epoxidation rates rise with higher x_{H_2O} due to a combination of increased thermodynamic activity of fluid phase C₆H₁₂ and increases in the entropy of the epoxidation transition state by the disruption of hydrogen bonds among intrapore H₂O molecules. In contrast, H₂O molecules likely enthalpically stabilize the hydrophilic transition state for H₂O₂ decomposition through hydrogen bonding but more significantly stabilize fluid phase H₂O₂ and Ti-OOH, leading to lower decomposition rates at higher x_{H_2O} . These interpretations agree with differences among 1,2-epoxyhexane adsorption enthalpies measured by isothermal titration calorimetry as functions of solvent composition. Analysis of the activation barriers for both reaction pathways and the trends in epoxide adsorption enthalpies show that multiple kinetic and thermodynamic parameters depend sensitively on the values of x_{H_2O} and vary more significantly with x_{H_2O} in Ti-BEA-OH than Ti-BEA-F. These comparisons agree with differences among intrapore solvent compositions between zeolites and organic solvents, which show that (SiOH)_x

necks facilitate preferential uptake of H₂O within pores and lead to greater interaction among H₂O molecules and surface intermediates at any given x_{H_2O} for the bulk fluid. Cumulatively, these findings show how the stability of reactive intermediates and transition states for epoxidation vary due to interactions with intrapore H₂O molecules and demonstrate the ubiquity of these effects across solvent mixtures and zeolites with distinct hydrophilic or hydrophobic nature.

3.2 Materials and Methods

3.2.1 Catalyst Synthesis

Ti-BEA-OH was prepared by post-synthetic modification of commercial Al-BEA, following previously published procedures.^{148, 179} Al-BEA (TOSOH, lot no. 94HA6X02Y; Si:Al = 20) was treated in refluxing HNO₃ (Macron Chemicals, 68 – 70 wt%, 20 cm³ g⁻¹) at 433 K for ~24 h to remove Al atoms from the *BEA framework by forming soluble Al(NO₃)₃. The dealumination treatment was carried out 3 times to ensure thorough dealumination (Si:Al > 1200). Between dealuminations, the *BEA sample was washed with deionized H₂O (18.2 MΩ cm, Elga Purelab Flex 2, 50 cm³ g_{zeolite}⁻¹) and recovered by vacuum filtration. After the last dealumination, the dealuminated *BEA was heated to 823 K (5 K min⁻¹) in flowing air (200 cm³ min⁻¹; Airgas, Ultra Zero grade) and held at 823 K for 6 h to remove organic residues. The resulting material (Si-BEA-OH) was heated in a round-bottom flask under vacuum (< 5 Pa, 473 K) to create a moisture-free environment, after which dichloromethane (CH₂Cl₂, Fisher Chemicals, 20 cm³ g_{zeolite}⁻¹) solvent was added to the flask. Titanium atoms were then incorporated into the framework by adding TiCl₄ to the Si-BEA-OH and CH₂Cl₂ mixture under an inert atmosphere (328 K, refluxing CH₂Cl₂, ~16 h, 50 cm³ min⁻¹ Ar, Airgas, Ultra High Purity). The resulting Ti-BEA-OH was recovered by rotary evaporation and was heated to 823 K (5 K min⁻¹) in flowing air (200 cm³ min⁻¹) and held at 823 K for 6 h, resulting in a white powder sample.

Ti-BEA-F was synthesized by following a previous procedure.^{136, 150} 16.82 g of tetraethylammonium fluoride hydrate (TEAF, Sigma-Aldrich, 98%) was dissolved in 27 cm³ of deionized H₂O (18.2 MΩ cm, Elga Purelab Flex 2) in a polypropylene container. 39.87 cm³ of tetraethylorthosilicate (TEOS, Sigma-Aldrich, >98 wt%) was added, and the mixture was stirred for 30 min at room temperature. 0.351 cm³ of titanium (IV) isopropoxide (TIPO, Sigma-Aldrich, 99.999%) was added, and the solution was covered and stirred for an additional 16 h to produce a white, opaque homogeneous solution. The cover was removed, and the mixture was stirred for 12 h to evaporate the alcohols formed from the hydrolysis of TIPO (isopropanol) and TEOS (ethanol). The mass of alcohols formed was estimated by assuming complete and stoichiometric hydrolysis of all TIPO and TEOS added. The solution was left uncovered to allow the alcohols to evaporate until the mass of the solution decreased by an amount equal to 115% of the calculated mass of the alcohols to increase the likelihood of complete evaporation of these alcohols. The alcohols are assumed to evaporate preferentially before water based on their greater volatility. A mass of deionized H₂O equivalent to the difference between the total mass evaporated (36.8 g) and the calculated mass of alcohols formed (31.0 g) was added to account for the H₂O lost during evaporation. The mixture was then transferred to a Teflon liner (Parr Instruments, 125 cm³, Model 4748). This yielded a gel with an approximate molar composition of 1 Si:0.006 Ti:0.56 TEAF:8.89 H₂O. A small amount of Si-BEA-OH seeds (3% by mass relative to SiO₂ in the synthesis gel) from a previous synthesis was added to promote crystallization. The Teflon liner was loaded into a stainless-steel autoclave (Parr Instruments, 125 cm³, Model 4748) and heated to 413 K at dynamic conditions (60 rpm) in a convection oven (Yamato, DKN602C) for 20 days. The resulting material was recovered by centrifugation, washed with H₂O, and dried in an oven for 12 h at 343 K. The

dried solid was heated at 5 K min^{-1} to 823 K in flowing air ($200\text{ cm}^3\text{ min}^{-1}$) and held at 823 K for 6 h to produce a white powder Ti-BEA-F sample.

3.2.2 Catalyst Characterization

The titanium (Ti), silicon (Si), and aluminum (Al) contents of the Ti-BEA catalysts were determined with energy-dispersive X-ray fluorescence (EDXRF). Finely ground samples of Ti-BEA (~50 mg) were loaded into a polypropylene cup (1 cm diameter) sealed with ultralene film. The sample cups were loaded into the He-purged chamber of the spectrometer (Shimadzu, EDX-7000). The samples were scanned between 0 and 30 keV, and the intensities of the fluorescence features were used to calculate the mass of Ti, Si, and Al within the sample. The EDXRF measurements show that Ti-BEA-OH (Si:Al ~1200) and Ti-BEA-F (Si:Al ~1750) contain only trace quantities of Al. The trace amount of Al in Ti-BEA-F may result from Al impurities from the components used in the synthesis. Compositions of the Ti-BEA samples were also assessed by ICP-OES, which confirmed each sample contained negligible quantities of Al (Si:Al > 2800) and possessed Ti quantities consistent with the results from EDXRF. Ti loadings and Si:Al ratios for each zeolite are shown in **Table 3.1**.

The dispersity of the Ti atoms in the Ti-BEA catalysts was measured with diffuse reflectance UV-vis (DRUV-vis) spectroscopy. Magnesium oxide (MgO, Sigma-Aldrich, 99.9995%) was used as a background. Ti-BEA samples were mixed and ground into a fine powder with magnesium oxide at a MgO:Ti-BEA mass ratio of 10:1 to measure sample spectra on a UV-vis spectrophotometer (Varian, Cary 5G). The total reflectance spectra were measured under ambient conditions, and the band gap energies (**Table 3.1**) were determined by extrapolating the linear portion of the Tauc plots to the horizontal axis to determine the minimum energy of photons absorbed (eV) (**Appendix Figure B1**).

The crystallinities of the Ti-BEA samples were confirmed using an X-ray diffractometer (Bruker, D8 Advance) with Cu K α radiation under ambient conditions. The Ti-BEA samples were ground into a fine powder and loaded into a polypropylene sample holder for the measurements. The diffractograms of the Ti-BEA samples match previously reported powder diffraction patterns for zeolite *BEA (**Figure B2**).¹⁵¹ These diffractograms confirm that all Ti-BEA samples possess the *BEA zeolite framework. Anatase TiO₂ contains a strong feature at ~ 25.5 degrees,²¹⁵ while the *BEA framework shows a weak feature in the same location. The patterns for each Ti-BEA and Si-BEA-OH in **Figure B2** possess a small feature in this region, suggesting that the feature either originates from a *BEA framework feature or minimal quantities of TiO₂ present within the Ti-BEA materials.

Ex situ Raman spectra of the Ti-BEA catalysts were measured with a Raman spectrometer (Renishaw, InVia) equipped with a 532 nm laser. The measurements were performed at ambient conditions on pressed catalyst pellets. The accumulation time was 20 s per scan, and each Raman spectra was calculated by averaging 10 scans. The delivered power density was approximately 2 mW μm^{-2} , as measured by a power meter (Gentec-EO, PRONTO-SI). The Raman spectra for each Ti-BEA (**Figure B3**) lack discernible features at 144 cm^{-1} , which indicates the absence of Ti-O-Ti bonds present in anatase TiO₂. In conjunction with the high band gaps (4.3 eV, **Table 3.1**) of these materials and the absence of strong TiO₂ features on the XRD patterns, these spectra indicate that Ti atoms reside in tetrahedral positions within the *BEA framework.

Catalyst	Si:Al	Ti wt%	Band Gap (eV) ^c	Φ_{IR} ^d	BET Surface Area ($\text{m}^2 \text{g}^{-1}$) ^e	Micropore Volume ($\text{cm}^3 \text{g}^{-1}$) ^f
Ti-BEA-OH	1220 ^a , 2800 ^b	0.36 ^a , 0.34 ^b	4.3	2.25	628	0.172
Ti-BEA-F	1750 ^a , 2880 ^b	0.26 ^a , 0.25 ^b	4.3	0.27	543	0.173

Table 3.1. Ti Content, Band Gap, and Relative Hydrophilicity of Synthesized Ti-BEA

^aDetermined with EDXRF. ^bMeasured with ICP. ^cExtracted from leading edge of Tauc plot from DRUV-vis. ^dCalculated from infrared transmission spectra of dehydrated Ti-BEA samples. ^eMeasured by volumetric Ar physisorption. ^fCalculated using the t-plots from Ar physisorption.

The surface area and micropore volumes of each Ti-BEA were determined using gas-phase adsorption isotherms of N₂ (77 K) and Ar (87 K). The effect of (SiOH)_x density on gaseous solvent uptake was determined from adsorption isotherms of H₂O and CH₃OH (295 K). All adsorption isotherms were collected on a volumetric adsorption instrument (Micromeritics, 3Flex). The Ti-BEA samples were pelletized and sieved to retain particles from 100 – 250 μm in diameter. The samples were degassed under dynamic vacuum prior to adsorption ($< 7 \times 10^{-4}$ Pa, 673 K, 3 h). The surface area was calculated using the Rouquerol-modified Brunauer-Emmett-Teller (BET) method,¹⁵⁷ and the micropore volume was determined from the *t*-plot method.¹⁵⁸ **Figure B4** shows the N₂ and Ar isotherms, and **Table B1** presents the total and external surface area, BET surface area and pore volume from N₂ adsorption, and total pore volume for each Ti-BEA. The H₂O and CH₃OH isotherms are displayed in **Figure B5**.

The relative density of (SiOH)_x groups within the Ti-BEA catalysts was measured using infrared spectroscopy. Catalyst pellets (~50 mg) were loaded into a transmission cell configured with CaF₂ windows. The transmission cell was connected to a temperature controller and gas manifold, then loaded into a Fourier-transform infrared spectrometer (Bruker, Vertex 70) equipped with a liquid N₂-cooled HgCdTe detector, as described previously.²¹⁶ The cell was first heated to 573 K at ~5 K min⁻¹ and held for 2 hours in flowing He (50 cm³ min⁻¹, 99.997%, Airgas) to desorb any water and volatile compounds. Infrared spectra (128 scans, 1 cm⁻¹) of the Ti-BEA samples were then taken at 573 K (**Figure B6**). Background spectra were obtained with the empty transmission cell at identical conditions. The vibrational modes on the dehydrated Ti-BEA spectra between 3300-3750 cm⁻¹ and 1800-2100 cm⁻¹ represent ν(O-H) of (SiOH)_x groups¹⁵⁵⁻¹⁵⁶ and Si-O-Si overtones¹⁵⁴ of the *BEA framework, respectively. The sharp feature at 3740 cm⁻¹ represents isolated SiOH groups that do not interact with other SiOH groups.¹⁵⁵⁻¹⁵⁶ The broader features from

3300 to 3700 cm^{-1} represent defects containing multiple interacting hydroxyl moieties present within $(\text{SiOH})_x$ groups. The ratio of the areas for $\nu(\text{O-H})$ and $\nu(\text{Si-O-Si})$ at 1865 and 2000 cm^{-1} gives a relative measure of SiOH density in each Ti-BEA (Φ_{IR} , **Equation 3.1**). The area of the isolated SiOH feature is excluded from $\nu(\text{O-H})$ in Φ_{IR} calculations. The $\nu(\text{O-H})$ region was deconvoluted into multiple peaks (see **Section B1.5**), and the isolated SiOH peak area was subtracted from the combined area of the $\nu(\text{O-H})$ region.

$$\Phi_{IR} = \frac{A_{\nu(\text{O-H})}}{A_{\nu(\text{Si-O-Si})}} \quad (3.1)$$

The Φ_{IR} values (**Table 3.1**) suggest that Ti-BEA-OH contains a density of $(\text{SiOH})_x$ groups nearly one order of magnitude greater than Ti-BEA-F.

Collectively, the characterization results provide strong evidence that Ti-BEA-OH and Ti-BEA-F materials contain atomically dispersed Ti atoms at framework positions within a crystalline *BEA framework. Moreover, these materials lack spectroscopically detectable quantities of TiO_2 nanoparticles or crystallites. Each zeolite contains ~ 1 Ti atom per 4 unit cells of *BEA, and Ti-BEA-OH contains 2.75 $(\text{SiOH})_x$ nests per unit cell (calculation in **Section B1.6**). The synthesis method of Ti-BEA-F prohibits a direct calculation of $(\text{SiOH})_x$ per unit cell, but previously established trends between Φ_{IR} and $(\text{SiOH})_x$ ⁷³ indicate that the Ti-BEA-F sample synthesized for this work ($\Phi_{IR} = 0.27$, **Table B1**) contains < 0.1 $(\text{SiOH})_x$ per unit cell.

3.2.3 Epoxidation Turnover Rate Measurements

Turnover rates for 1-hexene (C_6H_{12} , Sigma-Aldrich, $>99\%$) epoxidation with hydrogen peroxide (H_2O_2 , Fisher Chemical, 30 mol% in H_2O) in aqueous solutions of either acetonitrile (CH_3CN , Fisher Chemical, HPLC Grade), methanol (CH_3OH , Sigma-Aldrich, HPLC, $\geq 99.9\%$), or γ -butyrolactone (GBL, $\text{C}_4\text{H}_6\text{O}_2$, Sigma-Aldrich, $\geq 99\%$) were measured in three-necked round-

bottom flasks with magnetic stirring (700 rpm). The flasks were gently clamped to reflux condensers to avoid evaporative losses and submerged in a temperature-controlled H₂O (308 – 318 K) or oil (323 – 338 K) bath on a hot plate (Corning, PC-420D). The reagents (C₆H₁₂ and H₂O₂) were combined with H₂O (18.2 MΩ cm, Elga Purelab Flex 2) and CH₃CN, CH₃OH, or C₄H₆O₂ along with benzene as an internal standard (Sigma-Aldrich, thiophene-free, >99%) and stirred for 0.5 h before an initial aliquot (~0.5 cm³) was taken to determine the initial concentration of C₆H₁₂ and product, 1,2-epoxyhexane (C₆H₁₂O). Ti-BEA (~20-50 mg) was then added to initiate the reaction, and aliquots were taken as a function of time using a syringe equipped with a polypropylene filter (Tisch Scientific, 0.22 μm) to separate the sample from the catalyst particles. The concentrations of alkene, benzene standard, and epoxide product were quantified with a gas chromatograph (Agilent, 6850) equipped with a polysiloxane column (HP-1, Agilent, 19091Z-115E), flame ionization detector, and liquid autosampler (CTC Analytics, GC Pal). Initial turnover rates were determined by fitting turnover numbers (moles of C₆H₁₂O per moles of Ti) as a function of time to a second-order polynomial with the y-intercept fixed at zero and determining the derivative at time equal to zero. All reported turnover rates were measured at differential conversion (<5%), with an uncertainty of ~10% in reported rates, as shown with replicated measurements. The conditions used for rate measurements in this study avoid internal mass transfer constraints, as indicated by the linear dependence of turnover rates on alkene concentration (**Section 3.3.1**),¹⁵⁹ which is consistent with expectations based on prior studies of reactions of H₂O₂ with alkenes in Ti substituted MFI, *BEA, and FAU at similar conditions.^{30, 72, 76} A mass-transfer limited material would show a sub-linear dependence on alkene concentration because the mean concentration of alkenes throughout the pores would not depend linearly on the fluid phase alkene concentration.

H₂O₂ consumption rates ($-r_{H_2O_2}$) were measured with C₆H₁₂ present to calculate the selectivities for H₂O₂ consumption ($S_{H_2O_2}$) as a co-reactant for epoxidation, as opposed to decomposition between two H₂O₂ molecules to form H₂O and oxygen ($-r_{decomp}$). We note that solvent molecules may react with H₂O₂ to provide another contribution to $-r_{decomp}$, but rate changes with [H₂O₂] suggest that the bimolecular decomposition of H₂O₂ dominates contributions to $-r_{decomp}$ (**Figure 3.2c**). We define H₂O₂ selectivity as the ratio of the epoxidation rate (r_{epox}) to the overall H₂O₂ consumption rate ($-r_{H_2O_2}$):

$$S_{H_2O_2}(\%) = \frac{r_{epox}}{-r_{H_2O_2}} * 100 \quad (3.2)$$

Activation barriers for H₂O₂ decomposition were measured in the absence of C₆H₁₂. Solutions to measure H₂O₂ concentration were prepared using colorimetric titration with a titrant solution consisting of cupric sulfate (8.3 mM; VWR, 99%) and neocuproine hydrate (12 mM; SAGECHEM) in an aqueous solution of ethanol (4.3 M; Sigma-Aldrich, $\geq 99.5\%$). Aliquots from the reactions (0.15 cm³) were mixed with the titrant (1 cm³) and DI H₂O (0.85 cm³). The absorbance of this solution at 454 nm was then measured using a UV-Vis spectrophotometer (Spectronic, 20 Genesys) to obtain the H₂O₂ concentration. A calibration curve was developed with solutions of known H₂O₂ concentration to convert absorbance to concentration. The concentrations were used to calculate H₂O₂ decomposition rates by subtracting the formation rate of 1,2-epoxyhexane from the total rate of H₂O₂ consumption.

3.2.4 In Situ Analysis of H₂O₂ Activation

H₂O₂ activation over the Ti-BEA catalysts was examined using a UV-Vis spectrometer (Avantes, AvaSpec-2048) equipped with a pulsed xenon light source (Avantes, AvaLight-XE-Mini). Ti-BEA pellets (7 mm diameter) were loaded into a custom-built liquid flow cell attached

to cartridge heaters and a temperature controller (Watlow, EZ-ZONE PM) to hold the cell at 313 K. The cell and spectrometer were connected to a 45-degree fiber optic diffuse reflection probe (Avantes, FC-UVIR600-2-BX-SR). Solvents and H₂O₂ were introduced continuously to the cell (1 cm³ min⁻¹) using a high-performance liquid chromatography pump (Teledyne ISCO, ReaXus M1 Class). Background spectra were collected by flowing solvent without H₂O₂ (10 – 40 ms integration time, averaging 125 – 500 scans). Then solvent and H₂O₂ (0.1 M H₂O₂, 0.39 M H₂O) flowed through the cell until spectra stopped changing (~0.5 h), which indicated the coverage of H₂O₂-derived intermediates reached a steady state value. Finally, the cell was purged with flowing solvent without H₂O₂ for 1 h to examine the reversibility of H₂O₂ activation.

3.2.5 Liquid Phase Adsorption Enthalpies for 1,2-Epoxyhexane

The heat released upon adsorption of C₆H₁₂O (TCI Chemicals, >96%) was measured with an isothermal titration calorimeter (ITC) (TA Instruments, NanoITC) equipped with sample and reference cells. A multi-step cleaning procedure was performed to prepare the sample and reference cells for each experiment. A cleaning solution (75 vol % of 1 M NaOH, 20 volume % CH₃OH, 5 volume % dish soap) was first injected into the sample cell and left for 5 minutes at room temperature. The sample cell was then rinsed with 500 cm³ of DI H₂O (18.2 MΩ cm, Elga Purelab Flex 2). Next, a 4 M NaOH (VWR, 10 N) solution was left in the cell for 2 hours at 353 K, followed by another rinse with 500 cm³ of DI H₂O. Finally, the cell was treated with a solution of 4 M HNO₃ (Macron Chemicals, 68 – 70 wt%) for 2 hours at 353 K, then a third rinse with 500 cm³ of DI H₂O. The sample cell, reference cell, and 50 μL ITC syringe were then filled with H₂O, and the syringe was loaded into the instrument. A subsequent electrical calibration used sequential pulses to determine the heat released from a calibrated Pt resistor. Finally, pure DI H₂O was injected into DI H₂O to ensure that the sample cell was clean enough to begin experiments. The

cell was assumed to be clean when the H₂O-H₂O injection released negligible amounts of heat ($\pm$ 3 μ J for each injection of 1 μ L). The cleaning procedure was repeated if the H₂O-H₂O injection did not give sufficiently low heat rates.

In a typical experiment, a slurry of Ti-BEA (15-30 mg) in organic solvent with H₂O was titrated by a solution of epoxide (5-10 mM C₆H₁₂O) in the same solvent mixture. The mass of Ti-BEA in the sample cell was calculated by taking the difference between the mass added to the slurry and the mass remaining upon evaporation of the residual slurry after loading the cell. H₂O concentrations were chosen to match conditions for kinetic turnover rate measurements (**Section 3.3.1**). The titrations were carried out at 313 K with a stirring rate of 250 rpm. The enthalpies of epoxide adsorption were calculated by averaging the integrated heats released upon adsorption of the epoxides to Ti-BEA sites from a 1 μ L injection of titrant at low coverages (< 0.25 mol epoxide (mol Ti)⁻¹). The heats released in this low coverage regime remain approximately constant, suggesting that the calculated enthalpies represent the isosteric adsorption enthalpies for each epoxide.⁷³

3.2.6 Liquid Phase Absorption of Aqueous Solvents

A nuclear magnetic resonance (NMR) spectrometer (Unity, INOVA 500 NB) was used to calculate the equilibrium compositions of aqueous solutions of organic solvents contacted to and equilibrated with Ti-BEA-OH and Ti-BEA-F samples by measuring ¹H NMR peak areas. For each data point, an aliquot (~ 0.25 cm³) of organic solvent and H₂O was taken from a solvent solution (5 cm³) before and after 2 h contact with a Ti-BEA sample (~ 500 mg) at a stirring rate of 700 rpm and temperature of 313 K to measure the change in the bulk liquid phase concentration. The catalyst and solvent mixture were in contact for 2 h to ensure solvent absorption had reached equilibrium. The sample of organic solvent and H₂O was then mixed with deuterated methanol

(CD₃OD) as solvent and acetone or chloroform as an internal standard to prepare the NMR sample. The initial and final composition of the extrapore liquid was determined using areas of ¹H-NMR features for H₂O (4.5 ppm), acetone (2.2 ppm) or chloroform (7.8 ppm), and the organic solvent (CH₃CN at 2.1 ppm, CH₃OH at 3.3 ppm, C₄H₆O₂ features at 2.3, 2.6 and 4.5 ppm). The intrapore solvent composition was estimated from the amount of solvent absorbed by the catalyst and the difference in extrapore liquid phase concentration before and after contacting the solvent with the catalyst (Section B2).

3.3 Results and Discussion

3.3.1 Epoxidation and H₂O₂ Decomposition Rates Depend on Aqueous Solvent Composition

Figure 3.1 shows that turnover rates for C₆H₁₂ epoxidation and H₂O₂ decomposition depend strongly on the identity of the organic component of the aqueous solvent and the value of x_{H_2O} . Turnover rates span four-orders of magnitude and, consequently, lead to H₂O₂ selectivities ($S_{H_2O_2}$) that range from 0.1 – 98%. **Figure 3.1a** shows that rates of C₆H₁₂ epoxidation increase as x_{H_2O} increases for all organic solvents over both Ti-BEA-OH and Ti-BEA-F. Ti-BEA-OH gives greater rates than Ti-BEA-F for each organic solvent at all x_{H_2O} . This systematic difference was previously attributed to entropy gains that reflect the disruption of greater quantities of hydrogen bonded H₂O molecules in hydrophilic pores of Ti-BEA.^{72, 74, 211} Epoxidation turnover rates in C₄H₆O₂ are consistently lowest among these organic solvents at all x_{H_2O} . CH₃CN provides the greatest rates in all cases except when x_{H_2O} exceeds 0.4 over Ti-BEA-F, where rates in CH₃OH surpass those in CH₃CN.

Figure 3.1b shows that turnover rates for H₂O₂ decomposition (i.e., in the absence of C₆H₁₂) decrease with increasing x_{H_2O} for all combinations of organic solvent and zeolite, which

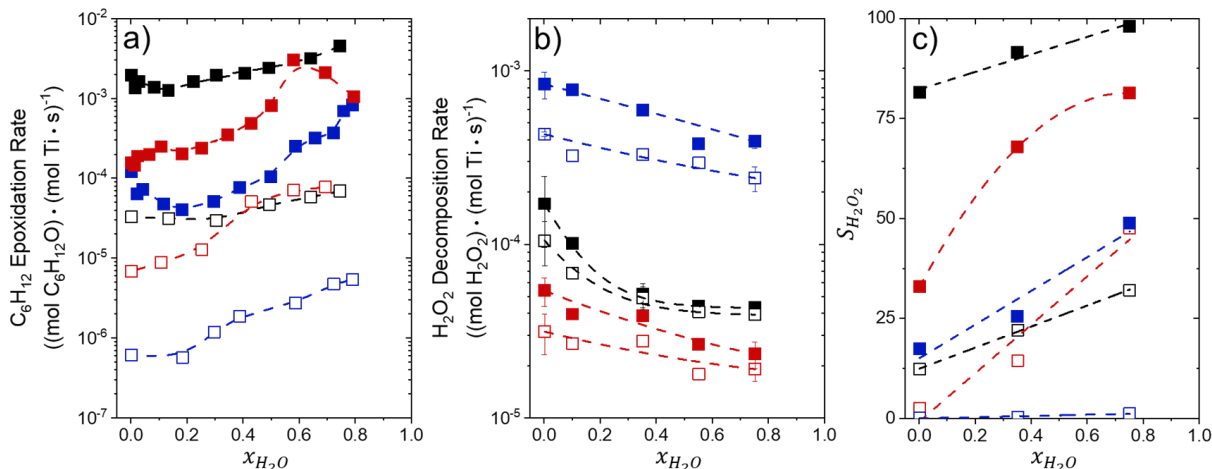


Figure 3.1. Turnover rates for a) C₆H₁₂ epoxidation to form C₆H₁₂O (1 mM C₆H₁₂, 10 mM H₂O₂, 313 K), b) H₂O₂ decomposition (1 mM H₂O₂, 313 K), and c) H₂O₂ selectivities for epoxidation (1 mM C₆H₁₂, 10 mM H₂O₂, 313 K) as a function of H₂O mole fraction (x_{H_2O}) in mixtures of CH₃CN (■, □), CH₃OH (■, □), and C₄H₆O₂ (■, □) with H₂O over Ti-BEA-OH (solid points) and Ti-BEA-F (hollow points). The furthest left data points represent $x_{H_2O} = 0.002$, which comes from the aqueous H₂O₂ reagent solution (39 mM).

opposes the trend for epoxidation turnover rates. Among organic solvents, C₄H₆O₂ gives the greatest H₂O₂ decomposition rates and CH₃OH gives the lowest rates at all x_{H_2O} . The lower H₂O₂ decomposition rates in CH₃OH than in CH₃CN mixtures agree with previous reports over Ti-incorporated zeolite materials,⁹⁰⁻⁹¹ while turnover rates for C₆H₁₂ epoxidation in CH₃CN that are greater than those in CH₃OH mixtures concur with findings over Ti-BEA materials.^{76, 86, 90, 213} Notably, H₂O₂ decomposition rates in **Figure 3.1b** span less than two-orders of magnitude, which shows the decomposition pathway senses the identity of the solvent and zeolite less strongly than C₆H₁₂ epoxidation. The contrasting effects of organic solvent and x_{H_2O} on epoxidation and H₂O₂ decomposition rates evince that solvent molecules influence the stability of the fluid phase reactants and transition states within pores for the two pathways in different ways.

Figure 3.1c reveals that all combinations of organic solvents and zeolites show significantly higher $S_{H_2O_2}$ for C₆H₁₂ epoxidation at greater x_{H_2O} . Ti-BEA-OH gives greater values

of $S_{H_2O_2}$ than Ti-BEA-F in all cases, but $S_{H_2O_2}$ increases more with x_{H_2O} over Ti-BEA-F relative to Ti-BEA-OH (see **Section B3**). The greatest $S_{H_2O_2}$ (98%) occurs in Ti-BEA-OH with aqueous CH₃CN ($x_{H_2O} = 0.75$) (*Note*: values of x_{H_2O} greater than 0.8 were not used due to miscibility issues with C₆H₁₂). Overall, CH₃CN mixtures lead to the highest $S_{H_2O_2}$ and C₄H₆O₂ leads to the lowest $S_{H_2O_2}$ at all x_{H_2O} in Ti-BEA-OH. This trend holds at lower x_{H_2O} values (≤ 0.35) in Ti-BEA-F, but CH₃OH gives the highest $S_{H_2O_2}$ at higher x_{H_2O} (≥ 0.75). Collectively, the data presented in **Figure 3.1** shows that increasing x_{H_2O} within each organic solvent provides greater epoxidation rates and more selective use of H₂O₂ for epoxidation over Ti-BEA zeolites with different (SiOH)_x densities.

The differences in turnover rates for C₆H₁₂ epoxidation (**Fig. 3.1a**) and H₂O₂ decomposition (**Fig. 3.1b**) may result from changes in the coverage of reactive species, the reaction mechanism, or the kinetically relevant step; alternatively, these differences may reflect changes in the free energies of reagents, reactive intermediates, or key transition states due to direct interactions with solvent molecules. The coming sections distinguish these possibilities using the molecular interpretation of turnover rate expressions for the epoxidation and H₂O₂ decomposition reactions.

3.3.2 x_{H_2O} Does Not Influence Reaction Mechanisms

Turnover rates for epoxidation and H₂O₂ decomposition reflect the stabilities of the associated transition states together with the coverages of reactive surface species formed during catalysis, which depend on the concentrations of the reactants and products present. **Figure 3.2a** shows that C₆H₁₂ epoxidation rates depend linearly on C₆H₁₂ concentration ($[C_6H_{12}]$, where brackets denote the concentration of a species or the number of surface intermediates) at low ratios of $[C_6H_{12}]$ to $[H_2O_2]$ (< 0.5) in aqueous CH₃OH mixtures over both Ti-BEA-OH and Ti-BEA-F.

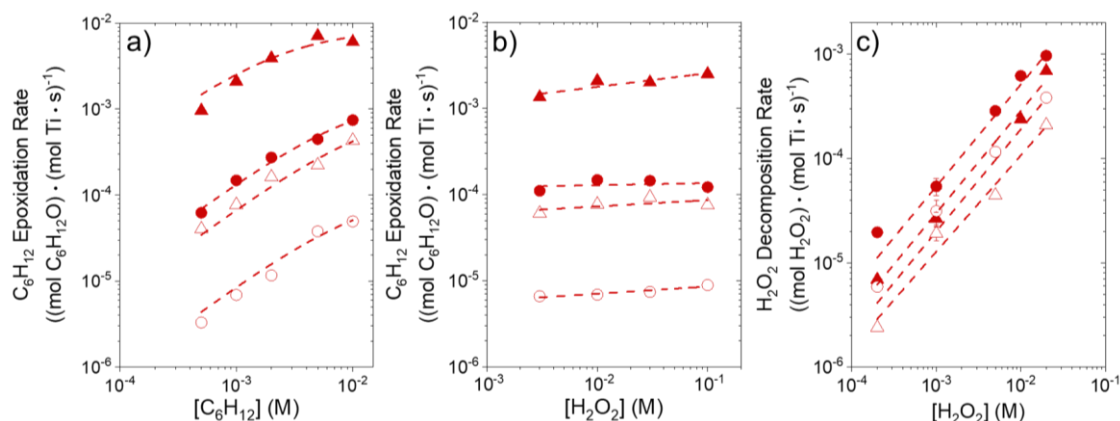
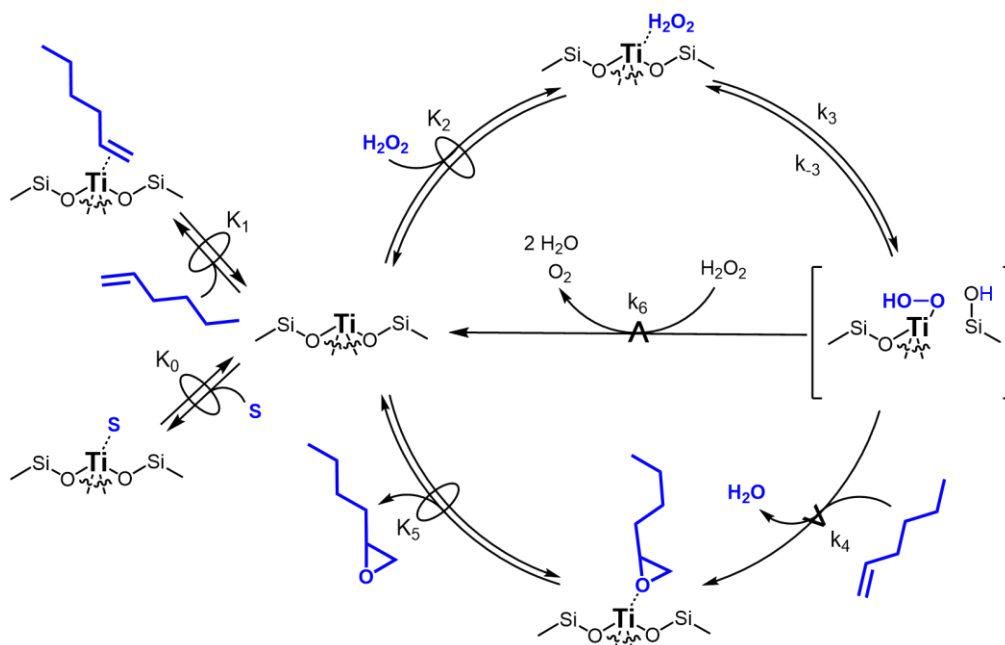


Figure 3.2. Turnover rates for C_6H_{12} epoxidation as a function of a) C_6H_{12} concentration (10 mM H_2O_2 , 313 K), and b) H_2O_2 concentration (1 mM C_6H_{12} , 313 K), and turnover rates for c) H_2O_2 decomposition (313 K) as a function of H_2O_2 concentration for CH_3OH mixtures with the minimum or maximum water contents examined (39 mM H_2O , $x_{H_2O} = 0.002$ (●,○); ~31.6 M H_2O , $x_{H_2O} = 0.75$ (▲,△)) over Ti-BEA-OH (solid points) and Ti-BEA-F (hollow points).

At these low ratios of $[C_6H_{12}]$ to $[H_2O_2]$, rates do not depend on values of $[H_2O_2]$ (**Figure 3.2b**). Rates show a sublinear dependence on $[C_6H_{12}]$ at higher ratios of $[C_6H_{12}]$ to $[H_2O_2]$, which signifies a change in the most abundant reactive intermediate (MARI). In contrast, turnover rates for epoxidation depend weakly on $[C_6H_{12}]$, linearly on $[H_2O_2]$, and inversely on epoxide product concentration ($[C_6H_{12}O]$) at sufficiently high ratios of $[C_6H_{12}]$ to $[H_2O_2]$ ($[C_6H_{12}]:[H_2O_2] > 50$), consistent with previous work.³⁰⁻³¹ **Figure 3.2c** demonstrates, however, that H_2O_2 decomposition turnover rates increase linearly with $[H_2O_2]$ on both Ti-BEA materials for all x_{H_2O} examined. Measurements obtained from aqueous solutions of CH_3CN and $C_4H_6O_2$ (**Section B4**) exhibit effects of reactant concentrations on epoxidation and H_2O_2 decomposition turnover rates that match the behavior in aqueous CH_3OH (**Figure 3.2**). Collectively, these observations match the manner in which turnover rates for epoxidation of 1-alkenes (C_6H_{12} to $C_{18}H_{36}$),^{30, 72, 74, 76, 85, 180, 211} cyclohexene,³¹ and styrene^{32, 217-218} with H_2O_2 depend upon concentrations of reactants and products in CH_3CN ^{30-32, 72, 74, 76, 85, 180, 217-218} and CH_3OH ^{76, 218} upon a range of titanasilicates (Ti-MFI,^{72, 76} Ti-BEA,^{30-32, 74, 76, 85, 217} Ti-FAU,^{72, 217} Ti-SiO₂^{32, 85, 180, 217}) and Fe- and Cr-incorporated



Scheme 3.2. Proposed mechanism for C_6H_{12} epoxidation with H_2O_2 and H_2O_2 decomposition on Ti-BEA catalysts. $\rightleftharpoons$ denotes a quasi-equilibrated step, while $\xrightarrow{k}$ signifies kinetically relevant steps for formation of distinct products. The degree of reversibility of H_2O_2 activation (step 3) varies with the quantity of protic molecules in the solvent. The blue H atom in the Si-OH group adjacent to Ti-OOH originates from H_2O_2 during Ti-OOH formation. Solvent molecules have been omitted for clarity, except for the adsorption of a solvent molecule (S) to Ti sites in step 0.

metal-organic frameworks,²¹⁸ which implies that conclusions for the effects of x_{H_2O} on epoxidation kinetics for C_6H_{12} should extend broadly across alkenes.

Scheme 3.2 depicts a plausible system of elementary steps that describe the epoxidation of C_6H_{12} and the bimolecular decomposition of H_2O_2 . The catalytic cycle begins with quasi-equilibrated adsorption of a solvent molecule (step 0), C_6H_{12} (step 1), or H_2O_2 (step 2). Then, H_2O_2 activates to form a pool of Ti-OOH^{30, 181-186} and titanium-peroxo ($Ti-(\eta^2-O_2)$)^{30, 32, 185-186} intermediates (step 3). The H_2O_2 -derived intermediates may protonate to reform H_2O_2 (reverse of step 3), react with C_6H_{12} to form $C_6H_{12}O$ (step 4), or react with a fluid phase H_2O_2 molecule to decompose to water and oxygen (step 6) in kinetically relevant processes. Radical clock experiments performed with *cis*-stilbene³⁰ give evidence that Ti-OOH intermediates, commonly

invoked as the reactive intermediate for epoxidations,^{30, 32, 185, 187-188} primarily participate in the transfer of O-atoms to alkenes to form epoxides (rather than Ti-(η^2 -O₂)). We, therefore, refer to the pool of H₂O₂-derived intermediates as Ti-OOH for simplicity. The formed epoxide then desorbs in a quasi-equilibrated manner to release the 1,2-epoxyhexane (C₆H₁₂O) product (step 5) and complete the catalytic cycle. This scheme accounts for differences in the apparent dependence of rates on reactant concentrations at low and high ratios of [C₆H₁₂] to [H₂O₂]. While O-atom transfer from Ti-OOH to C₆H₁₂ remains the kinetically relevant step for each kinetic regime,³⁰ the MARI differs between the regimes. Ti-OOH intermediates saturate active sites at low ratios of [C₆H₁₂] to [H₂O₂], and the C₆H₁₂O product covers these sites at high ratios of [C₆H₁₂] to [H₂O₂]. Based upon **Scheme 3.2** and the kinetic relevance of each step depicted, epoxidation rates (r_{epox}) follow a simple rate expression:

$$r_{epox} = k_4[Ti - OOH][C_6H_{12}] \quad (3.3)$$

where k_4 is the rate constant for step 4 (**Scheme 3.2**) and [Ti-OOH] represents the number of the H₂O₂-derived surface intermediates. Applying the pseudo-steady state hypothesis to Ti-OOH intermediates and a site balance yields a turnover rate expression (see **Section B6** for full derivation) consistent with rate measurements:

$$\frac{r_{epox}}{[L]} = \frac{\frac{k_3 k_4 K_2 [C_6H_{12}] [H_2O_2]}{k_{-3} + k_4 [C_6H_{12}] + k_6 [H_2O_2]}}{K_0 [S] + K_1 [C_6H_{12}] + K_2 [H_2O_2] + \frac{k_3 K_2 [H_2O_2]}{k_{-3} + k_4 [C_6H_{12}] + k_6 [H_2O_2]} + \frac{[C_6H_{12}O]}{K_5}} \quad (3.4)$$

Figure 3.3 presents evidence that the values of k_{-3} depend on the identity of the organic solvent and x_{H_2O} . *In situ* UV-Vis spectra give strong evidence that the H₂O₂-derived intermediates form reversibly in H₂O (**Figure 3.3a**) and irreversibly in C₄H₆O₂ (**Figure 3.3b**). Notably, the peak areas for Ti-OOH and Ti-(η^2)-O₂ attenuate by ~60% in H₂O (**Figure 3.3a**) and by ~6% in C₄H₆O₂ (**Figure 3.3b**) over a 1 h period after switching from an aqueous H₂O₂ solution to the neat solvent.

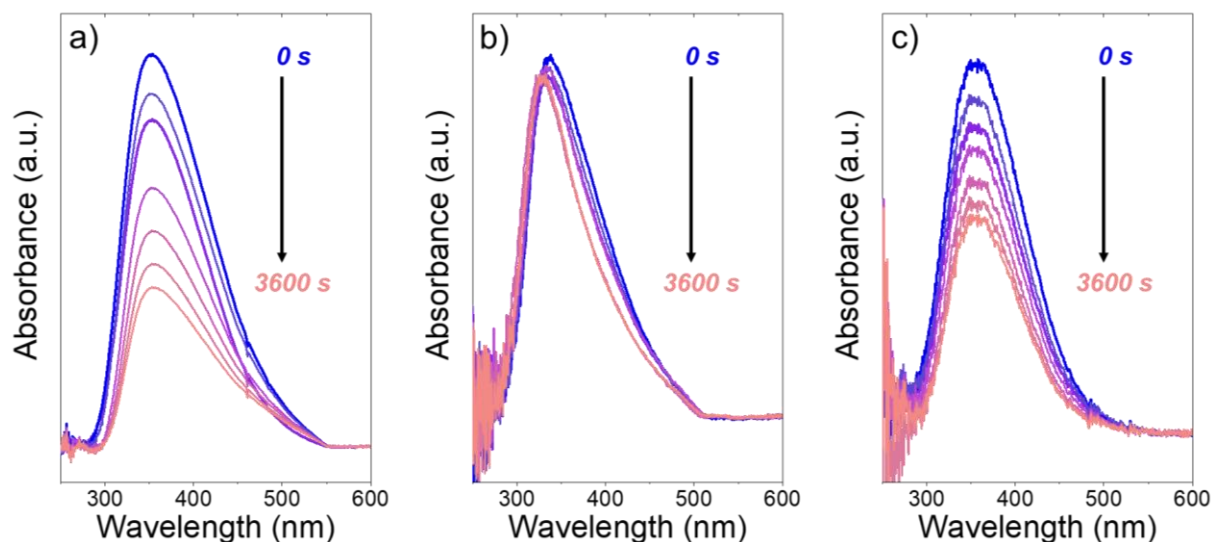


Figure 3.3. *In situ* UV-Vis spectra of Ti-BEA-OH as a function of time within continuously flowing neat a) H₂O, b) C₄H₆O₂, and c) equimolar H₂O and C₄H₆O₂ (313 K, 1 cm³ min⁻¹) after H₂O₂ activation (100 mM H₂O₂, 390 mM H₂O, 313 K, 1 cm³ min⁻¹). Spectra were acquired every 600 s after H₂O₂ activation. Spectra for Ti-BEA-F and desorption rate constants are included in **Section B5**.

Prior UV-Vis spectra suggest irreversible H₂O₂ activation in CH₃CN^{31-32, 76} and reversible activation in CH₃OH.^{76, 185} Therefore, these findings lead to the broader conclusion that protic solvents (i.e., H₂O, CH₃OH) protonate Ti-OOH and Ti-(η^2 -O₂), which then desorb as H₂O₂, but these steps are much slower in aprotic solvents (i.e., CH₃CN, C₄H₆O₂). The H₂O₂ intermediate peak areas also attenuate by ~40% in 1 h in an equimolar mixture of H₂O and C₄H₆O₂ (**Figure 3.3c**), which indicates that including a sufficient quantity of a protic component within a solvent mixture allows for reversible H₂O₂ activation. These findings demonstrate that H₂O₂ may reform from Ti-OOH and Ti-(η^2 -O₂) within all aqueous solvent combinations utilized here, where the rate of reformation depends on the concentration of protic solvent molecules present. Values of k_{-3} over Ti-BEA zeolites in CH₃OH are up to 10-times greater than in neat H₂O (**Table B3**),⁷⁶ which suggests that CH₃OH facilitates the reformation of H₂O₂ more readily than H₂O.

Despite the variations in the reversibility of H₂O₂ activation across solvent mixtures, the

full rate expression (**Equation 3.4**) simplifies to a common form when Ti-OOH intermediates saturate active sites (i.e., $[\text{Ti-OOH}] \approx [\text{L}]$).

$$\frac{r_{\text{epox}}}{[\text{L}]} = k_4[\text{C}_6\text{H}_{12}] \quad (3.5)$$

Equation 3.5 predicts rates that match the data in **Figures 3.2a** (at $[\text{C}_6\text{H}_{12}]:[\text{H}_2\text{O}_2] < 0.5$) and **3.2b**, implicating Ti-OOH intermediates as the MARI for epoxidation. Notably, **Figure B9** and **Figure 3.2** together demonstrate that the regime of a Ti-OOH MARI and first-order kinetics with respect to $[\text{C}_6\text{H}_{12}]$ holds for each combination of catalyst, organic solvent, and $x_{\text{H}_2\text{O}}$ when molar ratios of H_2O_2 to C_6H_{12} exceed two.

Rates for H_2O_2 decomposition depend on the coverage of Ti-OOH and $[\text{H}_2\text{O}_2]$ because H_2O_2 decomposition involves a reaction between a Ti-OOH intermediate and a fluid phase H_2O_2 molecule. Therefore, H_2O_2 decomposition rates correspond to:

$$-r_{\text{decomp}} = k_6[\text{Ti-OOH}][\text{H}_2\text{O}_2] \quad (3.6)$$

where k_6 is the rate constant for step 6 in **Scheme 3.2**. Substituting terms for $[\text{Ti-OOH}]$ and using the site balance for $[\text{L}]$ gives a full rate expression:

$$\frac{-r_{\text{decomp}}}{[\text{L}]} = \frac{\frac{k_3 k_4 K_2 [\text{H}_2\text{O}_2]^2}{k_{-3} + k_4 [\text{C}_6\text{H}_{12}] + k_6 [\text{H}_2\text{O}_2]}}{K_S [\text{S}] + K_1 [\text{C}_6\text{H}_{12}] + K_2 [\text{H}_2\text{O}_2] + \frac{k_3 K_2 [\text{H}_2\text{O}_2]}{k_{-3} + k_4 [\text{C}_6\text{H}_{12}] + k_6 [\text{H}_2\text{O}_2]} + \frac{[\text{C}_6\text{H}_{12}\text{O}]}{K_5}} \quad (3.7)$$

Once again, the rate expression simplifies when Ti-OOH intermediates saturate active sites, such that **Equation 3.7** collapses to the form:

$$\frac{-r_{\text{decomp}}}{[\text{L}]} = k_6[\text{H}_2\text{O}_2] \quad (3.8)$$

The rate expression in **Equation 3.8** reproduces the turnover rate dependencies on $[\text{H}_2\text{O}_2]$ shown in **Figure 3.2c**. This interpretation also agrees with prior studies that invoked a mechanism in which fluid phase H_2O_2 reacts with an H_2O_2 -derived intermediate over Ti-,^{181, 219} Nb-,²²⁰ and Ta-incorporated¹⁴⁹ microporous and mesoporous catalysts.

Notably, applying Ti-OOH as the MARI yields equations that match the data for C₆H₁₂ epoxidation (**Equation 3.5**) and H₂O₂ decomposition (**Equation 3.8**) in **Figure 3.2** simultaneously. The two pathways, therefore, proceed through the common reaction intermediate (Ti-OOH) that remains the MARI at all x_{H_2O} examined here in each zeolite. As shown for epoxidation rates, the simplified decomposition rate expression (**Equation 3.8**) does not reflect the value of k_{-3} , which implies that the reversibility of H₂O₂ activation does not impact rates of alkene epoxidation and H₂O₂ decomposition within the regime where Ti-OOH intermediates saturate active sites. This analysis indicates that kinetic measurements made under these conditions provide the requisite platform for quantitative comparisons between solvent – catalyst pairs.

To summarize, similar rate dependences for Ti-BEA-OH and Ti-BEA-F at high (0.002) and low (0.75) x_{H_2O} in each organic solvent suggest that epoxidation and H₂O₂ decomposition proceed through the same reaction mechanisms. Differences in epoxidation rates with different organic solvents, concentrations of water, and (SiOH)_x defect densities within pores of *BEA (**Figure 3.1**) do not result from changes in the reaction mechanisms or coverage of reactive species. These findings resemble the interpretation of prior investigations for homogeneous acid-catalyzed alcohol dehydration reactions that concluded solvent molecules influence the stability of fluid phase reactive species.^{203-204, 221-222} Our group and others showed that solvent molecules within zeolite pores affect the stability of adsorbed reactive species for alkene epoxidation with H₂O₂,^{72, 74, 76} glucose isomerization,^{109, 132, 136, 178} and alcohol dehydration.^{99, 191-193, 223} With mechanistic differences excluded, the rate differences for epoxidation and H₂O₂ decomposition in **Figures 3.1** and **3.2** must reflect interactions among solvent molecules and reactive species located both within pores and the bulk solvent that drive changes in k_4 (**Equation 3.5**) and k_6 (**Equation 3.8**).

3.3.3 Activity Coefficients Show Differences in Intrapore and Fluid Phase Species Stability

Activity coefficients (γ) of the fluid phase reactants (C_6H_{12} and H_2O_2 ; $\gamma_{C_6H_{12}}$ and $\gamma_{H_2O_2}$) contribute to observed differences between turnover rates. Prior studies correlated values of fluid phase γ for 5-hydroxymethylfurfural²²⁴ and glucose¹³⁶ to etherification and isomerization rates, respectively. Here, thermodynamic models were used to directly quantify γ values to determine how reagent stability changes with x_{H_2O} and organic solvent identity (**Section B7**). **Figure 3.4** shows turnover rates for C_6H_{12} epoxidation and H_2O_2 decomposition normalized by γ values of the respective reactant at each x_{H_2O} , which accounts for the influence of intramolecular interactions (i.e., excess contributions) on the stability of the reactant in the fluid phase. When normalized by solvent-dependent values of $\gamma_{C_6H_{12}}$, the epoxidation turnover rates still span three-orders of magnitude and depend on both x_{H_2O} and the identity of the organic component of the solvent (**Figure 3.4a**). In addition, the changes in activity-normalized turnover rates $\left(\frac{r_{epox}}{[L] \cdot \gamma_{C_6H_{12}}}\right)$ as functions of x_{H_2O} exhibit complex non-monotonic dependences, which may reflect the influence of pore confinement on the solvation shells of reactive species and transition states within *BEA pores. Indeed, these data indicate that the stabilities of reactive species in the pore (G_{Ti-OOH} , $G_{epox}^\ddagger$) change with x_{H_2O} and affect rates significantly. Accounting for $\gamma_{C_6H_{12}}$ and $\gamma_{H_2O_2}$ values within turnover rate expressions for C_6H_{12} epoxidation and H_2O_2 decomposition when Ti-OOH covers sites (**Equations 3.5 and 3.8**) and defining alternate rate constants (k_4^* and k_6^*) yields:

$$\frac{r_{epox}}{[L] \cdot \gamma_{C_6H_{12}}} = k_4^*[C_6H_{12}] \quad (3.9)$$

$$\frac{-r_{decomp}}{[L] \cdot \gamma_{H_2O_2}} = k_6^*[H_2O_2] \quad (3.10)$$

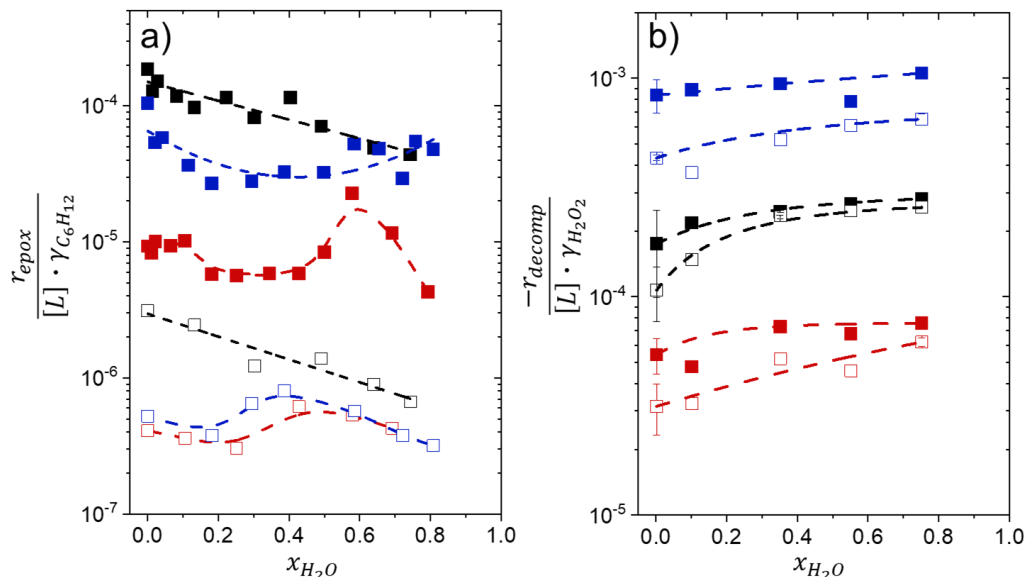


Figure 3.4. Turnover rates for a) $\text{C}_6\text{H}_{12}\text{O}$ formation (1 mM C_6H_{12} , 10 mM H_2O_2 , 313 K) normalized by $\gamma_{\text{C}_6\text{H}_{12}}$ and b) H_2O_2 decomposition (1 mM H_2O_2 , 313 K) normalized by $\gamma_{\text{H}_2\text{O}_2}$ as a function of $x_{\text{H}_2\text{O}}$ in mixtures of CH_3CN (■,□), CH_3OH (■,□), and $\text{C}_4\text{H}_6\text{O}_2$ (■,□) with H_2O over Ti-BEA-OH (solid points) and Ti-BEA-F (hollow). Activity coefficients of C_6H_{12} were calculated using the Volume-Translated Peng-Robinson (VTPR) method on ChemCAD, while activity coefficients of H_2O_2 were calculated with the nonrandom two-liquid (NRTL) method.

where k_4^* and k_6^* depend on corresponding alternate apparent activation free energies ($\Delta G_{app}^{\ddagger}$) (see **Section 3.3.4**). The non-monotonic trends in **Figure 3.4a** must stem from differences in the structure and composition of the solvation shells for Ti-bound intermediates and transition states as a function of organic solvent, $x_{\text{H}_2\text{O}}$, and zeolite $(\text{SiOH})_x$ density. The Ti-OOH intermediate and epoxidation transition state likely have different sizes and polarities (**Scheme 3.3a**), which promote different stoichiometries of water and co-solvent within their solvation shells.

Figure 3.4b reveals that rates for H_2O_2 decomposition normalized by $\gamma_{\text{H}_2\text{O}_2} \left(\frac{-r_{decomp}}{[L] \cdot \gamma_{\text{H}_2\text{O}_2}} \right)$ increase systematically with increasing $x_{\text{H}_2\text{O}}$ in all combinations of zeolite and organic solvent. The decomposition transition state and Ti-OOH plausibly form hydrogen bonds with multiple H_2O molecules (**Scheme 3.3b**), which stabilize these species at higher $x_{\text{H}_2\text{O}}$. Transition state

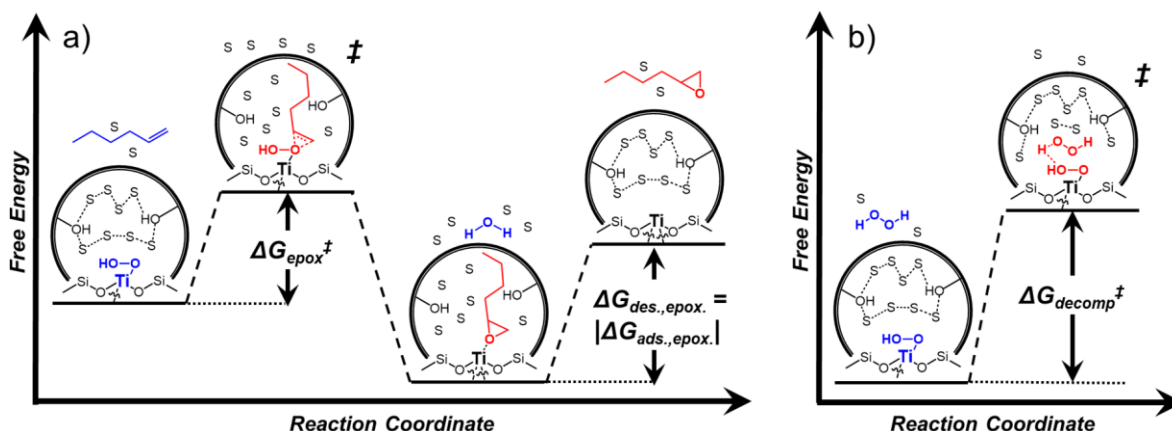
stabilization through hydrogen bonds with H₂O may outweigh the same effect for Ti-OOH because the transition state contains more hydrogen bonding functions. This disparity in hydrogen bond donating and accepting interactions generates the trends in activity-normalized turnover rates in **Figure 3.4b (Equation 3.10)**. Overall, $\frac{-r_{decomp}}{[L] \cdot \gamma_{H_2O_2}}$ values change less significantly with x_{H_2O} than $\frac{r_{epox}}{[L] \cdot \gamma_{C_6H_{12}}}$, indicating that differences in Ti-OOH stability largely cancel out with the decomposition transition state but differ more significantly from epoxidation transition state stability. The differences between the sensitivities of these reaction pathways to x_{H_2O} reflect the distinct size and structure of solvation shells surrounding the corresponding transition states within the pores of Ti-BEA catalysts and indicate that solvent molecules assist with the selective stabilization of certain transition states for these parallel pathways.

Variations between the trends for turnover rates in **Figure 3.1** and for $\frac{r_i}{[L] \cdot \gamma_i}$ values in **Figure 3.4** and their dependence on x_{H_2O} directly reflect the stabilization of fluid phase C₆H₁₂ and H₂O₂ by interactions with fluid phase solvent molecules. As x_{H_2O} increases ($0.002 \leq x_{H_2O} \leq 0.8$), $\gamma_{C_6H_{12}}$ increases by factors of 12-15 while $\gamma_{H_2O_2}$ decreases by 3-6 fold (**Figures B13 and B14**). These opposing changes result from destabilizing interactions between hydrophobic C₆H₁₂ and H₂O and stabilizing interactions between hydrophilic H₂O₂ and H₂O. These γ trends correspond to the rate trends for C₆H₁₂ epoxidation and H₂O₂ decomposition in **Figure 3.1**. The persistent dependence of $\frac{r_i}{[L] \cdot \gamma_i}$ values in **Figure 3.4** on organic solvent identity, x_{H_2O} , and (SiOH)_x density establishes that the stability of transition states and Ti-OOH intermediates in the pore respond to changes in fluid composition within the pores of *BEA. The following section provides further insight and quantitatively assesses the effect of x_{H_2O} on the stability of reactive species in the pores with activation barrier measurements.

3.3.4 Stability of Reactive Species Vary with Organic Solvent, x_{H_2O} , and $(SiOH)_x$ Density

Turnover rate measurements (**Figures 3.1 and 3.2**) show that C_6H_{12} epoxidation and H_2O_2 decomposition turnover rates depend on the organic solvent, x_{H_2O} , and $(SiOH)_x$ density of Ti-BEA. The first two factors alter the solvent environment around reactive species in the bulk fluid phase, whereas all three factors influence the solvation of species at active sites within the pores of Ti-BEA. Consequently, these variables impact apparent activation enthalpies ($\Delta H_{app}^\ddagger$) and entropies ($\Delta S_{app}^\ddagger$) for epoxidation ($\Delta H_{app,epox}^\ddagger$, $\Delta S_{app,epox}^\ddagger$) and H_2O_2 decomposition ($\Delta H_{app,decomp}^\ddagger$, $\Delta S_{app,decomp}^\ddagger$). Values of $\Delta H_{app}^\ddagger$ and $\Delta S_{app}^\ddagger$ were measured in identical kinetic regimes, where C_6H_{12} or H_2O_2 react with the Ti-OOH MARI to form the corresponding transition states (**Scheme 3.3**). The apparent activation free energy ($\Delta G_{app}^\ddagger$) depends on $\Delta H_{app}^\ddagger$ and $\Delta S_{app}^\ddagger$ and can be defined as the difference between the free energy of the transition state and reference state components, shown here for C_6H_{12} epoxidation:

$$\Delta G_{app,epox}^\ddagger = (G_{epox}^{\ddagger,0} + G_{epox}^{\ddagger,\varepsilon}) - (G_{Ti-OOH}^0 + G_{Ti-OOH}^\varepsilon) - (G_{C_6H_{12}}^0 + G_{C_6H_{12}}^\varepsilon) \quad (3.11)$$



Scheme 3.3. Proposed reaction coordinate diagrams for a) C_6H_{12} epoxidation and b) H_2O_2 decomposition over Ti-BEA zeolites, where solvent molecules are organic solvent or H_2O and are denoted with an “S”. In a), the alkene adsorbs into the pore and reacts with the Ti-OOH MARI to form the epoxide. The epoxide then desorbs to complete the reaction. In b), the liquid phase H_2O_2 adsorbs and binds to the Ti-OOH MARI to form the transition state. The remainder of the reaction coordinate in which the products form ($2 H_2O + O_2$) is not shown for brevity.

where free energies contain both standard state (G^0) and excess (G^ε) contributions. The excess free energy for a species i can be calculated from the activity coefficient for that species (γ_i), which depends on interactions with solvating molecules or nearby surfaces:

$$G_i^\varepsilon = RT * \ln(\gamma_i) \quad (3.12)$$

The excess free energies equal zero for ideal solutions (i.e., when the activity coefficient equals one) but are non-zero in non-ideal solutions and at solid-liquid interfaces.³⁹ We can define apparent free energy terms ($\Delta G_{app}^{\ddagger}$) that exclude the activity coefficient of the reactant (i.e., C_6H_{12}), which correspond to the k_4^* term represented in **Equation 3.9**:

$$k_4^* = \frac{k_B T}{h} \exp\left(-\frac{\Delta G_{app,epox}^{\ddagger}}{RT}\right) \quad (3.13)$$

To define $\Delta G_{app}^{\ddagger}$ values, we must simply add $G_{C_6H_{12}}^\varepsilon$ to each side of **Equation 3.11**:

$$\Delta G_{app,epox}^{\ddagger} = \Delta G_{app,epox}^{\ddagger} + G_{C_6H_{12}}^\varepsilon = (G_{epox}^{\ddagger,0} + G_{epox}^{\ddagger,\varepsilon}) - (G_{Ti-OOH}^0 + G_{Ti-OOH}^\varepsilon) - G_{C_6H_{12}}^0 \quad (3.14)$$

Note, an identical derivation of equations for H_2O_2 decomposition is included in the **Appendix (Section B6)**. Values for $\gamma_{C_6H_{12}}$ were used to compute $H_{C_6H_{12}}^\varepsilon$ (**Section B7**). The $H_{C_6H_{12}}^\varepsilon$ values allow for the derivation of an enthalpy term ($\Delta H_{app,epox}^{\ddagger}$) analogous to $\Delta G_{app,epox}^{\ddagger}$:

$$\Delta H_{app,epox}^{\ddagger} = \Delta H_{app,epox}^{\ddagger} + H_{C_6H_{12}}^\varepsilon = (H_{epox}^{\ddagger,0} + H_{epox}^{\ddagger,\varepsilon}) - (H_{Ti-OOH}^0 + H_{Ti-OOH}^\varepsilon) - H_{C_6H_{12}}^0 \quad (3.15)$$

Likewise, $\gamma_{H_2O_2}$ values yield values for $H_{H_2O_2}^\varepsilon$ (**Section B7**), which allows for the calculation of a similar enthalpic term for H_2O_2 decomposition ($\Delta H_{app,decomp}^{\ddagger}$):

$$\Delta H_{app,decomp}^{\ddagger} = \Delta H_{app,decomp}^{\ddagger} + H_{H_2O_2}^\varepsilon = (H_{decomp}^{\ddagger,0} + H_{decomp}^{\ddagger,\varepsilon}) - (H_{Ti-OOH}^0 + H_{Ti-OOH}^\varepsilon) - H_{H_2O_2}^0 \quad (3.16)$$

Section B9 includes the measured $\Delta H_{app}^{\ddagger}$ and $\Delta S_{app}^{\ddagger}$ for each pathway and discusses the entropy trends, which align with the interpretation of the enthalpy trends that follow. **Equations 3.15** and **3.16** account for the dependence of enthalpy values on organic solvent identity, x_{H_2O} , and $(SiOH)_x$

density. The values of $H_{C_6H_{12}}^0$ and $H_{H_2O_2}^0$ do not depend on these variables, so differences in $\Delta H_{app,epox}^{\ddagger}$ and $\Delta H_{app,decomp}^{\ddagger}$ arise entirely from changes in H^ε values for the Ti-OOH intermediate and respective transition states.

Figure 3.5 shows that $\Delta H_{app,epox}^{\ddagger}$ varies as a function of x_{H_2O} between Ti-BEA-OH and Ti-BEA-F, which indicates that the organization, density, and composition of solvent molecules within the pores of *BEA differ between these materials. Across organic solvents, $\Delta H_{app,epox}^{\ddagger}$ values span 4 – 19 kJ mol⁻¹ between the lowest and highest x_{H_2O} for Ti-BEA-F and 12 – 32 kJ mol⁻¹ over Ti-BEA-OH. These comparisons give evidence that the solvent structure in Ti-BEA-OH pores changes more significantly with increasing x_{H_2O} than in Ti-BEA-F. $\Delta H_{app,epox}^{\ddagger}$ increases with increasing x_{H_2O} for CH₃OH (**Figure 3.5a**) and CH₃CN (**Figure 3.5b**) mixtures over Ti-BEA-OH, which may indicate the transition state disrupts a greater quantity of H₂O within pores, which increases $H_{epox}^{\ddagger,\varepsilon}$. For C₄H₆O₂ mixtures (**Figure 3.5c**), $\Delta H_{app,epox}^{\ddagger}$ may decrease with increasing x_{H_2O} because the transition state needs to displace a smaller quantity of bulky C₄H₆O₂

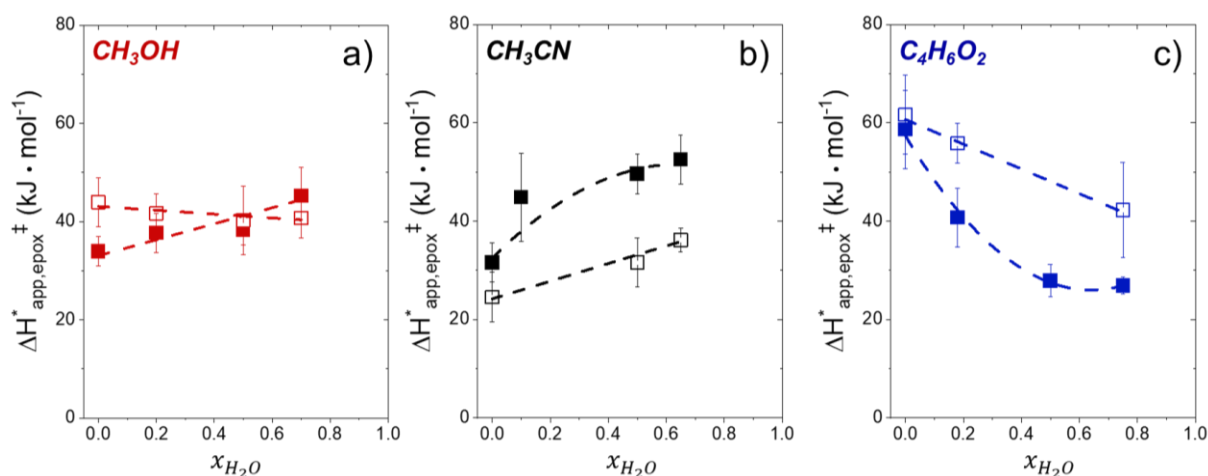


Figure 3.5. $\Delta H_{app,epox}^{\ddagger}$ values for C₆H₁₂ epoxidation (1 mM C₆H₁₂, 10 mM H₂O₂, 308-333 K) as a function of x_{H_2O} in mixtures of a) CH₃OH (■, □), b) CH₃CN (■, □), and c) C₄H₆O₂ (■, □) with H₂O over Ti-BEA-OH (solid) and Ti-BEA-F (hollow).

molecules, offsetting the enthalpic penalty of disrupting hydrogen bonded solvent molecules and reducing $H_{epox}^{\ddagger,\varepsilon}$.

Figure 3.6 demonstrates that values of $\Delta H_{app,decomp}^{\ddagger}$ also depend strongly on x_{H_2O} in each organic solvent. $\Delta H_{app,decomp}^{\ddagger}$ decreases with increasing x_{H_2O} in both Ti-BEA-OH and Ti-BEA-F because greater quantities of H_2O near sites enthalpically stabilize the hydrophilic transition state for H_2O_2 decomposition more significantly than Ti-OOH (**Scheme 3.3b**). For a given organic solvent and x_{H_2O} , Ti-BEA-F gives greater $\Delta H_{app,decomp}^{\ddagger}$ values than Ti-BEA-OH. More H_2O molecules may adsorb and hydrogen bond with the transition state within Ti-BEA-OH, which yields lower $H_{decomp}^{\ddagger,\varepsilon}$ values. $\Delta H_{app,decomp}^{\ddagger}$ depends more strongly on x_{H_2O} for Ti-BEA-OH than Ti-BEA-F in each organic solvent, showing that x_{H_2O} affects the stability of adsorbed reactive species more significantly in Ti-BEA-OH than Ti-BEA-F. Between organic solvents, $\Delta H_{app,decomp}^{\ddagger}$ values differ by 4 kJ mol⁻¹ over Ti-BEA-F and 8 kJ mol⁻¹ over Ti-BEA-OH at the highest x_{H_2O} (0.75). The smaller changes observed in Ti-BEA-F imply that H_2O

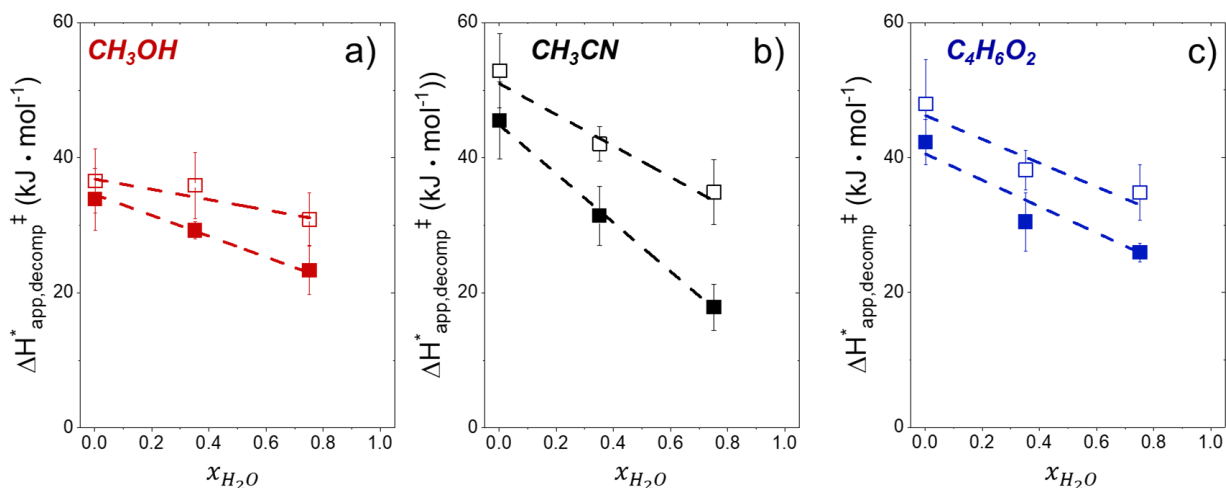


Figure 3.6. $\Delta H_{app,decomp}^{\ddagger}$ values for H_2O_2 decomposition (1 mM H_2O_2 , 313-343 K) as a function of x_{H_2O} in mixtures of a) CH_3OH (■, □), b) CH_3CN (■, □), and c) $C_4H_6O_2$ (■, □) with H_2O over Ti-BEA-OH (solid) and Ti-BEA-F (hollow).

molecules form similar first coordination solvation shells around the transition state and Ti-OOH intermediate at the highest x_{H_2O} . In contrast, the differences among Ti-BEA-OH may reflect contributions from extended hydrogen bonding networks of H₂O and organic solvent molecules within Ti-BEA-OH that influence both the decomposition transition state and Ti-OOH intermediate. $\Delta H^*_{app,epox}^\ddagger$ values differ by 6 kJ mol⁻¹ for Ti-BEA-F and 26 kJ mol⁻¹ over Ti-BEA-OH at the highest x_{H_2O} values, and the spans of values and differences between zeolites exceed that for $\Delta H^*_{app,decomp}^\ddagger$. This finding agrees with chemical intuition that the larger transition state for C₆H₁₂ epoxidation depends more sensitively on the secondary coordination sphere of solvent molecules within the pore than the smaller transition state for H₂O₂ decomposition (**Scheme 3.3**). Recent work demonstrated that solvent displacement dominates $\Delta H_{app,epox}$ differences as a function of alkene carbon number in aqueous CH₃CN, suggesting that changes in (SiOH)_x and intrapore solvent composition more significantly affect the stability of larger transition states that displace more solvent.²¹¹

The differences in the functional dependencies of $\Delta H^*_{app,decomp}^\ddagger$ and $\Delta H^*_{app,epox}^\ddagger$ on x_{H_2O} must reflect differences in the hydrophilicity of the transition state complexes for these competing reaction pathways. Greater x_{H_2O} may increase H^ε of the hydrophobic transition state for epoxidation from a combination of increased disruption of H₂O molecules and unfavorable interactions between the transition state and intrapore H₂O. In contrast, greater quantities of H₂O molecules likely lower H^ε for the transition state for H₂O₂ decomposition in all organic solvents. Among organic solvents, changing x_{H_2O} in CH₃OH mixtures has the least significant effect on both $\Delta H^*_{app,epox}^\ddagger$ and $\Delta H^*_{app,decomp}^\ddagger$ values. The weak effects of x_{H_2O} in CH₃OH likely reflect the more similar hydrogen bonding ability of CH₃OH to H₂O than CH₃CN or C₄H₆O₂ (see **Section**

B10 for solvent parameters). Therefore, CH₃OH molecules may hydrogen bond with reactive species in the pore similarly to H₂O, which lessens the differences in the solvent organization within pores brought about by replacing a fraction of CH₃OH with H₂O.

Overall, activation barrier measurements for epoxidation and H₂O₂ decomposition in **Figures 3.5** and **3.6** suggest that the organic solvent, x_{H_2O} , and (SiOH)_x density in Ti-BEA affect the stability of the Ti-OOH intermediate and transition states for epoxidation and H₂O₂ decomposition. The differences in stability result from differences between the organization and composition of fluid-like molecules within Ti-BEA pores, as described next.

3.3.5 Intrapore Solvent Composition Depends on Bulk Solvent Composition, (SiOH)_x Density

The bulk solvent composition^{178, 225-226} and intrapore (SiOH)_x density^{131, 227-228} affect the intrapore composition of solvent molecules and other adsorbates in aqueous-organic solvent mixtures. **Figure 3.7** presents measured mole fractions of H₂O within pores ($x_{H_2O,pore}$) (see **Section B2**) in equilibrated mixtures of H₂O with CH₃CN, CH₃OH, and C₄H₆O₂ as a function of the bulk H₂O fraction ($x_{H_2O,bulk}$). For each organic solvent and zeolite, increasing $x_{H_2O,bulk}$ leads to greater $x_{H_2O,pore}$ values across the full range of conditions examined. These observations agree with the interpretations of changes in turnover rates and activation parameters as functions of x_{H_2O} (**Sections 3.3.1** and **3.3.4**) and explains how altering $x_{H_2O,bulk}$ influences the stabilities of reactive species both in the bulk (i.e., C₆H₁₂ and H₂O₂) and in pores (i.e., Ti-OOH and transition states). Ti-BEA-OH adsorbs a greater fraction of H₂O than Ti-BEA-F for all combinations of organic solvents and $x_{H_2O,bulk}$, consistent with vapor adsorption results (**Appendix Figure B8a**) that show (SiOH)_x groups promote H₂O adsorption. The ratio of $x_{H_2O,pore}$ between Ti-BEA-OH and Ti-BEA-

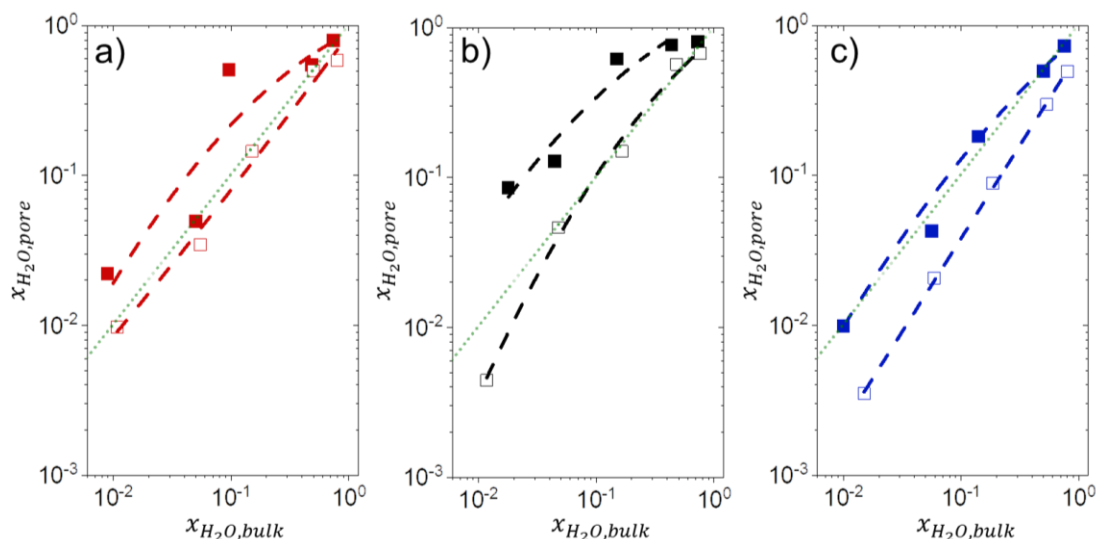


Figure 3.7. Intrapore mole fraction of H₂O ($x_{H_2O,pore}$) as a function of the equilibrium bulk H₂O fraction ($x_{H_2O,bulk}$) at 313 K in mixtures of a) CH₃OH (■, □), b) CH₃CN (■, □), and c) C₄H₆O₂ (■, □) with H₂O over Ti-BEA-OH (solid points) and Ti-BEA-F (hollow points). The faint green lines signify the parity line.

F generally decreases as $x_{H_2O,bulk}$ increases. This suggests that (SiOH)_x functions carry a stronger influence on H₂O adsorption at low $x_{H_2O,bulk}$, because the pores contain fewer H₂O molecules. This interpretation agrees with previously published binary adsorption measurements that indicate values of $x_{H_2O,pore}$ in hydrophilic zeolites depend more strongly on $x_{H_2O,bulk}$ from mixtures with methanol,²²⁹ ethanol,²³⁰⁻²³¹ and acetic acid²³² at lower $x_{H_2O,bulk}$ values. As $x_{H_2O,bulk}$ increases, H₂O molecules associate with H₂O already within pores, which leads to a weaker influence of the (SiOH)_x density and organic co-solvent on adsorption. This explanation agrees with CH₃CN mixtures that give the greatest difference in $x_{H_2O,pore}$ between zeolites at low $x_{H_2O,bulk}$. CH₃CN contains a lower sum of hydrogen bond donors and acceptors (1) than CH₃OH (3) or C₄H₆O₂ (4) (**Scheme B1**), as such, CH₃CN molecules offer fewer sites for H₂O molecules to associate than other organic solvents. Furthermore, CH₃CN mixtures give greater uptakes of H₂O within Ti-BEA-OH than the other organic solvents at similar $x_{H_2O,bulk}$. CH₃OH and C₄H₆O₂ may interact with

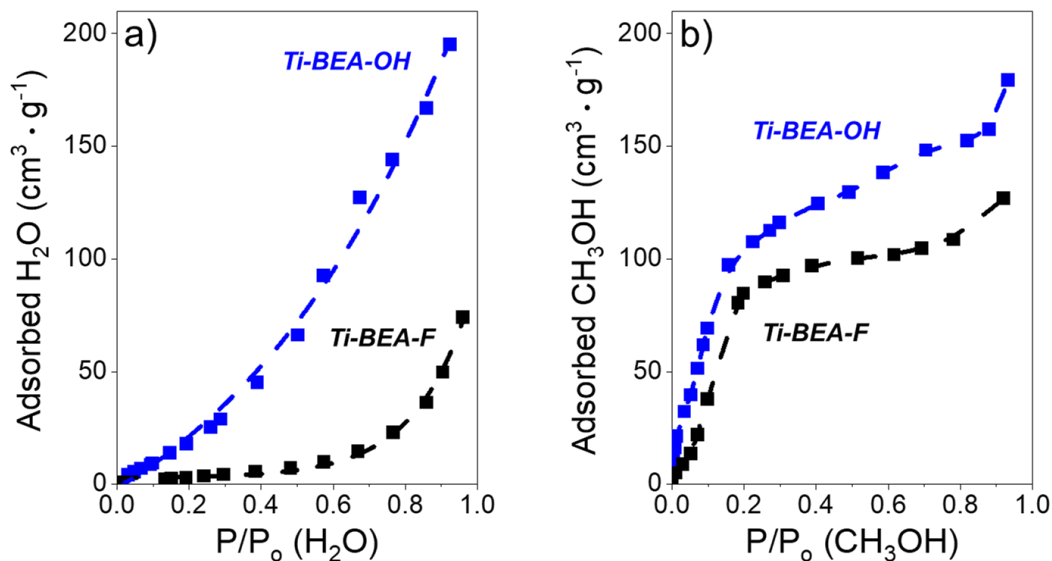


Figure 3.8. a) H_2O (295 K) and b) CH_3OH (295 K) adsorption isotherms over Ti-BEA-OH (blue) and Ti-BEA-F (black). The samples were degassed at 673 K under vacuum (<0.7 Pa) before adsorption.

$(\text{SiOH})_x$ more strongly than CH_3CN , which suggests those molecules may compete with H_2O for $(\text{SiOH})_x$ sites more effectively than CH_3CN . The bulky nature of $\text{C}_4\text{H}_6\text{O}_2$ may also lead to a lower available pore volume for H_2O molecules to co-adsorb.

For all organic solvents, Ti-BEA-OH shows greater $x_{\text{H}_2\text{O},\text{pore}}$ values than Ti-BEA-F, and an increase in $x_{\text{H}_2\text{O},\text{bulk}}$ leads to a corresponding increase in $x_{\text{H}_2\text{O},\text{pore}}$. These observations correspond to our interpretations of the effect of $x_{\text{H}_2\text{O}}$ on C_6H_{12} epoxidation and H_2O_2 decomposition, as outlined in the previous sections. While **Figure 3.7** demonstrates that Ti-BEA-OH promotes a more H_2O -rich pore solvent environment (higher $x_{\text{H}_2\text{O},\text{pore}}$), the vapor adsorption isotherms from **Figure 3.8a** also suggest that Ti-BEA-OH likely adsorbs greater numbers of H_2O molecules. Ti-BEA-OH adsorbs a greater volume of H_2O than Ti-BEA-F at all P/P_0 values, with the largest difference between the zeolites (~ 10 -fold) occurring at $0.5 P_{\text{H}_2\text{O}}/P_{\text{H}_2\text{O},0}$. The greater H_2O uptake in Ti-BEA-OH agrees with previous vapor H_2O adsorption measurements over MFI^{134, 196, 233} and *BEA^{74, 135-136} zeolites that observed increasing H_2O uptake with increasing $(\text{SiOH})_x$

density. Furthermore, the isotherm in **Figure 3.8b** signifies that Ti-BEA-OH preferentially adsorbs CH₃OH molecules, with the maximum difference between Ti-BEA-OH and Ti-BEA-F (~3.5-fold) at 0.03 $P_{CH_3OH}/P_{CH_3OH,0}$. The H₂O and CH₃OH uptake in Ti-BEA-OH exceeds Ti-BEA-F by more than 3 and 1.3 times, respectively, at all P/P_0 values greater than 0.01, which cannot stem from the differences between BET surface areas and pore volumes in **Table 3.1**. The experimental capabilities of the vapor adsorption instrument prohibit measurements with CH₃CN and C₄H₆O₂. Nevertheless, these observations provide strong evidence that (SiOH)_x defects promote the uptake of molecules with hydrogen bonding functions, an interpretation supported by prior infrared spectroscopy experiments and molecular dynamics simulations showing that Ti-BEA-OH adsorbs more CH₃CN molecules than Ti-BEA-F.²¹¹ Therefore, Ti-BEA-OH likely contains greater quantities of both H₂O and the organic co-solvent (i.e., CH₃CN, CH₃OH, C₄H₆O₂) at all conditions, which leads to higher solvent densities within pores. These differences in intrapore solvent densities lead to greater C₆H₁₂ epoxidation turnover rates through displacement and reorganization of hydrogen bonded solvent molecules, as reported for CH₃CN.²¹¹

More generally, the data in **Figure 3.7** and **Figure 3.8** demonstrate that the solvent composition and density within porous catalysts can be tuned by altering the bulk composition and catalyst (SiOH)_x density. This knowledge allows for control of the intrapore and bulk solvent environment for any liquid phase chemistry, which can significantly influence rates and selectivities for catalysis and adsorption processes.

3.3.6 Measured Enthalpies for Adsorption and Activation Reveal Influence of Intrapore Solvents on Surface Species

Brønsted-Evans-Polanyi relations propose that the intrinsic activation energy for an elementary step scales linearly with the enthalpy of reaction for the same process.^{202, 234-235}

Hammond postulated that the transition state structurally resembles the reaction state (i.e., reactant or product) most similar in energy, which leads to strong correlations between reaction kinetics and thermodynamics for adsorption of reactant or product molecules, as demonstrated frequently on metal surfaces and in computation.^{97, 198} Recently, the validity of these concepts were demonstrated within solvent-filled pore of zeolite catalysts used for alkene epoxidations. Values of $\Delta H_{app,epox}^\ddagger$ correlate with the liquid phase enthalpy of epoxide adsorption ($\Delta H_{ads,epox}$) for C₆H₁₂ epoxidation and C₆H₁₂O adsorption over *BEA zeolites containing different active metals (i.e., Ti, Nb, W)³⁰ and C₆ – C₁₈ alkenes and epoxides over Ti-BEA with varying (SiOH)_x densities.^{73, 211} The positive correlations between the enthalpies in these previous studies indicate that the transition state for epoxidation structurally resembles the adsorbed epoxidation product (**Scheme 3.3a**), because excess enthalpy contributions from interactions with surrounding solvent molecules affect epoxide adsorption and epoxidation transition state formation similarly. Measuring differences in $\Delta H_{ads,epox}$ provides a complementary method to examine how the composition of the organic solvent, x_{H_2O} , and (SiOH)_x density of Ti-BEA catalysts impact the structure of intrapore solvation structures and their influence on the stability of surface intermediates.

Isothermal titration calorimetry (ITC) experiments provided values of $\Delta H_{ads,epox}$ for C₆H₁₂O. The calorimeter releases heat upon each injection of C₆H₁₂O solution into a solution of Ti-BEA, as shown in a representative ITC thermogram in **Figure 3.9a**. **Figure 3.9b** shows the molar heats of adsorption from **Figure 3.9a** at low C₆H₁₂O coverages (< 0.25 mol C₆H₁₂O (mol Ti)⁻¹), a regime in which all epoxide molecules are assumed to adsorb to Ti sites.⁷³ Values of $\Delta H_{ads,epox}$ for 1,2-epoxyhexane within each combination of solvent and Ti-BEA zeolite were

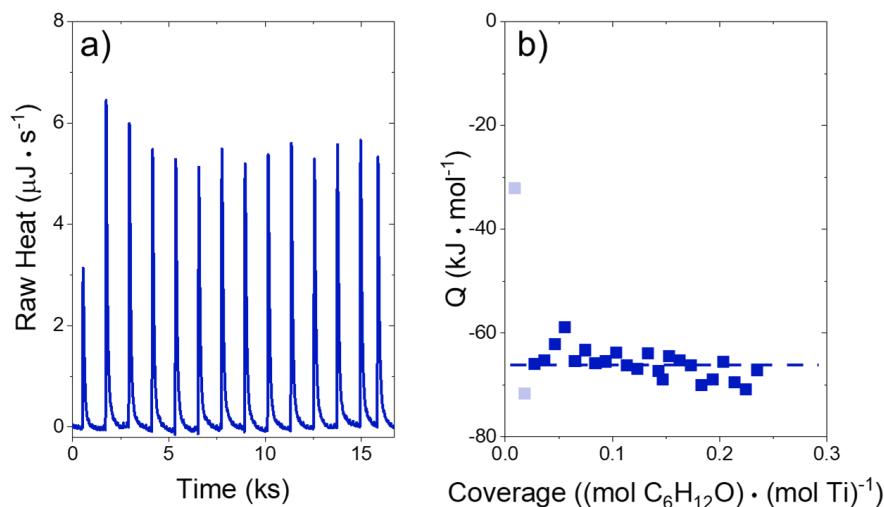


Figure 3.9. a) Thermogram from the titration of Ti-BEA-OH with 1,2-epoxyhexane (10 mM C₆H₁₂O in $x_{C_4H_6O_2} = 0.25$ (7.6 M) with H₂O (22.8 M), 313 K, 1 μL per injection) during isothermal titration calorimetry (ITC), and b) the corresponding heats released as a function of 1,2-epoxyhexane coverage. Transparent points are omitted due to common errors associated with early injections.

calculated from the average value of the heat released in this low coverage regime. The first injection (transparent) was omitted from the $\Delta H_{ads,epox}$ calculation, because these values exhibit lower heat than other points due to well-known instrumental errors (e.g., evaporation of titrant from syringe needle, leading to smaller than expected injected volumes). **Section B11** includes the thermograms and integrated heat data for the remaining solvent and zeolite combinations.

Figure 3.10a displays $\Delta H_{ads,epox}$ values for C₆H₁₂O as a function of x_{H_2O} . Notably, aqueous CH₃CN mixtures and neat CH₃CN give significantly more exothermic $\Delta H_{ads,epox}$ values than either CH₃OH or C₄H₆O₂ solutions, which suggests that CH₃CN mixtures provide the greatest stability to adsorbed C₆H₁₂O. These comparisons appear to explain why CH₃CN mixtures show greater C₆H₁₂ epoxidation turnover rates (**Figure 3.1**) than the other solvents examined. **Figure 3.10b** shows that $\Delta H_{ads,epox}$ values correlate with $\Delta H_{app,epox}^{\ddagger}$ values across all combinations of

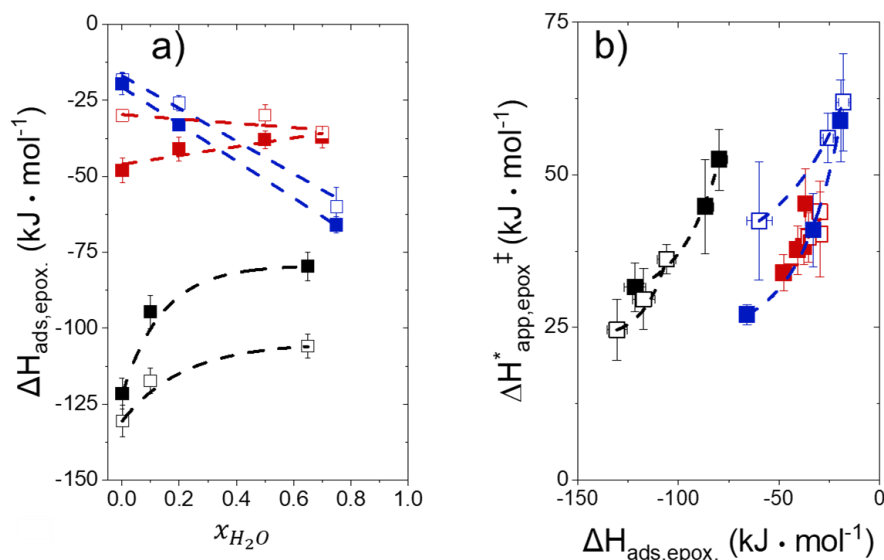


Figure 3.10. a) $\text{C}_6\text{H}_{12}\text{O}$ enthalpies of adsorption (5-10 mM $\text{C}_6\text{H}_{12}\text{O}$, 313 K) as a function of $x_{\text{H}_2\text{O}}$ and b) difference between the enthalpy of the transition state for C_6H_{12} epoxidation (1 mM C_6H_{12} , 308-333 K) and the Ti-OOH and standard state C_6H_{12} enthalpies as a function of $\text{C}_6\text{H}_{12}\text{O}$ enthalpies of adsorption in aqueous mixtures of a) CH_3OH (■, □), b) CH_3CN (■, □), and c) $\text{C}_4\text{H}_6\text{O}_2$ (■, □) over Ti-BEA-OH (solid points) and Ti-BEA-F (hollow points).

solvent composition and zeolites, which signifies the strong structural similarities between the intrapore solvation environment of 1,2-epoxyhexane bound to Ti active sites and the transition states for epoxidation that form in these same environments. The dependence of $\Delta H^*_{app,epox}^\ddagger$ and $\Delta H_{ads,epox}$ on $x_{\text{H}_2\text{O}}$ is weaker over Ti-BEA-F than Ti-BEA-OH (see **Figure 3.5** and **Figure 3.10a**) for all solvents, which shows that increases in $x_{\text{H}_2\text{O}}$ lead to less significant changes in the solvent structure within Ti-BEA-F (see **Section 3.3.5**). Based on insight gained from quantitative comparisons between GCMD simulations and ITC measurements of $\Delta H_{ads,epox}$ values,²¹¹ the more endothermic $\Delta H^*_{app,epox}^\ddagger$ and $\Delta H_{ads,epox}$ values in CH_3CN mixtures at higher $x_{\text{H}_2\text{O}}$ reflect the disruptions of greater numbers of hydrogen bonds that involve H_2O molecules upon adsorption of the epoxide. Presumably, the changes of $\Delta H^*_{app,epox}^\ddagger$ and $\Delta H_{ads,epox}$ with $x_{\text{H}_2\text{O}}$ in CH_3OH mixtures over Ti-BEA-OH reflect similar processes that displace solvent molecules, however, the

lower magnitude of these changes in CH₃OH likely stems from the greater hydrogen bonded character of neat CH₃OH relative to neat CH₃CN. Hence, the addition of small quantities of H₂O leads to more significant changes in the organization of CH₃CN molecules within pores than CH₃OH. In contrast, the values of $\Delta H^*_{app,epox}^\ddagger$ and $\Delta H_{ads,epox}$ become more exothermic with increasing x_{H_2O} in C₄H₆O₂ mixtures. While the full reasons for this trend remain unclear presently, these results give evidence that the spatial positioning of C₄H₆O₂ within pores responds to the presence of water.

Notably, $\Delta H^*_{app,epox}^\ddagger$ and $\Delta H_{ads,epox}$ show a positive and super-linear correlation for every combination of solvent and zeolite (**Figure 3.9b**). The derivative of the correlation increases at more endothermic enthalpies, which indicates that the transition state for epoxidation resembles the epoxide product more closely at more endothermic $\Delta H_{app,epox}^\ddagger$ values, following Hammond's postulate.¹⁹⁸ We cannot, however, exclude the possibility that H_{Ti-OOH}^ϵ varies systematically with x_{H_2O} and contributes to the non-linear trend. Nevertheless, the positive correlations between $\Delta H^*_{app,epox}^\ddagger$ and $\Delta H_{ads,epox}$ suggests that interactions with solvent molecules affect the stability of the epoxidation transition state and the adsorbed epoxide in similar ways. These findings show that solvent molecules and solvent composition influence the stability of solutes in bulk solvents and at solid-liquid interfaces during catalysis. These concepts can guide the design of not only heterogeneously catalyzed reactions, but also liquid phase homogeneously catalyzed and organic reactions in which reactant γ values carry significance.

3.4. Conclusions

The organic solvent choice, x_{H_2O} , and zeolite (SiOH)_x density influence rates and selectivities of liquid phase zeolite-catalyzed reactions by altering G^ϵ values of reactants in the

bulk fluid phase and at solid-liquid interfaces, as demonstrated with interpretations of alkene epoxidation kinetics. While the organic solvent identity and x_{H_2O} influence the reversibility of H_2O_2 activation, neither the solvent nor zeolite choice influences the mechanisms for alkene epoxidation or H_2O_2 decomposition. Instead, differences among turnover rates and selectivities stem from the distinct dependence of G^ε values of reactive species for C_6H_{12} epoxidation and H_2O_2 decomposition on x_{H_2O} . Greater rates of C_6H_{12} epoxidation in each zeolite and organic solvent at greater x_{H_2O} appear to be primarily driven by incommensurate changes in the activity coefficients of C_6H_{12} and for epoxidation transition states. However, H_2O_2 decomposition rates decrease at higher x_{H_2O} for both Ti-BEA-OH and Ti-BEA-F, likely because stabilization of the hydrophilic transition state by H_2O outweighs the stabilization of H_2O_2 and the Ti-OOH intermediate.

The findings reported here demonstrate the significance of interactions between solvent molecules and reactants in the liquid phase and at solid-liquid interfaces during catalytic reactions. Broadly, the findings suggest that introducing a more polar reaction environment promotes zeolite-catalyzed reaction pathways with predominantly hydrophobic reactants and transition states while suppressing pathways with hydrophilic reactive species. For industrial purposes, diluting organic solvents with H_2O increases separation costs for epoxidation, may increase rates of ring-opening of the epoxide^{87, 89, 236} (not observed at differential conversion in this study), and may influence the long-term stability of zeolite catalysts.²³⁷⁻²³⁹ The results presented here show that simply adding more H_2O increases rates and H_2O_2 selectivities for C_6H_{12} epoxidation in confined environments. Evidently, proper selection of organic solvent, x_{H_2O} , and catalyst polarity and topology can improve the performance of liquid phase reactions. These concepts can guide the design of adsorption and catalytic processes in the liquid phase and at solid-liquid interfaces.

CHAPTER 4

**UNDERSTANDING RATES AND REGIOSELECTIVITIES FOR EPOXIDE
METHANOLYSIS WITHIN ZEOLITES: MECHANISM AND ROLES OF COVALENT
AND NON-COVALENT INTERACTIONS^{iv}**

4.1 Introduction

The nucleophilic ring-opening of epoxides with alcohols, amines, thiols, or water yields high-value intermediates. These reaction products find use in the manufacturing of resins, solvents, biologically active products, and antifreeze, among other products.^{50, 240-241} Epoxide ring-opening catalysts include soluble homogeneous complexes⁵⁷⁻⁵⁹ and solid catalysts such as ion-exchange resins,⁶⁰⁻⁶² mesoporous silicates,^{63, 242-243} and microporous silicates (i.e., zeolites).⁶³⁻⁶⁵ Homogeneous catalysts can provide high rates but present challenges for catalyst recovery and regeneration,²⁴⁴⁻²⁴⁵ whereas ion-exchange resins may swell and deactivate under reaction conditions.⁶⁰⁻⁶² Ring-opening processes that use these catalysts require higher temperatures and pressures,^{59-61, 246-249} high nucleophile to epoxide ratios that increase costs,^{60, 246-248, 250} and suffer from secondary polymerizations that reduce selectivities.^{59, 247-249} Catalytically active silicates avoid many of these challenges and provide high turnover rates for related chemical transformations, separate readily from products, and resist deactivation (e.g., by structural collapse).^{115-116, 251}

^{iv} This chapter has been reprinted with permission from the following publication:
David S. Potts, Jessica K. Komar, Huston Loch, and David W. Flaherty, “Understanding Rates and Regioselectivities for Epoxide Methanolysis within Zeolites: Mechanism and Roles of Covalent and Non-covalent Interactions”, *ACS Catalysis* **2023**, 13, 22, 14928-14944. Copyright 2023 American Chemical Society.

Isolated Lewis and Brønsted acid sites in zeolite frameworks provide greater turnover rates and selectivities than oligomeric metal oxide sites in zeolites or isolated sites within mesoporous silicas for epoxide ring-opening,⁶³⁻⁶⁴ glucose isomerization,^{137, 252-253} and alkene epoxidation,^{32, 85, 254} among other chemistries.^{40, 255-257} The identity of the active metal atom inserted at tetrahedral positions within the zeolite framework strongly influences rates and selectivities for liquid-phase reactions. For example, Ti-incorporated zeolites give the greatest rates for epoxidation of linear and cyclic alkenes with H₂O₂ among transition metals.^{30-32, 69-70} Rate differences among metals reflect, in part, the energy of unoccupied orbitals that accept charge from reagents, as suggested by density functional theory (DFT) calculations⁷⁰ and measured enthalpies of adsorption of gaseous acetonitrile³¹ and liquid 1,2-epoxyalkanes.³⁰ For similar reasons, Sn-incorporated zeolites provide greater rates than Hf-, Zr-, and Ti-zeolites for the ring-opening of linear and cyclic epoxides with CH₃OH⁶³ or H₂O.⁶⁴ Sn was proposed to possess the greatest Lewis acid strength among these metals, based on ¹⁵N NMR chemical shifts^{63, 71} and desorption temperatures for pyridine.⁶⁴ The nature of these active sites also influences the competitive adsorption of nucleophiles and epoxides. For example, Zr sites within *BEA zeolite gave greater rates than Ti and Sn for the ring-opening of styrene oxide by reactions with amines because Zr sites bind styrene oxide in the presence of amines.⁶⁵ These works demonstrate that the choice of active metal significantly influences rates, selectivities, and stabilities of solid catalysts for ring-opening.

Beyond the influence of the active metal (i.e., covalent or inner-sphere effects), the environment introduced by surrounding solvent molecules and hydrogen-bonding species (i.e., non-covalent or outer-sphere effects) also influences rates and selectivities of catalytic reactions.¹²⁴⁻¹²⁵ Zeolites that contain high densities of silanol ((SiOH)_x) groups provide greater rates for alkene epoxidation with aqueous hydrogen peroxide (H₂O₂) than hydrophobic zeolites

(i.e., low Si(OH)_x density).^{74-75, 77-78, 211, 258-259} The hydrophilic pores of these materials stabilize clusters of H_2O molecules that provide entropic gains when disrupted by the adsorption or formation of hydrophobic reactive intermediates. These phenomena seem likely to influence the kinetics of epoxide ring-opening and provide strategies to control product formation rates and regioselectivities. Rates and regioselectivities for the reaction between 1,2-epoxyoctane and sodium azide (NaN_3) over ion-exchanged FAU zeolites show greater selectivities but lower turnover rates to secondary alcohols in polar solvents compared to non-polar solvents,⁷⁹ although the reasons for these differences were not clearly assigned. Recently, molecular simulations and kinetic measurements from Broadbelt, Notestein, and co-workers gave evidence that the addition of water increases selectivities to terminal alcohols during tris(pentafluorophenyl)borane-catalyzed alcoholysis of 1,2-epoxyoctane.⁸⁰⁻⁸² Water molecules coordinate to boron atoms and hydrogen bond with epoxide substrates and other hydrogen bond acceptors.⁸⁰ The hydrogen bond acceptors in these complexes stabilize the approach of the alcohol nucleophile to the more substituted epoxide carbon, thereby facilitating the formation of the terminal alcohol over the terminal ether.⁸¹⁻⁸²

The choice of element for the active center of Lewis acid catalysts and the solvent clearly influences rates and regioselectivities for epoxide ring-opening. The type of acid used to catalyze the reaction carries equal importance. Brønsted and Lewis acid catalysts perform differently in the ring-opening of epoxides by water,^{64, 101} amines,^{65, 102} and alcohols.^{63, 103} Both Brønsted⁹²⁻⁹⁴ and Lewis^{59, 95-96} acid catalysts commonly find use in industrial processes for epoxide ring-opening, yet, few quantitative comparisons or explanations for differences between mechanisms, turnover rates, and regioselectivities over Lewis and Brønsted acidic materials exist. The solvent choice and composition likely influence these classes of acids differently through excess free energy

contributions (G^ε) that originate from thermodynamic non-idealities which influence the activity coefficients of reactive species.^{39, 124} Protons of Brønsted acid zeolites can detach from the framework and delocalize across cluster of solvent molecules,⁹⁸⁻¹⁰⁰ whereas, the active metal of Lewis acid zeolites remain fixed to the framework. The concentration of reagents serves as another critical consideration in a liquid-phase catalytic reaction, as it can influence both the dominant reaction pathway and the solvent structure surrounding active sites, which can significantly affect rates and selectivities.^{80, 82, 124-125} Creating materials with greater performance for epoxide ring-opening requires knowledge of the effects of metal identity, acid type, reagent concentrations, and solvation effects within pores on rates, regioselectivities, and the reaction mechanism.

Here, we examine the consequences of varying the active metal in zeolite *BEA (M-BEA, where M = Al, Sn, Ti, or Zr) on rates and regioselectivities for 1,2-epoxybutane (C_4H_8O) ring-opening with methanol (CH_3OH). Rates for C_4H_8O ring-opening measured as functions of reagent concentrations suggest that products form by the kinetically relevant nucleophilic attack to the epoxide ring. Despite high concentrations of CH_3CN in most conditions, surface intermediates derived from C_4H_8O , and less commonly CH_3OH , saturate active sites of M-BEA catalysts across all conditions. Turnover rates and regioselectivities depend on the metal identity and fluid-phase composition in ways that reflect preferential stabilization of ring-opening transition states by combinations of covalent and non-covalent interactions. Here, we utilize covalent interactions to describe interactions between the active metal centers and reactive species, which encompasses the coordinate covalent bonds²⁶⁰ between Lewis acid sites and reactant molecules (i.e., Lewis bases) and the ionic interactions between protonated reactive species and the zeolite anion within the Brønsted acid. Non-covalent interactions describe the interactions of reactive species with surrounding solvent molecules (e.g., hydrogen bonding) and the pore walls of the zeolite (e.g., van

der Waals interactions). Strong correlations between activation enthalpies for ring-opening (obtained from rate measurements) and enthalpies for the adsorption of C_4H_8O to active sites (measured by isothermal titration calorimetry) demonstrate the ability to control rates and selectivities by these orthogonal factors. Collectively, these findings give insight into the reaction pathways for epoxide ring-opening that prevail on solid acid catalysts and describe why the identity of the active metal, the class of acid catalyst (Lewis or Brønsted acids), and interactions with intrapore solvent molecules influence the kinetics for epoxide ring-opening reactions.

4.2 Methods and Materials

4.2.1 Catalyst Synthesis

M-BEA (M = Al, Sn, Ti, Zr) were prepared by post-synthetic modification of commercial Al-BEA-20 (TOSOH, lot no. 94HA6X02Y; Si/Al = 20). For each Lewis acid, Al-BEA-20 was treated in refluxing HNO_3 (Macron Chemicals, 68 – 70 wt%, $20\text{ cm}^3\text{ g}^{-1}$) at 433 K for ~24 h to remove Al atoms from the *BEA framework by forming soluble $(AlNO_3)_3$ complexes. The HNO_3 treatment was repeated three times to give a thoroughly dealuminated material (Si:Al > 1200) denoted Si-BEA. Between acid treatments, the catalyst sample was washed with deionized H_2O ($18.2\text{ M}\Omega\text{ cm}$, Elga Purelab Flex 2, $50\text{ cm}^3\text{ g}_{zeolite}^{-1}$) and recovered with vacuum filtration. For Al-BEA, the parent Al-BEA-20 material was treated in dilute HNO_3 (1 M) for ~3 h to partially remove Al atoms from the framework. The gentle HNO_3 treatment led to an Al-BEA with similar metal loading and $(SiOH)_x$ density to the other M-BEA materials. After the acid treatments, the dealuminated *BEA materials were placed into a quartz boat and loaded into a three-zone furnace (Applied Test Systems, 3210), which was heated to 823 K (5 K min^{-1}) in flowing air ($200\text{ cm}^3\text{ min}^{-1}$; Airgas, Ultra Zero grade) and held at 823 K for 6 h to remove organic residues.

Sn-, Ti-, and Zr-BEA were synthesized by incorporating metal atoms into Si-BEA. Sn-BEA was prepared by dry impregnation and calcination, adapted from previously published procedures.^{64, 148} Si-BEA was first dried at 393 K overnight to remove residual H₂O molecules. Then, Si-BEA (5 g) was ground with dimethyl tin dichloride (350 mg; (CH₃)₂SnCl₂, Alfa Aesar, ≥98.5%) for 600 s in the fume hood using a mortar and pestle. *Note: Take precaution when using (CH₃)₂SnCl₂, as it is highly toxic if inhaled or swallowed.* The solid mixture was transferred to a quartz boat, loaded into the three-zone furnace, and heated to 823 K (2 K min⁻¹) in flowing air and held at 823 K for 8 h to yield Sn-BEA. We postulate the slow heating rate and extended treatment at 823 K are needed to ensure sufficient time for (CH₃)₂SnCl₂ to diffuse throughout the pores of Si-BEA and to react to yield Sn atoms within tetrahedral positions of the *BEA framework. Notably, Sn atoms can form oxide clusters during this process, which can be alleviated by introducing a pre-pyrolysis treatment in an inert environment (i.e., Ar, N₂).²⁶¹⁻²⁶² Ti- and Zr-BEA were prepared by liquid-phase metal incorporation based on previously reported procedures.^{30, 74} Si-BEA was heated in a round-bottom flask under vacuum (< 5 Pa, 473 K) for 2 h to create a moisture-free environment. Dichloromethane (CH₂Cl₂, Fisher Chemicals, 20 cm³ g_{zeolite}⁻¹) solvent was then added to the flask for Ti-BEA, and isopropanol (C₂H₇OH, Fisher Chemicals, 20 cm³ g_{zeolite}⁻¹) was added for Zr-BEA. A rubber seal was removed from the sidearm of the flask, and the solvents were poured into the flask under a high flow of Ar (500 cm³ min⁻¹) to minimize the adsorption of moisture from the air. Ti and Zr atoms were incorporated by later adding liquid TiCl₄ (Sigma-Aldrich, ≥99.0%) or solid ZrCl₄ (Sigma-Aldrich, ≥99.9% trace metals basis) to the Si-BEA and solvent mixture under Ar flow. TiCl₄ was loaded into a glass syringe and injected through a rubber seal on the flask sidearm. ZrCl₄ was introduced by removing the rubber seal and depositing the powder into the flask under flowing Ar (500 cm³ min⁻¹). These mixtures were then

heated and left overnight under an inert atmosphere (328 K for Ti, 373 K for Zr, refluxing solvent, ~16 h, 50 cm³ min⁻¹ Ar, Airgas, Ultra High Purity). The resulting materials were recovered by vacuum filtration and were heated to 823 K (5 K min⁻¹) in flowing air (200 cm³ min⁻¹) and held at 823 K for 6 h, resulting in white powder Ti-BEA and Zr-BEA samples.

4.2.2 Catalyst Characterization

The dispersity of the M atoms in the M-BEA catalysts was examined with diffuse reflectance UV-visible (DRUV-vis) spectroscopy. The total reflectance sample spectra were obtained with a UV-vis spectrophotometer (Varian, Cary 5G) under ambient conditions. M-BEA samples were mixed and finely ground with magnesium oxide (MgO, Sigma-Aldrich, 99.9995%) at a MgO:M-BEA mass ratio of 10:1. MgO was used as a background for the measurement. The band gap energies (**Table 4.1**) were determined by extrapolating the linear portion of the Tauc plots ($[F(R) \cdot h\nu]^{1/2}$) to the horizontal axis to determine the minimum energy of photons adsorbed (eV) (**Figure C1**). The band gaps of SnO₂, anatase TiO₂, and ZrO₂ were measured in a similar manner as the M-BEA materials (**Appendix Figure C1**). Sn-, Ti-, and Zr-BEA show greater band gaps than the respective metal oxides, supporting that each heteroatom is substituted within the framework at dispersed locations. The metal oxide materials were purchased commercially and used as received: γ -Al₂O₃ (US Research Nanomaterials, Inc., 20 nm, 99%), SnO₂ (Sigma-Aldrich, EMPLURA®, ≥99.0%), anatase TiO₂ (Sigma-Aldrich, 99.8% trace metals basis), ZrO₂ (Sigma-Aldrich, 5 μ m 99% trace metals basis).

The crystallinities of the M-BEA catalysts were confirmed with an X-ray diffractometer (Bruker, D8 Advance) with Cu K α radiation under ambient conditions. The M-BEA powders were loaded into a polypropylene sample holder for the measurements. The diffractograms of M-BEA (**Figure C2a**) match previously reported diffraction patterns for *BEA,¹⁵¹ supporting that all M-

BEA possess the *BEA framework. Notably, the patterns for M-BEA do not possess strong features in the characteristic peak locations for the respective metal oxides (**Figure C2b**), supporting that negligible quantities of each incorporated metal exist in metal oxide form.

The metal contents of the M-BEA samples were calculated with energy-dispersive X-ray fluorescence (EDXRF) and inductively coupled plasma optical emission spectroscopy (ICP-OES). M-BEA powders (~50 mg) were loaded into a polypropylene cup (1 cm diameter) sealed with ultralene film. The sample cups were loaded into the He-purged chamber of the spectrometer (Shimadzu, EDX-7000). The samples were scanned between 0 and 30 keV, and the intensities of the fluorescence features were used to calculate the mass of metals within the sample. The EDXRF measurements show that Sn-, Ti-, and Zr-BEA contain only trace quantities of Al (Si:Al ~ 1200-1400), while Al-BEA has Si:Al ~70. M-BEA metal compositions were also obtained from ICP-OES (PerkinElmer, Optima 8300), which confirmed Sn-, Ti-, and Zr-BEA contained negligible quantities of Al (Si:Al ~ 4000). Notably, Al- and Ti-BEA show similar loadings of active metal between ICP-OES and EDXRF, while ICP-OES gives loadings ~1.5 times greater than EDXRF for Sn-BEA and ~1.25 times lesser than EDXRF for Zr-BEA. Reported turnover rates are calculated by normalizing rates with metal loadings determined by ICP-OES. Metal loadings and Si:Al ratios for each zeolite are shown in **Table 4.1**.

The coordination of metal atoms within M-BEA was probed with Raman spectroscopy. *Ex situ* Raman spectra were measured at ambient conditions on pressed catalyst pellets with a Raman spectrometer (Renishaw, InVia) equipped with a 532 nm laser. The power density at the sample was approximately 2 mW μm^{-2} (Gentec-EO, PRONTO-SI). The accumulation time was 20 s per scan, and each Raman spectra was calculated by averaging 10 scans. The Raman spectra for each M-BEA (**Figure C3**) lack discernible features in the regions where the respective metal oxides

show strong features, indicating the absence of M-O-M bonds. Together with the high band gap energies (**Table 4.1**), these spectra support that the M atoms in each material reside in tetrahedral positions within *BEA and not within octahedral coordinations outside of the zeolite framework.

The incorporation of heteroatoms (Sn, Ti, Zr) into the *BEA framework was examined with attenuated total reflectance-infrared spectroscopy. The M-BEA samples were pressed onto the diamond internal reflection element of the spectrometer (Bruker, Alpha). The spectra (**Figure C4**) were then collected at ambient conditions (16 scans, 2 cm^{-1}). Analysis of the spectra is provided in **Section C1.4**.

The relative density of $(\text{SiOH})_x$ groups within M-BEA were measured with infrared spectroscopy. A background spectrum was first taken with an empty transmission cell configured with CaF_2 windows. The cell was loaded into a Fourier-transform infrared spectrometer (Bruker, Vertex 70) equipped with a liquid N_2 -cooled HgCdTe detector, as described previously.²¹⁶ The cell was connected to a temperature controller and gas manifold, then heated to 573 K ($\sim 5\text{ K min}^{-1}$) and held for 2 h in flowing Ar ($50\text{ cm}^3\text{ min}^{-1}$, 99.997%, Airgas) to desorb volatile compounds and H_2O . The background spectrum was then collected at 573 K (128 scans, 4 cm^{-1}). Subsequently, each M-BEA was pressed into a pellet and loaded in the transmission cell. The cell was loaded into the spectrometer, and the spectra for M-BEA (**Figure C5**) were obtained in the same manner as the background measurement. The vibrational features on the FTIR spectra at $1800\text{--}2100\text{ cm}^{-1}$ and $3300\text{--}3750\text{ cm}^{-1}$ represent Si-O-Si overtones¹⁵⁴ of the *BEA framework and $\nu(\text{O-H})$ of $(\text{SiOH})_x$ groups¹⁵⁵⁻¹⁵⁶, respectively. The broad features from $3300\text{--}3700\text{ cm}^{-1}$ arise from SiOH defects containing multiple hydroxyl moieties within $(\text{SiOH})_x$ groups. The sharper feature at $\sim 3750\text{ cm}^{-1}$ represents isolated SiOH defects that do not interact with other SiOH.¹⁵⁵⁻¹⁵⁶ The ratio of the areas for $\nu(\text{O-H})$ and $\nu(\text{Si-O-Si})$ at 1865 and 2000 cm^{-1} gives a relative measure of SiOH density defined

Catalyst	M wt%	Si:M	Si:Al	Band Gap (eV) ^c	Φ_{IR}^d	Active Site Density (mol g ⁻¹) ^e
Al-BEA	0.71 ^a , 0.64 ^b	63 ^a , 71 ^b	63 ^a , 71 ^b	--	1.44	2.72 x 10 ⁻⁴
Sn-BEA	0.73 ^a , 1.24 ^b	268 ^a , 144 ^b	1060 ^a , 4060 ^b	4.7	1.63	9.19 x 10 ⁻⁵
Ti-BEA	0.76 ^a , 0.80 ^b	103 ^a , 91 ^b	1100 ^a , 4110 ^b	4.1	1.56	1.52 x 10 ⁻⁴
Zr-BEA	1.25 ^a , 1.03 ^b	121 ^a , 131 ^b	1030 ^a , 3980 ^b	5.8	1.41	1.10 x 10 ⁻⁴

Table 4.1. Characterization of Synthesized M-BEA.

^aDetermined with EDXRF. ^bMeasured with ICP-OES. ^cExtracted from leading edge of Tauc plot from DRUV-vis. ^dCalculated from infrared transmission spectra of dehydrated M-BEA samples. ^eMeasured from *in situ* 1,2-diphenylethylenediamine site titrations.

as Φ_{IR} (**Equation 4.1**) in each M-BEA. The isolated SiOH feature is excluded from $A_{\nu(O-H)}$ in **Equation 4.1**. The $\nu(O-H)$ region was deconvoluted into multiple peaks (see **Figure C6**), and the isolated SiOH peak area was subtracted from the combined area of the $\nu(O-H)$ region.

$$\Phi_{IR} = \frac{A_{\nu(O-H)}}{A_{\nu(Si-O-Si)}} \quad (4.1)$$

The values of Φ_{IR} for M-BEA (**Table 4.1**) indicate that each material contains a similar density of (SiOH)_x.

The presence of Lewis and Brønsted acid sites in M-BEA was characterized by infrared spectra of adsorbed pyridine (C₅H₅N, Sigma-Aldrich, >99%) and deuterated acetonitrile (CD₃CN, Cambridge Isotope Laboratories, 99.8% D atom). The catalysts were pelletized, loaded into the spectrometer, and pre-treated at 573 K as described above. The cell was then cooled to either 393 K (C₅H₅N) or 303 K (CD₃CN). A background spectrum was taken before flowing the adsorbates. C₅H₅N or CD₃CN were then introduced with a syringe pump (KD Scientific, Legato) and vaporized into a stream of flowing Ar (20 cm³ min⁻¹) within the heated gas-transfer lines. Reported spectra were collected after the absorbance features had reached a steady state. The spectra and a detailed analysis of the results are provided in **Section C1.7**.

Collectively, the characterization of the M-BEA materials gives strong evidence that each material possesses a crystalline *BEA framework containing similar densities of (SiOH)_x. All M-BEA contain atomically dispersed metal atoms incorporated at framework positions and lack spectroscopically detectable quantities of the respective metal oxides that exist outside of the *BEA framework.

4.2.3 Epoxide Ring-Opening Turnover Rate Measurements

Turnover rates for 1,2-epoxybutane (C₄H₈O, TCI Chemicals, >99.0%) ring-opening with methanol (CH₃OH, Sigma-Aldrich, ≥99.9%) in acetonitrile (CH₃CN, Fisher Chemical, HPLC Grade) were measured in three-necked round-bottom flasks with magnetic stirring (700 rpm). The reagents were combined with CH₃CN and benzene as an internal standard (Sigma-Aldrich, thiophene-free, >99%). The flasks were connected to reflux condensers to prevent evaporative losses and submerged in a temperature-controlled H₂O (298 – 318 K) or silicone oil (Sigma-Aldrich, viscosity 100 cSt) (323 – 328 K) bath on a hot plate (Corning, PC-420D). The reagents were combined and stirred for 0.5 h at the reaction temperature before taking an initial aliquot (~0.5 cm³) to determine the initial concentration of C₄H₈O and the products, 1-methoxy-2-butanol (C₅H₁₂O₂, 1M2B) and 2-methoxy-1-butanol (C₅H₁₂O₂, 2M1B). M-BEA (~15-80 mg) was then added to initiate the reaction, and aliquots were taken as a function of time with a syringe equipped with a polypropylene filter (Tisch Scientific, 0.22 μm) to separate the sample solution from the catalyst. The concentrations of the epoxide, benzene, and ring-opening products were quantified with a gas chromatograph (GC) (Agilent, 6850) equipped with a liquid autosampler, flame ionization detector, and polysiloxane column (HP-1, Agilent, 19091Z-115E). Elution times and sensitivity factors for the reaction products were determined using commercially obtained samples of 1M2B (TCI Chemicals, >93.0%) and 2M1B (TCI Chemicals, >98.0%) (**Section C2**). All

reported turnover rates were measured at differential conversion (<10%) with an uncertainty of ~10%, as demonstrated with replicated measurements. The carbon balance closes within 90 – 110% for all reported measurements.

Carbon selectivity to the desired 1M2B and 2M1B products exceeds 90% across all measurements and >95% for nearly all measurements. Two side products appear with similar GC retention times to the ring-opening products. While the identity of these side products remains unclear, a comparison of the retention times of these species to known standards excludes the possibility that these represent formation of dibutyl ether or the formation of butanal or butanone from Meinwald rearrangement of the epoxide. One remaining possibility is that these peaks correspond to 1,1-dimethoxybutane ($C_6H_{14}O_2$) from the reaction of either ring-opening product with CH_3OH . Each ring-opening product may also react with a second epoxide molecule to form an oligomerization product, although we expect minimal contribution from these pathways at differential conversion.

Initial turnover rate values were calculated by fitting turnover numbers (moles of product per moles of active metal) as a function of time to a second-order polynomial with the turnover rate fixed at zero at time equal to zero, then determining the derivative at time equal to zero. The conditions used for rate measurements here avoid internal and external mass transfer constraints because turnover rates do not depend on the loading of metal atoms for all materials within the range of loadings studied (**Figure C13a** in **Appendix Section C4**). These measurements demonstrate that all M-BEA satisfy the Madon-Boudart criterion²⁶³ and are free of mass transfer artifacts. In addition, turnover rates exhibit combinations of first- and zero-order dependencies on the concentrations of C_4H_8O and CH_3OH at limiting conditions (**Section 4.3.1**).¹⁵⁹ A mass-transfer limited material would show a sub-linear dependence on reactant concentrations because the mean

concentration of the reactants throughout the pores would not depend linearly on the fluid phase reactant concentrations for a zero-order reactant.

Hot filtration tests were utilized to determine if metal atoms or catalytic protons leach from the *BEA framework and form homogeneous complexes active for ring-opening. A large aliquot ($\sim 5\text{ cm}^3$) was taken $\sim 600\text{--}900\text{ s}$ after adding the catalyst, filtered with a polypropylene filter (Tisch Scientific, $0.22\text{ }\mu\text{m}$), then transferred into a scintillation vial (20 cm^3 , Trident Technology). The vial was heated at 308 K and stirred at 700 rpm . Aliquots were taken from the vial as a function of time, and concentrations of all relevant species were quantified with GC. **Figure C11** in **Section C3** shows that the product concentrations change negligibly after filtering out the solid catalyst but continue to increase in the presence of the catalyst. In addition, turnover rates normalized to the amount of residual Al within a dealuminated *BEA material (Si:Al ~ 1300 from EDXRF) are lower than all M-BEA by more than an order of magnitude (**Figure C12b**), which demonstrates that residual Al atoms within the Lewis acidic M-BEA materials contribute negligibly to measured turnover rates. Together, these experiments provide strong evidence that the ring-opening of $\text{C}_4\text{H}_8\text{O}$ with CH_3OH proceeds solely at metal atoms substituted within the *BEA framework.

In situ site titration experiments with (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine (DPED, Sigma-Aldrich, 97%) were carried out to probe the number of active sites within each M-BEA material. DPED was added to a mixture of CH_3CN , benzene, $\text{C}_4\text{H}_8\text{O}$, and M-BEA at a ratio of DPED to metal atom of two. The reaction flask was stirred for 0.5 h at 308 K to allow DPED to selectively bind to the active sites. The reaction was then initiated by adding CH_3OH , after which aliquots were taken as a function of time, as described above. The concentration of DPED in the liquid phase during the reaction was quantified via GC and used to determine the quantity of DPED that binds to the catalyst. Each bound DPED molecule is assumed to titrate one active site in the

catalyst. Therefore, the number of active sites is estimated by the quantity of DPED adsorbed (**Table 4.1**). A full analysis of the titration experiments is provided in **Appendix Section C4**.

4.2.4 Liquid-Phase Uptake Measurements of CH₃OH

The mole fraction of CH₃OH in the pores of M-BEA was estimated via liquid-phase uptake measurements from CH₃CN. First, varying concentrations of CH₃OH were mixed with CH₃CN in a 5 cm³ solution, from which an initial aliquot was taken. ~100 mg of M-BEA was then added to the CH₃OH and CH₃CN solution, after which the solution was mixed for 2 h at a stir rate of 250 rpm and a temperature of 308 K. The catalyst and solution were left in contact for 2 h to ensure that the adsorption of CH₃CN and CH₃OH had reached equilibrium. A second aliquot was taken after this mixing period. The concentrations of CH₃CN and CH₃OH in each aliquot were quantified with GC. The intrapore solvent composition was estimated from the amount of solution absorbed by M-BEA and the difference in the liquid phase composition before and after mixing the solution with the catalyst (**Appendix Section C5**).

4.2.5 Liquid-Phase Adsorption Enthalpies for Reactants

The heat released upon adsorption of C₄H₈O and CH₃OH was measured with an isothermal titration calorimeter (ITC) (TA Instruments, NanoITC) equipped with sample and reference cells. A brief cleaning procedure was performed to prepare the sample and reference cells for each experiment. First, 500 cm³ of a cleaning solution consisting of 2 volume % detergent in DI H₂O (18.2 MΩ cm, Elga Purelab Flex 2) flowed through the cell at room temperature. The sample cell was then rinsed with 1000 cm³ of DI H₂O. The sample cell and reference cell were then filled with 350 μL of H₂O (maximum cell volumes are 500 μL). A 50 μL ITC syringe was filled with H₂O, then loaded into the instrument. A subsequent electrical calibration used sequential pulses to

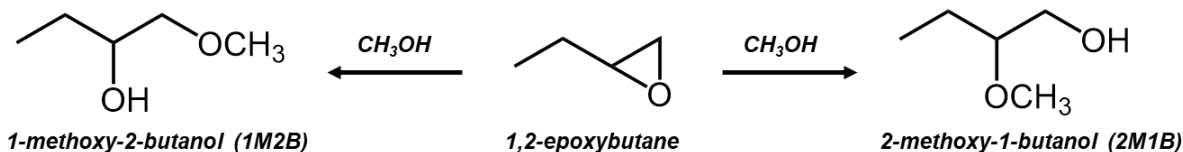
determine the heat released from a calibrated Pt resistor. Finally, pure DI H₂O was injected into DI H₂O to ensure the sample cell was clean enough to begin experiments. The cell was assumed to be clean when the H₂O-H₂O injection released negligible amounts of heat ($\pm 3 \mu\text{J}$ for each injection of 1 μL). The cleaning procedure was repeated if the H₂O-H₂O injection did not give sufficiently low heat rates. Notably, this cleaning procedure is less harsh than treatments using HNO₃ and NaOH^{30, 73, 211, 258, 264} we reported previously. This method reduces the risk of corrosion and metal dissolution at components of the ITC cell while still leading to measurements with a consistent baseline and high signal-to-noise ratio.

In a typical experiment, a slurry of M-BEA (20-40 mg) in CH₃CN or CH₃OH was titrated by a solution of C₄H₈O or CH₃OH (5 mM) in the same solvent. The mass of M-BEA in the sample cell was calculated by taking the difference between the mass added to the slurry and the mass remaining upon evaporation of the residual slurry after loading the cell. The titrations were carried out at 308 K with a stirring rate of 250 rpm. The sample cell was filled with 350 μL of M-BEA and solvent, while the reference cell was filled with 350 μL of solvent. The enthalpies of adsorption were calculated by averaging the integrated heats released upon adsorption of the titrant molecules to M-BEA sites from a 1 μL injection of titrant at low coverages ($< 0.25 \text{ mol titrant (mol M)}^{-1}$). The heat released in this low coverage regime remains approximately constant, suggesting that the calculated enthalpies represent the isosteric adsorption enthalpies for each titrant.⁷³

4.3 Results and Discussion

4.3.1 Mechanistic Interpretations of Epoxide Ring-Opening Rates

Turnover rates for C₄H₈O ring-opening with CH₃OH over M-BEA were measured in CH₃CN solvent to allow for control of both C₄H₈O and CH₃OH concentrations ([C₄H₈O], [CH₃OH], where [x] denotes the concentration of species x). Measurements were made in neat



Scheme 4.1. Primary reaction products formed by $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH over M-BEA zeolite catalysts.

CH_3OH (24.7 M CH_3OH) as well. **Scheme 4.1** shows that the reaction yields either 1-methoxy-2-butanol (1M2B, a terminal ether) or 2-methoxy-1-butanol (2M1B, a terminal alcohol).

Turnover rates for $\text{C}_4\text{H}_8\text{O}$ ring-opening depend strongly on both $[\text{CH}_3\text{OH}]$ (**Figure 4.1**) and $[\text{C}_4\text{H}_8\text{O}]$ (**Figure 4.2**), as well as the elemental identity of the framework substituted metal. Among Lewis acids, turnover rates increase from Ti to Zr to Sn, such that rates upon Sn-BEA are 10-50 times greater than those on Ti-BEA across the conditions examined. The Bronsted acidic Al-BEA gives lesser turnover rates than Sn-BEA with exceptions in extreme stoichiometric excess of CH_3OH ($[\text{CH}_3\text{OH}]:[\text{C}_4\text{H}_8\text{O}] > 1000$). **Figure 4.1** shows turnover rates depend linearly on $[\text{CH}_3\text{OH}]$ for all M-BEA at ratios of $[\text{CH}_3\text{OH}]$ to $[\text{C}_4\text{H}_8\text{O}]$ less than 40. Turnover rates on all

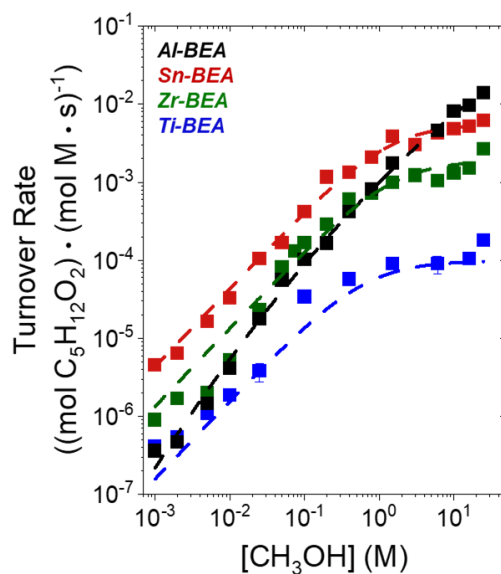


Figure 4.1. Turnover rates for $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH as functions of CH_3OH concentration over Al- (black), Sn- (red), Zr- (green), and Ti-BEA (blue) (0.005 M $\text{C}_4\text{H}_8\text{O}$, CH_3CN solvent, 308 K).

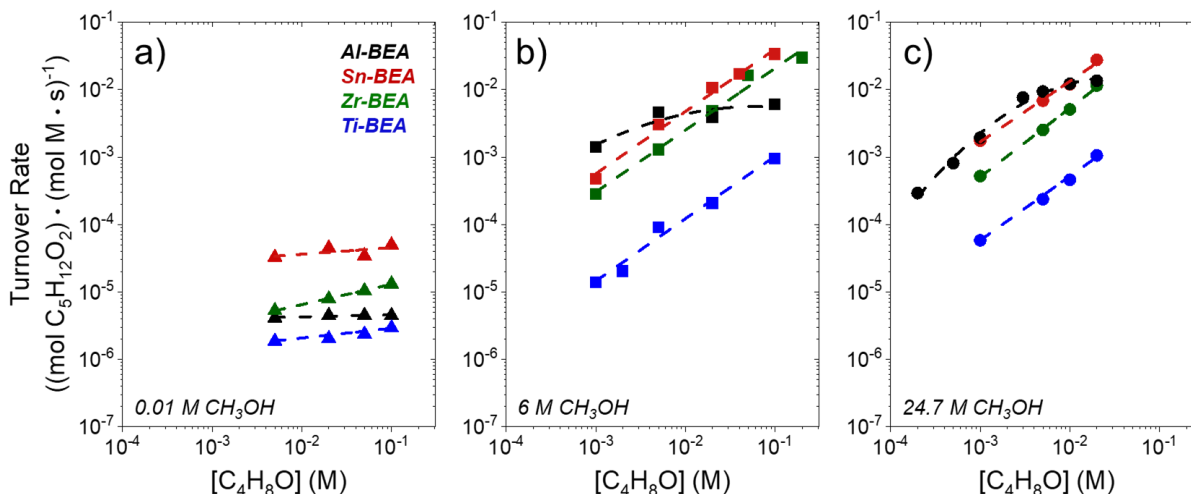
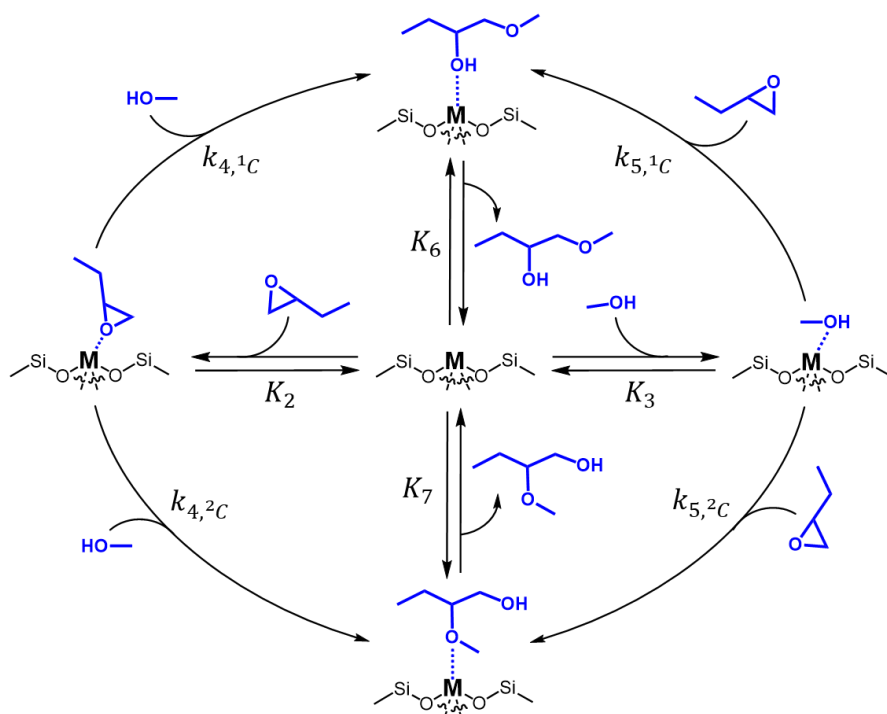


Figure 4.2. Turnover rates for C_4H_8O ring-opening with CH_3OH as functions of C_4H_8O concentration at a) 0.01 M CH_3OH , b) 6 M CH_3OH , or c) neat (24.7 M) CH_3OH (CH_3CN solvent, 308 K) over Al- (black), Sn- (red), Zr- (green), and Ti-BEA (blue).

catalysts depend weakly on $[C_4H_8O]$ within this regime (**Figure 4.2a**). At high molar ratios of CH_3OH to C_4H_8O ($[CH_3OH]:[C_4H_8O] > 500$), turnover rates depend linearly on $[C_4H_8O]$ for Lewis acidic catalysts (**Figures 4.2b** and **4.2c**). However, turnover rates upon Al-BEA show a linear dependence on $[C_4H_8O]$ only when ratios of $[CH_3OH]$ to $[C_4H_8O]$ exceed 5000. Taken together, these rate measurements (**Figures 4.1** and **4.2**) suggest that all M-BEA materials catalyze epoxide ring opening by an analogous sequence of elementary steps that proceed on active sites saturated by either C_4H_8O - or CH_3OH -derived species. Intermediates derived from C_4H_8O occupy active sites of Al-BEA at nearly all conditions examined, and CH_3OH -derived species dominate only at the greatest $[CH_3OH]$ to $[C_4H_8O]$ ratios. Over Lewis acidic catalysts, the transitions between these regimes occur at lower molar ratios ($100 \leq [CH_3OH]:[C_4H_8O] \leq 500$). These differences may arise from distinct preferences to bind reactants or mechanistic differences between Lewis and Brønsted acid zeolite catalysts.

Scheme 4.2 depicts a plausible set of elementary steps for the ring-opening of C_4H_8O with CH_3OH over Lewis acidic M-BEA materials. CH_3CN (step 1, not shown for clarity), C_4H_8O (step



Scheme 4.2. Proposed catalytic cycle for $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH in CH_3CN solvent over Lewis acidic M-BEA zeolites. We expect an identical set of steps over the Brønsted acid. All adsorption steps are assumed to be reversible. Steps to form 1M2B and 2M1B are denoted with ^1C or ^2C to signify nucleophilic attack to the primary or secondary carbon atom in the oxirane ring, respectively. For clarity, we do not show the reversible adsorption of CH_3CN molecules (step 1) in this cycle.

2), or CH_3OH (step 3) adsorb to active sites. The epoxide ring opens either by nucleophilic attack of CH_3OH toward bound $\text{C}_4\text{H}_8\text{O}$ (step 4) or by the reaction of $\text{C}_4\text{H}_8\text{O}$ with bound CH_3OH (step 5).⁶³ For concision, we portray only reactions with molecularly adsorbed CH_3OH and $\text{C}_4\text{H}_8\text{O}$ (e.g., CH_3OH^* , where * indicates species associated with the active site) and not dissociatively bound oxygenates. The distinct ring-opening products ($\text{C}_5\text{H}_{12}\text{O}_2$, 1M2B and 2M1B) may form through either process (steps 4 or 5) by similar elementary steps that possess unique rate constants (e.g., $k_{4,1\text{C}}$, $k_{4,2\text{C}}$) and transition states that account for regioselectivity. Here, steps denoted as ^1C represent nucleophilic attack at the primary carbon in the $\text{C}_4\text{H}_8\text{O}$ ring to form 1M2B, while ^2C signifies attack at the secondary carbon to form 2M1B. The 1M2B and 2M1B products desorb

(steps 6 and 7) to complete the catalytic cycle. We note that a CH₃CN molecule may co-adsorb to the Lewis acid sites with a CH₃OH or C₄H₈O molecule to form an octahedral configuration, consistent with previous reports of framework Ti and Sn atoms in zeolites binding with two H₂O molecules.^{136, 265-266} However, we are unable to distinguish between reaction pathways with or without a spectating CH₃CN molecule coordinating to the active sites. An analogous sequence of steps forms ring-opening products on Al-BEA (**Scheme C1**); however, the structure of the intermediates involved differs due to proton transfer to the reactive species.²⁶⁷⁻²⁷⁰ Notably, the formation rates of the 1M2B and 2M1B products show nearly identical dependences on [CH₃OH] and [C₄H₈O] (see **Section C6**), providing evidence that the products form from common intermediates as depicted in **Scheme 4.2** and **Scheme C1**.

Rates for ring-opening (r_{RO}) equal the sum of the rates of reactions through bound C₄H₈O- (r_4) or CH₃OH-derived intermediates (r_5):

$$r_{RO} = r_4 + r_5 = k_4[C_4H_8O^*][CH_3OH] + k_5[C_4H_8O][CH_3OH^*] \quad (4.2)$$

where k_4 and k_5 represent the sum of the rate constants to form products in steps 4 ($k_{4,1C}$, $k_{4,2C}$) and 5 ($k_{5,1C}$, $k_{5,2C}$) in **Scheme 4.2**, and [C₄H₈O*] and [CH₃OH*] represent the number of C₄H₈O* and CH₃OH* intermediates, respectively. The application of the pseudo-steady state hypothesis to the bound intermediates and a site balance yields a turnover rate expression that accounts for each reaction path (see **Section C7** for full derivation):

$$\frac{r_{RO}}{[L]} = \frac{\frac{k_2 k_4 [C_4H_8O][CH_3OH]}{k_{-2} + k_4 [CH_3OH]} + \frac{k_3 k_5 [C_4H_8O][CH_3OH]}{k_{-3} + k_5 [C_4H_8O]}}{1 + K_1 [CH_3CN] + \frac{k_2 [C_4H_8O]}{k_{-2} + k_4 [CH_3OH]} + \frac{k_3 [CH_3OH]}{k_{-3} + k_5 [C_4H_8O]} + \frac{k_4 [CH_3OH] + k_5 [C_4H_8O] + k_{-6} [1M2B]}{k_6} + \frac{k_4 [CH_3OH] + k_5 [C_4H_8O] + k_{-7} [2M1B]}{k_7}} \quad (4.3)$$

The reaction likely does not proceed as a bimolecular Langmuir-Hinshelwood reaction between surface-bound CH₃OH and C₄H₈O because this would lead to squared dependences on the CH₃OH and C₄H₈O terms in the denominator at sufficiently high coverages of either species. Rates would

eventually decrease with increasing concentrations of CH₃OH and C₄H₈O in a bimolecular surface reaction. Rates show linear or zero order dependences over the wide range of conditions shown in **Figures 4.1** and **4.2**, providing support that the reaction proceeds through an Eley-Rideal mechanism as illustrated in **Scheme 4.1**.

The full rate expression (**Equation 4.3**) simplifies considerably when a single type of reactive intermediate dominates at active sites. In the limit when C₄H₈O-derived species saturate active sites and act as the most abundant reactive intermediate (MARI), the rate expression collapses to the form:

$$\frac{r_{RO}}{[L]} = \frac{k_2 k_4 [CH_3OH] (k_{-3} + k_5 [C_4H_8O]) + k_3 k_5 [CH_3OH] (k_{-2} + k_4 [CH_3OH])}{k_2 (k_{-3} + k_5 [C_4H_8O])} \quad (4.4)$$

The form of **Equation 4.4** predicts a superlinear dependence of rates on [CH₃OH] and a weak dependence on [C₄H₈O] at low ratios of [CH₃OH] to [C₄H₈O]. Yet, the form of this equation matches the trends observed in **Figures 4.1** and **4.2** at ratios of [CH₃OH] to [C₄H₈O] up to ~40 in Lewis acids and ~1000 over Al-BEA only when the first term in the numerator dominates, which leads to the following:

$$\frac{r_{RO}}{[L]} = k_4 [CH_3OH] \quad (4.5)$$

Neglecting the second term implies that the value of $k_2 k_4$ far exceeds $k_3 k_5$. C₄H₈O shows much larger adsorption enthalpies (~ -50 to -100 kJ mol⁻¹) than CH₃OH (~ 0 to -5 kJ mol⁻¹) over M-BEA, measured by ITC (see **Section C8**). These comparisons suggest that values for the equilibrium constants for binding C₄H₈O (K_2) exceed those for CH₃OH (K_3), which implies that C₄H₈O adsorbs more readily than CH₃OH (i.e., $k_2 \gg k_3$). The much greater values of k_2 relative to k_3 may lead to the first term in the numerator of **Equation 4.4** dominating up to [CH₃OH] to [C₄H₈O] ratios of ~40 in Lewis acids and ~1000 over Al-BEA, even if k_4 and k_5 have similar values. Consequently, these comparisons indicate that the difference in adsorption strength

between C₄H₈O and CH₃OH leads to rate trends that agree with the form of **Equation 4.4** at sufficiently low ratios of [CH₃OH] to [C₄H₈O]. These assumptions and adsorption enthalpy measurements justify the simplification of **Equation 4.4** to **Equation 4.5** and the conclusion that C₄H₈O-derived species dominate active sites at these conditions.

When CH₃OH-derived intermediates prevail and serve as the MARI, the complete rate expression (**Equation 4.3**) becomes:

$$\frac{r_{RO}}{[L]} = \frac{k_2 k_4 [C_4H_8O] (k_{-3} + k_5 [C_4H_8O]) + k_3 k_5 [C_4H_8O] (k_{-2} + k_4 [CH_3OH])}{k_3 (k_{-2} + k_4 [CH_3OH])} \quad (4.6)$$

Here, the numerator simplifies to a form that matches the linear rate dependence on [C₄H₈O] and weak dependence on [CH₃OH] under greater ratios of [CH₃OH]:[C₄H₈O] when the second term of the numerator dominates, which gives:

$$\frac{r_{RO}}{[L]} = k_5 [C_4H_8O] \quad (4.7)$$

At sufficiently high ratios of [CH₃OH] to [C₄H₈O] (>500 in Lewis acids and ~5000 over Al-BEA), [CH₃OH] likely dominates over all terms in **Equation 4.7**, leading to a negligible value for the first term in the numerator. These assumptions lead to the form of **Equation 4.7** in solutions with a large stoichiometric excess of CH₃OH, even if k_4 and k_5 possess values of a similar magnitude.

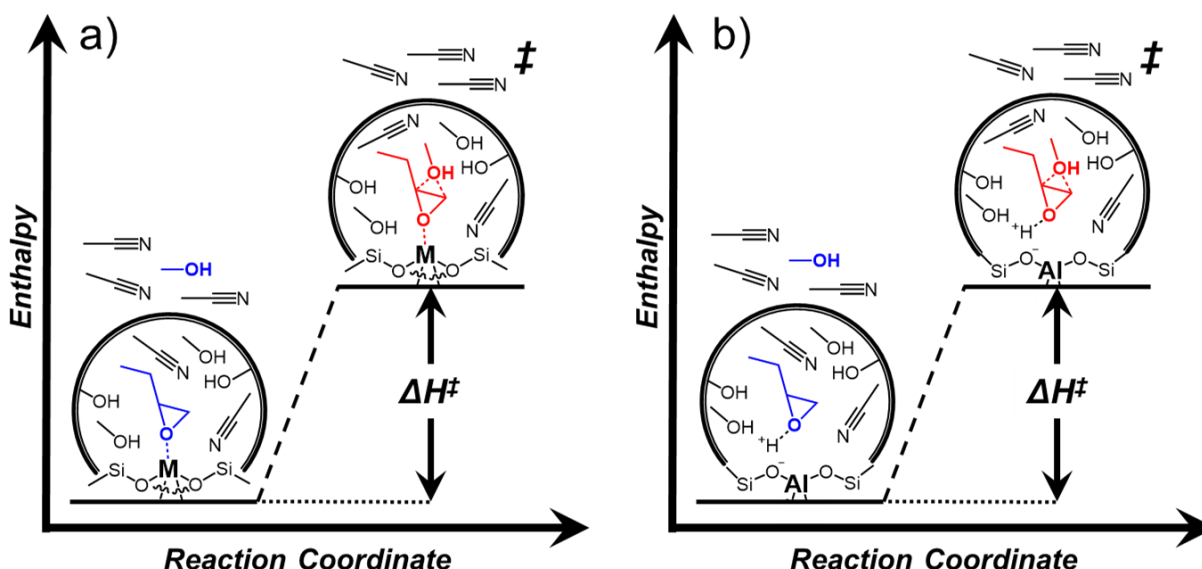
Turnover rates for Sn-, Ti-, and Zr-BEA agree with the forms of **Equations 4.5** and **4.7** in the limit of C₄H₈O- and CH₃OH-saturated sites, respectively, which suggests that Lewis acids share common surface intermediates and reaction mechanisms. Therefore, differences between turnover rates for the Lewis acidic M-BEA catalysts arise specifically from differences among rate constants for the nucleophilic attack to the epoxide intermediate (k_4 and k_5). The values of k_4 and k_5 reflect differences in the covalent interactions between reactive intermediates and active sites comprised of distinct elements. Brønsted acidic Al-BEA likely catalyzes epoxide conversion through a similar mechanism (**Scheme C1**), and here, differences between the values of k_4 and k_5

for Brønsted and Lewis acids should describe disparities in charge transfer (i.e., coordinate covalent bonds or ionic interactions) and solvation of the active site and reactive species (i.e., non-covalent interactions).

Previous studies demonstrate that changing the active metal³⁰⁻³² and intrapore solvent structure^{74, 211, 258-259, 264} strongly influence rates and selectivities for alkene epoxidation reactions through changes in the stability of reactive species. Intuitively, changing these variables must also influence the stability of reactive species for epoxide ring-opening. The stability of reactive species can be probed directly with measurements of activation barriers and adsorption enthalpies, as discussed in the following sections.

4.3.2 Inner and Outer Sphere Interactions Govern Differences in Activation Barriers

The ring-opening of C_4H_8O proceeds on M-BEA catalysts by steps illustrated in **Scheme 4.2** and with turnover rates that depend on the concentrations of reactants captured by **Equations**



Scheme 4.3. Proposed reaction coordinate diagrams for C_4H_8O ring-opening with CH_3OH in CH_3CN solvent under conditions of a MARI species derived from C_4H_8O over a) Lewis acidic and b) Brønsted acidic M-BEA. Liquid phase CH_3OH adsorbs to react with $C_4H_8O^*$ and form the product, which then desorbs to complete the reaction.

4.5 and **4.7**. Differences among turnover rates for the selection of M-BEA catalysts examined at identical conditions, therefore, stem from changes in the stability of surface intermediates and transition states that alter the rate constants for nucleophilic attack (k_4 and k_5), and not by differences in the mechanism for ring-opening or dominant surface intermediates. Transition state theory²⁷¹⁻²⁷² restates these rate constants in terms of activation free energies ($\Delta G^\ddagger$) and the corresponding activation enthalpies ($\Delta H^\ddagger$) and entropies ($\Delta S^\ddagger$):

$$k_x = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} = \frac{k_B T}{h} e^{-\frac{\Delta H^\ddagger}{RT}} e^{\frac{\Delta S^\ddagger}{R}} \quad (4.8)$$

Scheme 4.3 shows that the values of $\Delta H^\ddagger$ reflect differences between the enthalpy of the transition state for nucleophilic attack and the sum of the enthalpies of the bound $C_4H_8O^*$ intermediate and liquid-phase CH_3OH (note, identical states define $\Delta S^\ddagger$) when turnover rates depend linearly upon $[CH_3OH]$ (**Equation 4.5**). Under these conditions, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ equal:

$$\Delta H^\ddagger = H^\ddagger - H_{C_4H_8O^*} - H_{CH_3OH} \quad (4.9)$$

$$\Delta S^\ddagger = S^\ddagger - S_{C_4H_8O^*} - S_{CH_3OH} \quad (4.10)$$

These activation parameters account for the total formation rate of both products. Each term contains both standard state (H^0 , S^0) and excess (H^ε , S^ε) contributions:

$$\Delta H^\ddagger = \Delta H^{\ddagger,0} + \Delta H^{\ddagger,\varepsilon} = (H^{\ddagger,0} + H^{\ddagger,\varepsilon}) - (H_{C_4H_8O^*}^0 + H_{C_4H_8O^*}^\varepsilon) - (H_{CH_3OH}^0 + H_{CH_3OH}^\varepsilon) \quad (4.11)$$

$$\Delta S^\ddagger = \Delta S^{\ddagger,0} + \Delta S^{\ddagger,\varepsilon} = (S^{\ddagger,0} + S^{\ddagger,\varepsilon}) - (S_{C_4H_8O^*}^0 + S_{C_4H_8O^*}^\varepsilon) - (S_{CH_3OH}^0 + S_{CH_3OH}^\varepsilon) \quad (4.12)$$

Here, we define H^0 and S^0 values as the covalent interactions stemming from the coordinate covalent bonds between Lewis acids sites and reactive species and the ionic interactions between the zeolite anion and protonated intermediates and transition states in the Brønsted acid material. H^ε and S^ε values encompass non-covalent interactions of the transition state or reactive intermediates with surrounding solvent molecules and the pore walls of the zeolite.^{39, 124}

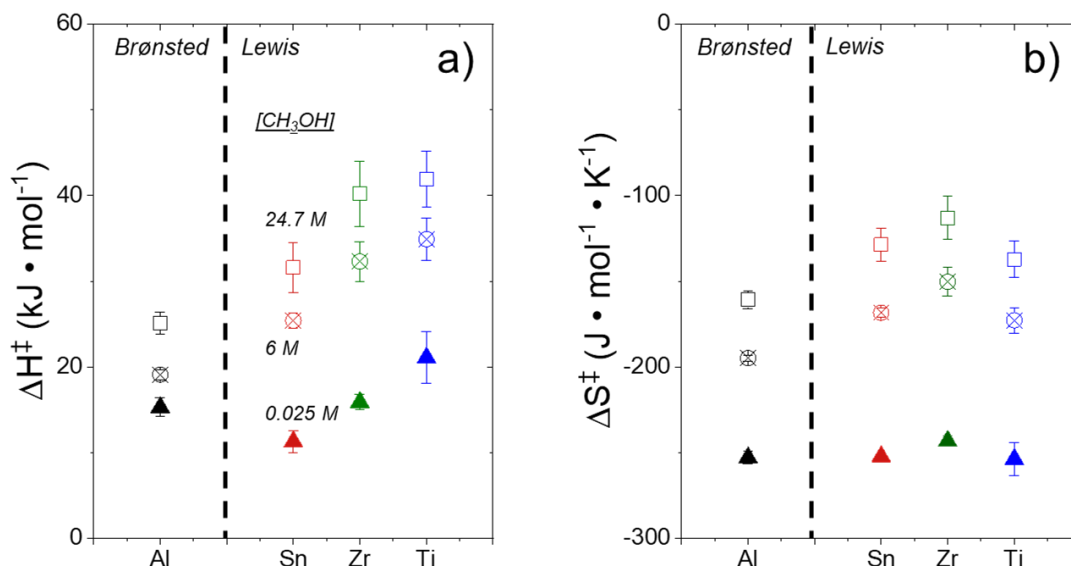


Figure 4.3. Activation a) enthalpies and b) entropies for C₄H₈O ring-opening with CH₃OH (solid triangles – 0.005 M C₄H₈O, 0.025 M CH₃OH in CH₃CN; crossed circles – 0.25 M C₄H₈O, 6 M CH₃OH in CH₃CN; hollow squares – 1 M C₄H₈O in neat (24.7 M) CH₃OH), 298-323 K) over Al- (black), Sn- (red), Zr- (green), and Ti-BEA (blue).

Figure 4.3 demonstrates that the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ depend strongly on the identity of the active metal within M-BEA and the composition of the solvent even when C₄H₈O* saturates active sites consistently (calculation details and barriers under a CH₃OH-derived MARI in **Section C9**; supplemental kinetics at high [C₄H₈O] in **Section C10**). Among Lewis acid metals, $\Delta H^\ddagger$ values span ~ 10 kJ mol⁻¹ with the lowest values on Sn-BEA and the greatest on Ti-BEA for any given [CH₃OH] value. In comparison, $\Delta S^\ddagger$ only spans ranges of ~10 to 20 J mol⁻¹ K⁻¹. Comparisons between these activation parameters and turnover rates (**Figures 4.1** and **4.2**) demonstrate that differences among values of $\Delta H^\ddagger$ (and not $\Delta S^\ddagger$) are primarily responsible for greater turnover rates for ring-opening over Sn-BEA in comparison to Zr- and Ti-BEA. These observations imply that differences among the covalent interactions between the metal atoms that comprise active sites (Sn, Zr, or Ti) and reactive species give rise to rate changes and $\Delta H^\ddagger$ differences among Lewis acids for a given reaction mixture. Furthermore, these differences do not give evidence for

significant changes in the solvation environment between these materials, which would likely manifest as large differences in $\Delta S^\ddagger$. Greater ring-opening turnover rates likely reflect the enthalpic stabilization of the transition states for ring-opening by charge transfer (i.e., decreased $H^{\ddagger,0}$).

While differences in the identity of the metal lead to consequential differences in $\Delta H^\ddagger$ values, **Figure 4.3** shows greater values of [CH₃OH] deliver more positive values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for all M-BEA catalysts. All Lewis acids show systematic and similar increases in $\Delta H^\ddagger$ (20 – 25 kJ mol⁻¹) and $\Delta S^\ddagger$ (115 – 130 J mol⁻¹ K⁻¹) from 0.025 CH₃OH to 24.7 M CH₃OH. These trends demonstrate that differences in the solvation of reactive species between a CH₃CN-rich and CH₃OH-rich solvent likely alter $\Delta H^\ddagger$ and $\Delta S^\ddagger$ by varying excess contributions that influence the stability of bulk fluid phase species and those bound to active sites within the pores of *BEA. Notably, H^ε values span a range of less than 3 kJ mol⁻¹ for liquid-phase C₄H₈O and CH₃OH across the range of solvent compositions examined, while activity coefficients vary by less than a factor of three (see **Section C11**). These weak dependences demonstrate that changes in the stability of the liquid-phase reactants do not contribute significantly to changes in rates (**Section 4.3.1**) or $\Delta H^\ddagger$ values, and therefore, changes in the stability of solvated reactive species within zeolite pores drive differences in rates and kinetics.

Barriers measured in the dilute limit for methanol (0.025 M CH₃OH) were selected as a reference state (i.e., assigning values for excess contributions to the activation parameters, $\Delta H^{\ddagger,\varepsilon}$ and $\Delta S^{\ddagger,\varepsilon}$, equal to zero), because this set of conditions represents systems with the minimum number of hydrogen bonding interactions among reactive species. Previous work showed that the disruption of hydrogen bonded solvent molecules within zeolite pores increases $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values through corresponding changes in $\Delta H^{\ddagger,\varepsilon}$ and $\Delta S^{\ddagger,\varepsilon}$ that occur when transition states for kinetically relevant steps occupy larger volumes within dense fluids than the preceding reactive

intermediates.^{74, 211, 259} Here, the formation of the transition state for ring-opening may similarly disrupt hydrogen bonds among CH₃OH molecules near active sites, leading to $\Delta H^{\ddagger,\varepsilon}$ and $\Delta S^{\ddagger,\varepsilon}$ values that increase with [CH₃OH] over all M-BEA catalysts. In addition, the presence of networked CH₃OH may enthalpically stabilize the reactive intermediates that saturate active sites (e.g., C₄H₈O*) more significantly than the transition state and increase $\Delta H^{\ddagger}$. The disruption and reorganization of solvating molecules appear as differences in $\Delta S^{\ddagger}$ values that rise from significant entropy losses in CH₃CN-rich solutions (0.025 M CH₃OH), which likely signify the formation of solvation shells with greater ordering around ring-opening transition states than C₄H₈O* complexes. Increasingly positive $\Delta S^{\ddagger}$ suggest that CH₃OH forms increasing numbers of cohesive clusters as [CH₃OH] rises, and the disruption of these clusters offsets a portion of the entropy lost when forming the bimolecular transition state. The trends in these values across Lewis acidic M-BEA catalysts indicate these differences reflect similar increases in $\Delta S^{\ddagger,\varepsilon}$ that are offset by concomitant rises in $\Delta H^{\ddagger,\varepsilon}$, which leads to rate differences primarily driven by changes in [CH₃OH].

Al-BEA shows increases in both $\Delta H^{\ddagger,\varepsilon}$ and $\Delta S^{\ddagger,\varepsilon}$ (10 kJ mol⁻¹ and 90 J mol⁻¹ K⁻¹) as [CH₃OH] increases (0.025 to 24.7 M CH₃OH), which are notably smaller than those for Lewis acid catalysts. Protonation of the reactive intermediate and transition state (**Scheme 4.3b**) clouds direct comparisons of $\Delta H^{\ddagger}$ between Al-BEA and the Lewis acids. Contributions from $\Delta H^{\ddagger,0}$ that reflect proton transfer to the transition state and reactive intermediate (i.e., C₄H₈O*) likely contribute to changes in $\Delta H^{\ddagger}$ between Lewis and Brønsted acids. The Brønsted acid sites within Al-BEA interact with the solvent in ways distinct from those observed in Lewis acid catalysts. Specifically, the proton from the acid site can delocalize across a cluster of many molecules comprised of the reactive species and solvent molecules with sufficient proton affinities. Here,

reactive species likely exist within mobile clusters of CH₃OH molecules in CH₃OH-rich solvents, as reported previously,^{100, 273-274} while the protonated reactant remains more tightly associated with the anionic Al-O⁻ moiety at higher values of [CH₃CN]. Differences in the nature of the active proton within Al-BEA as [CH₃OH] changes may explain why Al-BEA shows smaller increases in $\Delta H^{\ddagger,\varepsilon}$ and $\Delta S^{\ddagger,\varepsilon}$ with [CH₃OH] than the Lewis acids. Despite these convoluting factors, the consistent trends among all M-BEA suggest that differences in the solvation of reactive species play a strong role in the greater $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values at higher [CH₃OH] through changes in $\Delta H^{\ddagger,\varepsilon}$ and $\Delta S^{\ddagger,\varepsilon}$.

Figure 4.3 demonstrates that both covalent (i.e., changes in $\Delta H^{\ddagger,0}$ and $\Delta S^{\ddagger,0}$ in response to metal identity) and non-covalent interactions (i.e., changes in $\Delta H^{\ddagger,\varepsilon}$ and $\Delta S^{\ddagger,\varepsilon}$ in response to solution composition) differ considerably across relevant reaction conditions and contribute to the differences in rate constants that impact turnover rates for epoxide ring-opening (**Figures 4.1** and **4.2**). Measurements of C₄H₈O adsorption enthalpies, revealed in the next section, provide further insight into the effect of the active metal and solvent composition on the stability of reactive species along the reaction coordinate.

4.3.3 Adsorption and Activation Enthalpy Correlations Reveal Consequences of Active Metal on Ring-Opening Turnover Rates

The intrinsic activation energy for an elementary step scales proportionally with the enthalpy of reaction for that step, as described by Brønsted-Evans-Polanyi relations.^{202, 234-235} Hammond's postulate rationalizes this observation by describing the structure of transition states as resembling the reaction state (i.e., reactant or product) most similar in energy.^{97, 198} These findings motivate the measurement of reactant and product adsorption enthalpies to gain a better understanding of transition state structures through comparison to measured activation enthalpies.

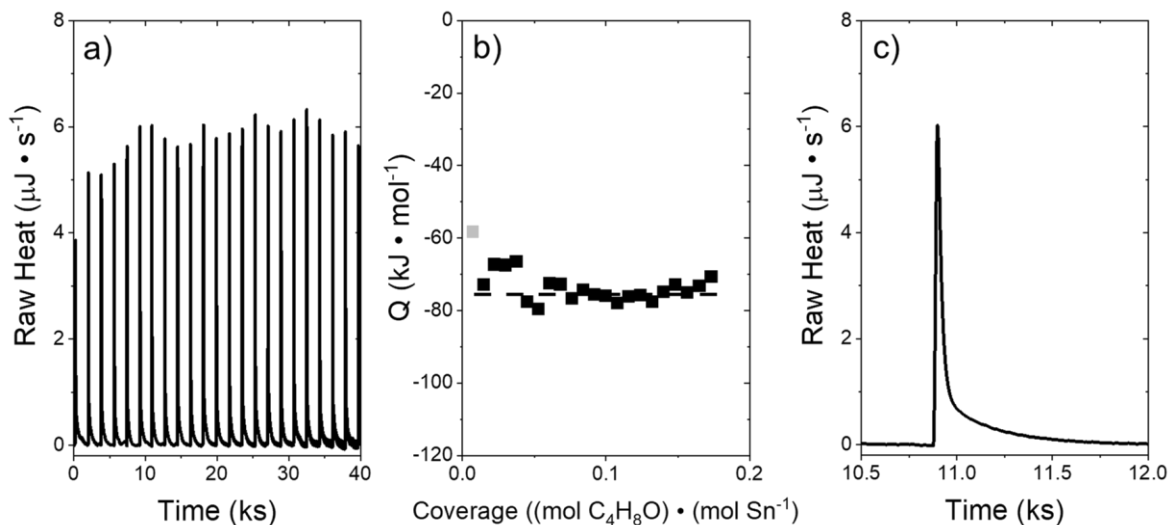


Figure 4.4. Isothermal titration calorimetry yields (a) thermograms from the titration of Sn-BEA with C₄H₈O (0.005 M C₄H₈O in CH₃OH, 308 K, 1 μL per injection), (b) corresponding heats released as a function of C₄H₈O coverage, and (c) a representative injection peak to illustrate baseline stability and signal-to-noise ratio. The transparent point in **Figure 4.4b** is omitted due to common errors associated with early injections.

Recent work demonstrates that $\Delta H^\ddagger$ values for epoxidation of linear alkenes correlate to liquid phase adsorption enthalpies for the corresponding product epoxides over *BEA zeolite substituted with different heteroatoms³⁰ and Ti-BEA zeolites containing varying (SiOH)_x densities^{73, 211} or submerged in organic solvents mixed with different quantities of H₂O.²⁵⁸ The positive correlations between enthalpies in these studies provide compelling evidence that the transition state for epoxidation resembled the adsorbed epoxide product, motivating the measurement of adsorption enthalpies for C₄H₈O (ΔH_{ads}) to gain a further understanding of the relevant transition states for C₄H₈O ring-opening.

Values of ΔH_{ads} for C₄H₈O adsorption were measured with isothermal titration calorimetry (ITC). **Figure 4.4a** presents the ITC thermogram for C₄H₈O adsorption into Sn-BEA (0.005 M C₄H₈O in CH₃OH, 308 K), during which the calorimeter quantifies heat released upon each injection of the C₄H₈O titrant solution into a slurry of Sn-BEA and CH₃OH. **Figure 4.4b** presents

heat evolved per quantity of C_4H_8O injected, which leads to calculated values of ΔH_{ads} equal to $-75 \text{ kJ} \pm 4 \text{ mol}^{-1}$ for Sn-BEA suspended in CH_3OH . All ΔH_{ads} measurements were obtained under a regime of low adsorbate coverage ($< 0.25 \text{ mol adsorbate (mol M}^{-1})$), where adsorbate molecules fully bind to active sites. The ΔH_{ads} value in **Figure 4.4b** was measured by averaging the non-opaques points, in which the integrated heat remains approximately constant, and is illustrated by the dashed line intersecting the points. The uncertainties were calculated from a single standard deviation among the points used to calculate ΔH_{ads} . A similar strategy was employed to obtain ΔH_{ads} values from the thermograms and integrated heat of adsorption plots for all other experiments, which are provided in **Section C12**. **Figure 4.4c** depicts a single heat flow feature (extracted from **Figure 4.4a**) that demonstrates the high signal-to-noise ratio of the ITC measurements.

Figure 4.5 demonstrates that values for ΔH_{ads} across M-BEA materials vary widely and depend on both the active metal identity and composition of the liquid-phase: trends that resemble those observed for $\Delta H_{app}^\ddagger$ (**Figure 4.3**). Among the Lewis acids, a more exothermic ΔH_{ads} corresponds to greater rates for C_4H_8O ring-opening in **Figures 4.1** and **4.2**. The most exothermic values of ΔH_{ads} appear for Sn-BEA and the most endothermic in Ti-BEA, regardless of the liquid composition. In comparisons between solvents, adsorption of C_4H_8O from CH_3CN provides more exothermic ΔH_{ads} values than from CH_3OH for each M-BEA material. Al-BEA shows more exothermic ΔH_{ads} values than each Lewis acid in both CH_3CN and CH_3OH . These measurements clearly quantify the extent to which covalent and non-covalent interactions contribute to differences among ΔH_{ads} values. Previous work from our group correlated more exothermic ΔH_{ads} values for $C_6H_{12}O$ to a greater intrinsic Lewis acid strength of M-BEA materials.³⁰ This trend aligns with expectations from reported Lewis acidities^{65, 71} for the M-BEA examined in this

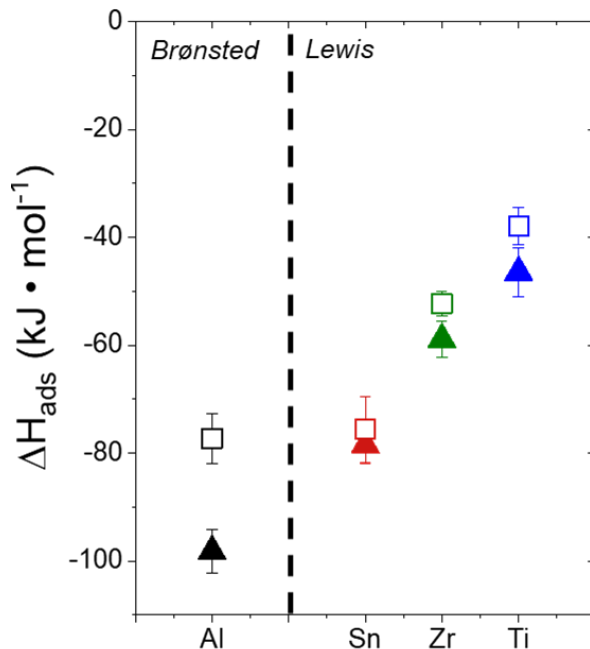


Figure 4.5. C₄H₈O adsorption enthalpies (ΔH_{ads}) (0.005 M C₄H₈O, 308 K) as a function of active metal in neat CH₃CN (solid triangles) and neat CH₃OH (hollow squares) over Al- (black), Sn- (red), Zr- (green), and Ti-BEA (blue).

study, further supporting that stronger Lewis acids give greater rates for epoxide ring-opening by binding C₄H₈O more strongly and lowering $H^{\ddagger,0}$. The more endothermic ΔH_{ads} values for all M-BEA in CH₃OH may originate from the displacement of CH₃OH, which likely binds more exothermically than CH₃CN, and disruption of hydrogen bonded CH₃OH molecules by C₄H₈O.^{73, 211} Significantly, the most exothermic ΔH_{ads} values in Al-BEA demonstrate that C₄H₈O adsorbs more strongly to the Brønsted acid sites than to any Lewis acid site here. This observation appears consistent with the weaker dependence of rates on [C₄H₈O] in Al-BEA than in the Lewis acids (Figure 4.1) and explains why C₄H₈O saturates sites on Al-BEA across nearly all conditions examined.

Figure 4.6 reveals that values for $\Delta H^{\ddagger}$ exhibit a linear dependence upon ΔH_{ads} among Lewis acids at a given solvent composition (i.e., CH₃CN-rich (solid points) or neat CH₃OH (hollow points)). Notably, values for Al-BEA fall well outside of the trend of the Lewis acids, as illustrated

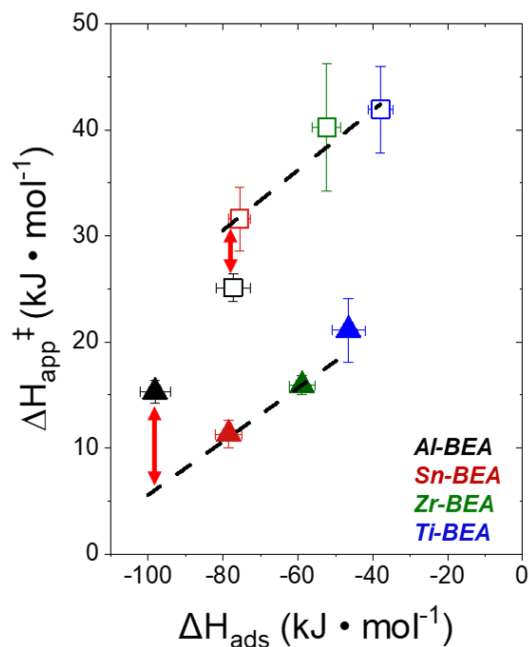


Figure 4.6. $\Delta H^{\ddagger}$ values for C_4H_8O ring-opening (from **Figure 4.3**, 0.025 M CH_3OH in CH_3CN (solid triangles) or 24.7 M CH_3OH (hollow squares)) as a function of ΔH_{ads} for C_4H_8O over Al- (black), Sn- (red), Zr- (green), and Ti-BEA (blue). Red arrows signify the deviation of Al-BEA from the trend between the Lewis acidic M-BEA materials.

by the red arrows (**Figure 4.6**). These linear correlations among Lewis acidic M-BEA suggest that the formation of the C_4H_8O ring-opening transition states upon $C_4H_8O^*$ saturated active sites and the adsorption of the C_4H_8O reactant respond similarly to changes in the electronic structure of the binding site because of structural similarities between the transition state and the bound reagent. Notably, the values of $\Delta H^{\ddagger}$ span a smaller range of values than ΔH_{ads} , and, consequently, the slopes of these correlations possess values of 0.25 – 0.35 (**Figure 4.6**). These comparisons appear to reflect differences among $\Delta H^{\ddagger,0}$ values that demonstrate the adsorption of C_4H_8O depends more sensitively upon the electronic structure of the active site than the formation of the ring-opening transition state, which agrees with expectations given the differences in proximity of the activated bonds from the transition metal center. When comparing an individual metal between CH_3CN and CH_3OH , the slope of the correlation between $\Delta H^{\ddagger}$ and ΔH_{ads} exceeds two for all Lewis acids.

These sharp slopes show that changing the solvent environment surrounding the metal sites influences the stability of the transition states for ring-opening more strongly than the stability of the adsorbed C_4H_8O intermediate, which likely reflects the differences between the excluded volume and extent of solvent reorganization required to accommodate these complexes. We cannot completely exclude the possibility that ring-opening by reaction of $C_4H_8O^*$ with CH_3OH contributes to measured ΔH_{ads} values in CH_3OH , which may convolute the comparison between these thermodynamic and kinetic parameters. Nevertheless, the strong dependences of $\Delta H^\ddagger$ and ΔH_{ads} upon solvent composition give direct evidence that intrapore solvent displacement and reorganization processes contribute to the excess enthalpies for adsorption and subsequent ring-opening of C_4H_8O .

Within **Figure 4.6**, values for Al-BEA deviate significantly from the linear correlations among Lewis acidic M-BEA catalysts. These differences signify that proton transfer to the epoxide (and transition state) and the solvation of reactive species by protonated solvent clusters involve distinct intermolecular forces that stabilize reactive species. The influence of proton transfer and delocalization may allow Al-BEA to stabilize reactive complexes more effectively than Lewis acid M-BEA materials in CH_3OH , whereas the opposite is true in CH_3CN . These differences may stem from CH_3OH showing a computed proton solvation free energy 20-40 kJ mol^{-1} more exergonic than CH_3CN ,²⁷⁵⁻²⁷⁷ which influence the favorability of solvating reactive complexes within solvent clusters associated by proton shuttling. Among measurements obtained from Al-BEA, $\Delta H^\ddagger$ increase in proportion to ΔH_{ads} values between CH_3CN -rich and CH_3OH -rich solvents, which suggests similar structures and sets of covalent and non-covalent interactions stabilize the protonated forms of C_4H_8O and the ring-opening transition state.

In summary, the measurements in **Figures 4.5** and **4.6** give insight into differences in the prevalence of kinetic regimes with C₄H₈O-covered surfaces between Brønsted and Lewis acids and provide evidence that Lewis acids that bind C₄H₈O more strongly give greater ring-opening rates. The positive correlations of ΔH_{ads} and $\Delta H^\ddagger$ provide strong evidence that changes in the stability of ring-opening transition states drive changes in activation barriers.

4.3.4 Regioselectivities Depend on Active Metal and Intrapore Solvent Composition

The stabilities of transition states for epoxide ring-opening depend on interactions with active sites that alter the values of $\Delta H^{\ddagger,0}$ (and $\Delta S^{\ddagger,0}$) and interactions with surrounding solvent molecules that alter $\Delta H^{\ddagger,\varepsilon}$ (and $\Delta S^{\ddagger,\varepsilon}$), as described above. These interactions influence rates and barriers for epoxide ring-opening and can stabilize transition states that lead to distinct products differently, thereby influencing the regioselectivity of epoxide ring-opening. The distribution of regioisomers for a liquid phase reaction likely depends on both covalent interactions with catalytic functions and non-covalent interactions with surrounding molecules.

Regioselectivities for C₄H₈O ring-opening with CH₃OH over M-BEA were quantified using calculated rate ratios as follows:

$$\beta = \frac{r_{1M2B}}{r_{2M1B}} \quad (4.13)$$

where r_{1M2B} and r_{2M1B} represent the formation rates of 1M2B and 2M1B, respectively, and depend on reactant concentrations and product-specific rate constants for kinetically relevant steps ($k_{4,1C}$, $k_{4,2C}$, $k_{5,1C}$, $k_{5,2C}$) (**Scheme 4.2**). The form of β greatly simplifies the analysis that seeks to understand the origins of regioselectivities because the forms of rate expressions that describe r_{1M2B} and r_{2M1B} differ in only a few terms, regardless of the solvent composition or prevailing surface intermediates. The product isomers form by parallel pathways that diverge from a shared

pair of reactive intermediates; therefore, the regioselectivities depend only upon differences between the activation free energies to form each product ($\Delta G_{1M2B}^\ddagger$ and $\Delta G_{2M1B}^\ddagger$). To quantify r_{1M2B} and r_{2M1B} in **Equation 4.13**, we consider only conditions of C₄H₈O*-covered active sites and substitute product-specific values of k_4 to **Equation 4.5** (*vide supra*). The concentration terms cancel, and the equation for β simplifies to the form:

$$\beta = \frac{k_{4,1C}}{k_{4,2C}} = \exp\left(\frac{\Delta G_{2M1B}^\ddagger - \Delta G_{1M2B}^\ddagger}{RT}\right) \quad (4.14)$$

where $\Delta G^\ddagger$ values quantify the difference in free energies between the transition state and reference state for the kinetically relevant steps. Assuming the isomers form from common surface intermediates and fluid-phase reactants upon the same set of active sites, the expression for β simplifies further to reflect only the differences between the free energies of the transition states that give each isomer (i.e., $G_{1M2B}^\ddagger$ and $G_{2M1B}^\ddagger$):

$$\beta = \exp\left(\frac{G_{2M1B}^\ddagger - G_{1M2B}^\ddagger}{RT}\right) \quad (4.15)$$

Figure 4.7 reveals that β values under conditions of C₄H₈O*-covered active sites depend on both the composition of the reaction mixture and the active metal substituted in *BEA. For all metals, increases in [CH₃OH] lead to lower values for β (**Figure 4.7a**), while increases in [C₄H₈O] increase β . These trends demonstrate an increased preference to form the terminal alcohol (2M1B) when the solution contains greater numbers of hydrogen bonds per unit volume. The weak dependences (sublinear) of β on [CH₃OH] and [C₄H₈O] imply that these changes reflect composition-dependent values for $G_{1M2B}^\ddagger$ and $G_{2M1B}^\ddagger$. All M-BEA catalysts show values of β that approach unity in CH₃OH-rich solutions. Ti- and Zr-BEA give greater β that approach values of 3-4 at the lowest [CH₃OH] (< 0.1 M CH₃OH); however, Sn-BEA and Al-BEA show weaker increases of β to values between 1-2 at the lowest [CH₃OH]. **Figure 4.7b** demonstrates that β

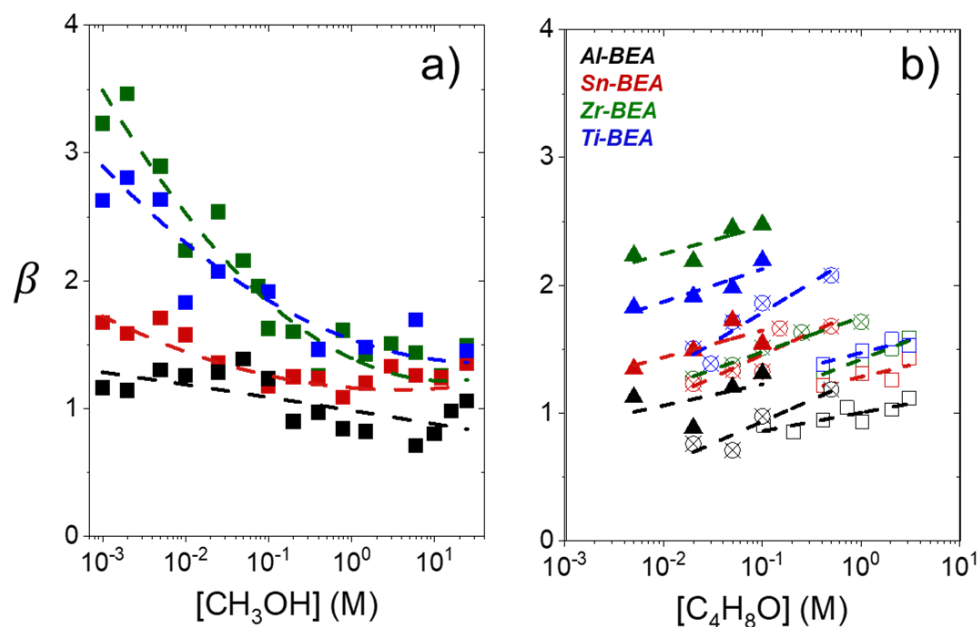


Figure 4.7. Values of β for $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH as a function of a) CH_3OH concentration (0.005 – 1 M $\text{C}_4\text{H}_8\text{O}$, $[\text{CH}_3\text{OH}]:[\text{CH}_3\text{CN}] = 0.2 - 100$, CH_3CN solvent, 308 K), and b) $\text{C}_4\text{H}_8\text{O}$ concentration at 0.01 M (solid triangles), 6 M (crossed circles), or 24.7 M CH_3OH (CH_3CN , 308 K) over Al- (black), Sn- (red), Zr- (green), and Ti-BEA (blue). All measurements were made under $\text{C}_4\text{H}_8\text{O}^*$ -covered active sites.

values increase gradually with $[\text{C}_4\text{H}_8\text{O}]$ across all M-BEA catalysts and a wide range of $[\text{CH}_3\text{OH}]$ (0.01 M, 6 M, and 24.7 M CH_3OH). **Figure 4.7** also shows that Al-BEA gives the lowest β values among M-BEA at nearly all $[\text{CH}_3\text{OH}]$ and $[\text{C}_4\text{H}_8\text{O}]$ values. Overall, the values in **Figure 4.7** span a range of 0.7 to 3.5. Previous studies examined $\text{C}_4\text{H}_8\text{O}$ ring-opening in neat (24.7 M) CH_3OH with homogeneous catalysts, where Lewis acidic aluminum triflate shows β values near 1.2^{57, 278} and sulfuric acid yields a β value near 1.1.²⁶⁷ Other studies have utilized zeolites for $\text{C}_4\text{H}_8\text{O}$ ring-opening in neat CH_3OH as well, in which Brønsted acid zeolites of varying pore size show β values from 0.8 to 1.3²⁶⁷ and Lewis acid zeolites with varying active metal give β values from 1.2 to 1.4.⁶³ The β values measured in neat CH_3OH range from 0.9 to 1.5 over M-BEA in **Figure 4.7**, which overlaps with the range of β values reported in previous studies. The introduction of CH_3CN as co-solvent provides opportunities to extend to higher β values. Differences in the β values between

M-BEA in **Figure 4.7** at an identical [CH₃OH] show that differences in the strength of the covalent interactions between the active metal and reactive species alter the preference towards the ring-opening products. Further, the dependence of β on [CH₃OH] for all M-BEA materials demonstrates that the non-covalent interactions between reactive species and solvent molecules also drive changes in regioselectivity.

Differences among β values (**Figure 4.7**) must originate from changes in the free energies of the transition states for 1M2B ($G_{1M2B}^\ddagger$) and 2M1B ($G_{2M1B}^\ddagger$) caused by subtle variations in their covalent and non-covalent interactions with the transition metal at the active site and the surrounding fluid. These contributions can be deconvoluted into activation enthalpies and entropies to form each product, which can be written as the differences in the enthalpy and entropy of the transition states because each product originates from a common reference state:

$$\Delta\Delta H^\ddagger = H_{2M1B}^\ddagger - H_{1M2B}^\ddagger \quad (4.16)$$

$$\Delta\Delta S^\ddagger = S_{2M1B}^\ddagger - S_{1M2B}^\ddagger \quad (4.17)$$

Figure 4.8 demonstrates that the active metal and solvent composition govern changes in $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ values between the ring-opening products, which lead to differences in regioselectivity across reaction conditions that result in C₄H₈O*-covered active sites (see **Section C10** for kinetics). **Figure 4.8a** shows the values of $\Delta\Delta H^\ddagger$ are negative across all combinations of catalysts and conditions, which demonstrates a consistent preference to enthalpically stabilize the transition state that leads to 2M1B (the terminal alcohol) with respect to that which forms 1M2B (terminal ether), despite regioselectivities toward 1M2B typically exceeding those for 2M1B (i.e., $\beta > 1$ in **Figure 4.7**). The positive correlation between values of $\Delta\Delta H^\ddagger$ and the average value of β (calculated from measurements extending from 298-323 K for each catalyst and solution composition) indicates that changes to the catalyst or solution composition that reduce the

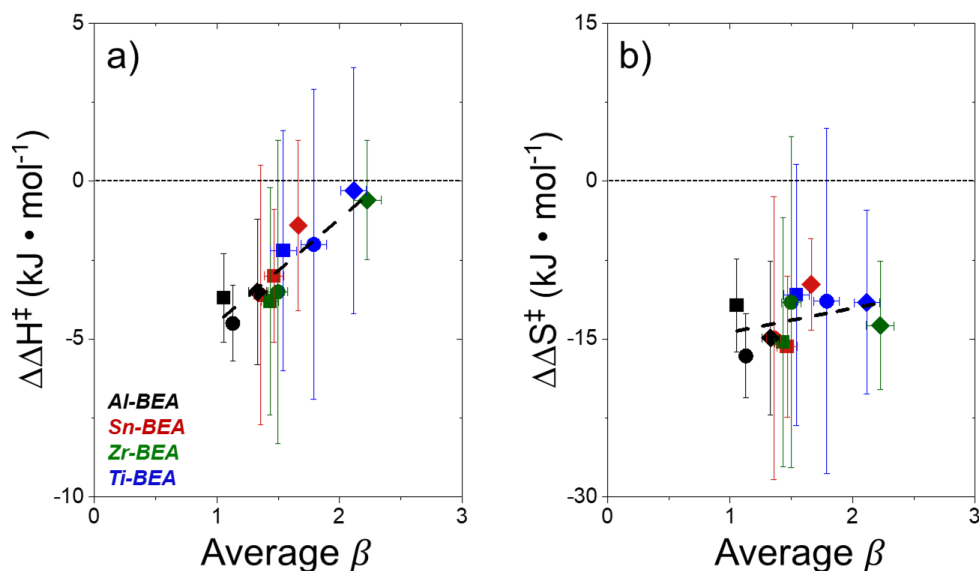


Figure 4.8. Values for a) $\Delta\Delta H^\ddagger$ and b) $\Delta\Delta S^\ddagger$ for C_4H_8O ring-opening and corresponding average values of β over Al- (black), Sn- (red), Zr- (green), and Ti-BEA (blue) from 298 – 323 K. Measurements were obtained in three distinct solution compositions with dilute CH_3OH (diamonds; 0.005 M C_4H_8O , 0.025 M CH_3OH in CH_3CN) and more concentrated CH_3OH solutions (squares; 0.25 M C_4H_8O , 6 M CH_3OH in CH_3CN ; circles; 1 M C_4H_8O , 24.7 M CH_3OH) with concentrations resulting in $C_4H_8O^*$ -covered active sites for all conditions (see Section C10).

magnitude of the enthalpic preference to form 2M1B result in greater regioselectivities to 1M2B. For a given metal, a CH_3CN -rich solution (0.025 M CH_3OH) generally provides a more positive $\Delta\Delta H^\ddagger$ and a greater average β than CH_3OH -rich solutions (6 and 24.7 M CH_3OH). While the consistent enthalpic preference to 2M1B may appear initially non-intuitive, **Figure 4.8b** reveals that the formation of the transition state for 2M1B incurs a consequential entropic penalty relative to that for 1M2B for all conditions ($-17 \text{ J mol}^{-1} \text{ K}^{-1} < \Delta\Delta S^\ddagger < -10 \text{ J mol}^{-1} \text{ K}^{-1}$). The preference to form 1M2B for nearly all points in **Figures 4.7** and **4.8** demonstrates that these differences between activation entropies for the two pathways surpass the enthalpic driving force. Significantly, the values of $\Delta\Delta S^\ddagger$ appear relatively insensitive to metal identity and solution composition; therefore, differences in regioselectivities across the span of conditions used here reflect the small but

distinguishable changes in $\Delta\Delta H^\ddagger$. These changes in $\Delta\Delta H^\ddagger$ plausibly stem from differences in $\Delta\Delta H^{\ddagger,0}$ from changing the active metal and $\Delta\Delta H^{\ddagger,\varepsilon}$ from changing the solvent composition.

Greater regioselectivities to terminal ethers (e.g., 1M2B) compared to terminal alcohols (e.g., 2M1B) during the ring-opening of terminal aliphatic epoxides, as demonstrated in **Figure 4.7**, appear frequently in prior studies and are commonly attributed to greater steric hindrance for nucleophilic attack at the more substituted C-atom of the oxirane ring that leads to the terminal alcohol.^{63, 104-106} This steric hindrance may correspond to the entropic penalty observed for 2M1B formation (**Figure 4.8b**) through a more negative $\Delta S^{\ddagger,0}$, which we speculate originates from a reduction in the freedom of motion of the transition state when CH₃OH coordinates at the more substituted C-atom, in closer proximity to the alkyl tail of the epoxide. An enthalpy-entropy compensation may lead to a lower $\Delta H^{\ddagger,0}$ value for 2M1B that partially offsets the entropic penalty. Despite these intrinsic structural contributions to regioselectivity, the dependence of $\Delta\Delta H^\ddagger$ values on active metal and solvent composition shows that altering the inner and outer sphere environment influences the stability of the transition states to form each product in different ways. Greater quantities of CH₃OH may lead to an increased preference to form 2M1B through hydrogen-bonding interactions that lower $\Delta H^{\ddagger,\varepsilon}$, which agrees with recent work that found adding hydrogen-bonding acceptors increases selectivities to the terminal alcohol for ring-opening over homogeneous borane complexes.⁸¹ **Figure C14** reveals that greater intrapore CH₃OH fractions correspond to lower β values, further supporting this interpretation.

While contributions from changes in [CH₃OH] may affect β , this does not immediately explain the differences in β between M-BEA. In particular, M-BEA materials show a large span of β at low [CH₃OH] (**Figure 4.7a**), with greater β values in Ti- and Zr-BEA than Al- and Sn-BEA. The intrinsic properties of each active site can likely influence the preference to form each

product through changes in $\Delta H^{\ddagger,0}$. Reported Mulliken electronegativities⁷¹ (see **Section C13**) indicate that Al- and Sn-incorporated zeolites may contain more electrophilic active sites than Ti- or Zr-incorporated materials, which may draw sufficient electron density from the epoxide oxygen atom to allow for easier cleavage of either C-O bond, leading to a more even split between the products. Alternatively, more electrophilic sites may preferentially stabilize the secondary partial positive charge that likely forms on the more-substituted epoxide carbon in the 2M1B transition state relative to the primary partial positive charge for 1M2B. The ionic environment induced by H^+ within Al-BEA may exacerbate this stabilizing effect and contribute to the consistently lowest β values in Al-BEA. Additionally, the formation of a protonated epoxide has been argued to promote the nucleophilic attack at the more substituted epoxide carbon,^{268, 270, 279-280} which also may increase the preference for the terminal alcohol in Al-BEA. Prior quantum chemical calculations reveal that protonation of the epoxide causes elongation of the weaker C-O bond between the more substituted carbon and epoxide oxygen atom, which promotes the attack at that carbon to form the terminal alcohol.²⁷⁰ Differences between the solvent structures that surround active sites comprised of distinct transition metals may also contribute to the differences in β across M-BEA by altering $\Delta H^{\ddagger,\varepsilon}$. **Figure C14** shows that the intrapore CH_3OH fraction changes among metals, which may contribute to differences in β . This result demonstrates that the choice of active metal not only influences G^0 values of reactive species through covalent interactions, but also can indirectly affect G^ε values by influencing the solvent structure surrounding active sites. Overall, the contributions from inner-sphere interactions (i.e., Lewis or Brønsted acidity altering standard state energies) may dominate at lower $[CH_3OH]$ values, but introducing sufficient quantities of CH_3OH may produce intrapore environments in which outer-sphere interactions (i.e.,

solvation altering excess energies) begin to dominate and lead to more similar β values among all materials in CH₃OH-rich solvents (**Figure 4.7a**).

Figures 4.7 and 4.8 demonstrate that changing the active metal and solvent environment within M-BEA leads to differences in regioselectivities by altering the stability of transition states to form the ring-opening products through changes in both G^0 and G^E values. Broadly, these findings indicate that inner-sphere and outer-sphere interactions warrant similar levels of consideration in the design of liquid-phase catalytic processes, as each class of interactions can influence rates and selectivities.

4.4 Conclusions

The active metal within zeolites and intrapore solvent environment alter rates and regioselectivities for epoxide ring-opening reactions through changes in the free energy of reactive species. Rates among Lewis acids proceed in the order Ti < Zr < Sn at all conditions, correlating with observed trends in activation enthalpies and reactant adsorption enthalpies and suggesting that rate differences are likely driven by differences in metal Lewis acidity. Activation enthalpies and entropies increase with increasing [CH₃OH] for all M-BEA, demonstrating that solvation influences the stability of transition states for ring-opening. Rate dependences on reactant concentrations suggest that kinetic regimes with a CH₃OH- or C₄H₈O-derived MARI exist over both Lewis and Brønsted acids. Still, the weaker dependence of rates on [C₄H₈O] over Al-BEA reflects different preferences to bind the reactants, which leads to differences in MARI trends. Comparisons among measured adsorption enthalpies demonstrate that inner-sphere effects (i.e., covalent and ionic interactions) among reactive species and active sites lead to significant differences in the stabilization of reactive intermediates; however, outer-sphere effects (i.e., non-

covalent interactions) can contribute to a similar extent to the energetics of binding events and reactions.

The regioselectivity to the terminal ether (β) decreases with increasing $[\text{CH}_3\text{OH}]$ and increases with greater $[\text{C}_4\text{H}_8\text{O}]$ over each M-BEA. Activation barrier differences between products show that these trends correspond to a greater enthalpic preference to form the terminal alcohol in CH_3OH -rich environments, providing evidence that differences in solvation between transition states contribute to regioselectivity changes. At low $[\text{CH}_3\text{OH}]$ ($< 0.01 \text{ M CH}_3\text{OH}$), Ti- and Zr-BEA deviate to significantly greater β values than Sn- or Al-BEA, whereas all materials collapse to similar β values at $[\text{CH}_3\text{OH}]$ above 1 M. These trends suggest that differences in intrapore solvent structure may dominate contributions to β in a CH_3OH -rich solvent, whereas the choice of active metal and acid type likely contributes more significantly in a CH_3CN -rich solvent.

The findings outlined here show that manipulating the inner- and outer-sphere environments within zeolite pores influences regioselectivities for epoxide ring-opening with CH_3OH , which likely extends to other alcohols or classes of nucleophiles (e.g., amines, thiols). Furthermore, these factors likely affect regioselectivities or other selectivities (i.e., chemoselectivity, enantioselectivity, and stereoselectivity) of many liquid-phase chemistries. The active metal in M-BEA zeolites²⁸¹ and the choice of solvent (water or CH_3OH)²⁸²⁻²⁸³ alter both chemoselectivities and stereoselectivities between the isomerization and epimerization of glucose over Sn-BEA zeolites. The choice of solvent also strongly influences the enantioselectivity of enzyme-catalyzed esterification reactions.²⁸⁴⁻²⁸⁷ Clearly, interactions with catalytic centers and surrounding solvent molecules play significant roles in the selectivities of liquid-phase catalysis and provide an exciting opportunity to tune reactions towards desired products and pathways.

CHAPTER 5

CONSEQUENCES OF PORE POLARITY AND SOLVENT STRUCTURES ON EPOXIDE RING-OPENING IN LEWIS AND BRØNSTED ACID ZEOLITES

5.1 Introduction

Zeolites serve as useful materials for catalysis and adsorption because the sub-nanometer pores within zeolites can stabilize guest molecules of selective shapes and sizes.^{115, 288} The zeolite pore walls stabilize these adsorbate molecules through nonspecific van der Waals interactions.^{40, 118} The introduction of a condensed intrapore phase adds further complexity to systems due to specific interactions (e.g., hydrogen bonds) between reactants, spectator molecules (e.g., solvent), and pore functions.^{122, 124-126} These interactions introduce thermodynamic nonidealities that alter the excess free energies (G^E) of adsorbates and transition states.³⁹ Altering the surface functions within zeolite pores leads to differences in the arrangement of solvent and reactant molecules near active sites, which provides an opportunity to influence the rates and selectivities of catalytic and separation processes.

The presence of intrapore silanol ((SiOH)_x) functions strongly affects both adsorption and catalysis in zeolites. Vega-Vila and Gounder demonstrated that hydrophobic Sn-incorporated zeolites stabilize 2-5 times greater densities of methanol molecules than hydrophilic materials, which contain (SiOH)_x groups that promote extended hydrogen-bonded structures of methanol (CH₃OH) that pack the pores less densely.¹³² In other reports, hydrophilic zeolites adsorb 5 to 100-fold more water (H₂O) than hydrophobic zeolites because (SiOH)_x groups stabilize networks of H₂O molecules.^{74, 134-135, 258} Pore polarity can also influence the selectivity of adsorption from binary mixtures, as Zhang et al. found that the selectivity for ethanol adsorption from ethanol and H₂O mixtures within hydrophobic pores exceeds that of hydrophilic pores by 5 times.¹³¹ The differences

(NaN_3), although the authors do not provide clear hypotheses for these trends.⁷⁹ Brunelli and co-workers found that the post-synthetic fluoride treatment of Sn-BEA increases the rate of epichlorohydrin ring-opening with CH_3OH by a factor of 2 compared to an untreated Sn-BEA material.¹⁰⁷ They attribute the rate increases to a decrease in the density of $(\text{SiOH})_x$ groups that leads to entropic gains for ring-opening. More recent work used site quantification, rate measurements, and ^{15}N NMR of adsorbed pyridine to show that Sn sites adjacent to $(\text{SiOH})_x$ nests provide greater turnover rates for epoxide ring-opening than Sn sites adjacent to a point SiOH defect.²⁹⁰ This shows that the $(\text{SiOH})_x$ structure near Sn atoms influences ring-opening kinetics, which may stem from differences in local solvent structure. Inspired by these findings, our group examined the mechanism of for ring-opening 1,2-epoxybutane ($\text{C}_4\text{H}_8\text{O}$) with CH_3OH over hydrophilic M-BEA zeolites and demonstrated that addition of an aprotic co-solvent (CH_3CN) increases the preference to form the terminal ether product (from ^{13}C attack).²⁹¹ Measurements of activation barriers provide evidence that differences in regioselectivity occur arise from differences in the solvent composition near active sites that affect the stability of transition states for each regioisomers to different extents. To summarize, the acid site and $(\text{SiOH})_x$ density significantly influence epoxide ring-opening and other liquid-phase chemistries. While industrial ring-opening processes commonly utilize Brønsted⁹²⁻⁹⁴ and Lewis^{59, 95-96} acid catalysts, the literature lacks comparisons of how these different acid types affect the solvent environment during liquid-phase catalysis. The ability of Brønsted acidic protons to detach from the zeolite framework and form ionic solvent clusters intuitively leads to different solvent structures near catalytic active sites than for Lewis acidic metal atoms that remain bound to the framework.^{74, 124, 199} Still, the effect of the interplay between $(\text{SiOH})_x$ functions and Lewis and Brønsted acid sites on the intrapore solvent environment in zeolites remains unclear. The strong influence of the

choice of solvent and zeolite hydrophilicity shown in previous ring-opening studies underscores the importance of establishing these connections.

Here, we reveal the impact of varying the $(\text{SiOH})_x$ density of Lewis acidic Zr- and Brønsted acidic Al-BEA zeolites on the intrapore solvent environment and, consequently, rates and regioselectivities of $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH in CH_3CN co-solvent. Despite apparently identical reaction mechanisms, turnover rates over $(\text{SiOH})_x$ -rich Zr-BEA (Zr-BEA-OH) exceed those over a $(\text{SiOH})_x$ -poor material (Zr-BEA-F) by ~ 10 times. In contrast, turnover rates over Al-BEA-OH and Al-BEA-F materials differ by less than two times. Measurements of liquid and vapor solvent uptake provide evidence that Zr-BEA-OH adsorbs greater quantities of CH_3OH and promotes greater intrapore ratios of CH_3OH to CH_3CN than Zr-BEA-F, while Al-BEA-OH and Al-BEA-F show more similar solvent uptakes. The Al-BEA materials show nearly identical activation enthalpies and entropies for ring-opening and adsorption enthalpies for $\text{C}_4\text{H}_8\text{O}$, which likely lead to similar rates between the catalysts. In contrast, Zr-BEA-OH shows more positive activation enthalpy, entropy, and $\text{C}_4\text{H}_8\text{O}$ adsorption enthalpy values than Zr-BEA-F. This trend provides strong evidence that the entropic gain from the disruption of hydrogen-bonded solvent molecules in the Zr-BEA-OH pores leads to greater ring-opening rates than Zr-BEA-F. Reaction regioselectivities depend strongly on the active metal choice and solvent composition but weakly on $(\text{SiOH})_x$ density, demonstrating that pore polarity influences rates and regioselectivities differently. Cumulatively, these findings show that the intrapore solvent structure depends intimately on the $(\text{SiOH})_x$ density and active site structure within the *BEA pores, which provides opportunities to control the kinetics and thermodynamics of catalytic reactions (i.e., epoxide ring-opening).

5.2 Methods and Materials

5.2.1 Catalyst Synthesis

M-BEA-OH (M = Al, Zr) were prepared by post-synthetic modification of a commercial Al-BEA material (TOSOH, lot no. 94HA6X02Y; Si/Al = 20). For Zr-BEA-OH, the commercial Al-BEA was treated in refluxing HNO₃ (Macron Chemicals, 68 – 70 wt%, 20 cm³ g⁻¹) at 433 K for ~24 h to remove Al atoms from the *BEA framework by forming soluble (AlNO₃)₃ complexes. The HNO₃ treatment was repeated three times to give a thoroughly dealuminated material denoted Si-BEA-OH (Si:Al > 1200 from EDXRF, > 3500 from ICP-OES, *vide infra*). Between acid treatments, the catalyst sample was washed with deionized H₂O (18.2 MΩ cm, Elga Purelab Flex 2, 50 cm³ g_{zeolite}⁻¹) and recovered with vacuum filtration. For Al-BEA-OH, the parent Al-BEA material was treated in dilute HNO₃ (1 M) for ~3 h to partially remove Al atoms from the framework. After the acid treatments, the dealuminated *BEA materials were loaded into quartz boats and placed in a three-zone furnace (Applied Test Systems, 3210), which was heated to 823 K (5 K min⁻¹) in flowing air (200 cm³ min⁻¹; Airgas, Ultra Zero grade) and held at 823 K for 6 h to remove organic residues. The heat treatment resulted in white powder Al-BEA-OH and Si-BEA-OH samples.

Zr-BEA-OH was synthesized by the liquid-phase incorporation of Zr atoms into the Si-BEA-OH material, based on previously reported procedures.^{30, 74} Si-BEA-OH was first heated in a round-bottom flask under vacuum (< 5 Pa, 473 K) for 2 h to create a moisture-free environment. A rubber seal was then removed from the sidearm of the flask, and isopropanol solvent (C₂H₇OH, Fisher Chemicals, 20 cm³ g_{zeolite}⁻¹) was poured into the flask under a high flow of Ar (500 cm³ min⁻¹) to minimize the adsorption of moisture from the air. Zr atoms were incorporated by then adding solid ZrCl₄ powder (Sigma-Aldrich, ≥99.9% trace metals basis) to the Si-BEA-OH and

solvent mixture under flowing Ar ($500\text{ cm}^3\text{ min}^{-1}$). The rubber seal was placed back onto the flask sidearm, and the mixture was then heated and left overnight under an inert atmosphere (373 K, refluxing solvent, $\sim 16\text{ h}$, $50\text{ cm}^3\text{ min}^{-1}$ Ar, Airgas, Ultra High Purity). The resulting material was recovered by vacuum filtration and was heated to 823 K (5 K min^{-1}) in flowing air ($200\text{ cm}^3\text{ min}^{-1}$) and held at 823 K for 6 h, resulting in a white powder Zr-BEA-OH sample.

M-BEA-F (M = Al, Zr) were synthesized by adapting previously published procedures for hydrothermal synthesis of Ti-BEA-F materials.^{136, 150} For each M-BEA-F, 20 g of tetraethylammonium fluoride hydrate (TEAF, Sigma-Aldrich, 98%) was dissolved in 32.1 cm^3 of deionized H_2O ($18.2\text{ M}\Omega\text{ cm}$, Elga Purelab Flex 2) in a polypropylene container. Next, 47.4 cm^3 of tetraethylorthosilicate (TEOS, Sigma-Aldrich, $>98\text{ wt}\%$) was added, and the mixture was stirred for 30 min at room temperature. Either 0.455 g of aluminum (III) isopropoxide ($\text{Al}[\text{OCH}(\text{CH}_3)_2]_3$, AIPO, Sigma-Aldrich, $\geq 98\%$) or 0.921 cm^3 of zirconium (IV) n-propoxide in n-propanol ($\text{Zr}[\text{OCH}(\text{CH}_3)_2]_4$, ZIPO, Alfa Aesar, 70 wt% in n-propanol) was added, and the solutions were covered and stirred for an additional 16 h to produce white, opaque homogeneous solutions. The covers were removed, and the mixtures were stirred for 12 – 24 h to evaporate the alcohols formed from the hydrolysis of AIPO or ZIPO (n-propanol) and TEOS (ethanol). The mass of alcohols formed was estimated by assuming complete and stoichiometric hydrolysis of all AIPO, ZIPO, and TEOS added. The solutions were left uncovered to allow the alcohols to evaporate until the mass of the solutions decreased by an amount equal to 115% of the calculated mass of the alcohols to increase the likelihood of complete evaporation of these alcohols. The alcohols are assumed to evaporate preferentially before water based on their greater volatility. A mass of deionized H_2O equivalent to the difference between the total mass evaporated (42 – 47 g) and the calculated mass of alcohols formed (40 – 41 g) was added to account for the H_2O lost during evaporation. The

evaporation procedure yielded gels with an approximate molar composition of 1 Si:0.006 Al or Zr:0.56 TEAF:8.89 H₂O. The gels were subsequently transferred to Teflon liners (Parr Instruments, 125 cm³, Model 4748). A small amount of Si-BEA-OH seeds (3% by mass relative to SiO₂ in the synthesis gel) from a previous synthesis was added to each gel to promote crystallization. The Teflon liners were loaded into a stainless-steel autoclave (Parr Instruments, 125 cm³, Model 4748) and heated to 413 K at dynamic conditions (60 rpm) in a convection oven (Yamato, DKN602C) for 22 days. The resulting materials were recovered by centrifugation, washed with H₂O, and dried in an oven for 12 h at 343 K. The dried solids were heated at 5 K min⁻¹ to 823 K in flowing air (200 cm³ min⁻¹) and held at 823 K for 6 h to produce white powder Al-BEA-F and Zr-BEA-F samples.

5.2.2 Catalyst Characterization

The crystallinities of the M-BEA materials were confirmed with an X-ray diffractometer (Bruker, D8 Advance) with Cu K α radiation under ambient conditions. The M-BEA powders were loaded into a polypropylene sample holder for the measurements. The diffractograms of M-BEA-OH (**Appendix Figure D1a**) and M-BEA-F (**Figure D1b**) match previously reported diffraction patterns for *BEA,¹⁵¹ supporting that all M-BEA possess the *BEA framework. Furthermore, the patterns for M-BEA do not possess strong features in the characteristic peak locations for the respective metal oxides (**Figure D1c**), supporting that negligible quantities of each incorporated metal exist in metal oxide form. Metal oxide samples were purchased commercially and used as received: γ -Al₂O₃ (US Research Nanomaterials, Inc., 20 nm, 99%) and ZrO₂ (Sigma-Aldrich, 5 μ m 99% trace metals basis).

The metal contents of the M-BEA samples were calculated with inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer, Optima 8300) measurements

carried out by staff scientists at the Microanalysis Laboratory at the University of Illinois. The measurements confirm that Zr-BEA-OH and Zr-BEA-F contain negligible quantities of Al (Si:Al ~ 4000). Each Zr-BEA possesses similar Si:Zr values (131 for Zr-BEA-OH, 103 for Zr-BEA-F), and each Al-BEA shows a similar Si:Al ratio (70 for Al-BEA-OH, 76 for Al-BEA-F). Reported turnover rates are calculated by normalizing rates with the metal loadings determined by ICP-OES. Metal loadings and Si:Al ratios for each zeolite are shown in **Table 5.1**.

The dispersity of the M atoms in the M-BEA catalysts was probed with diffuse reflectance UV-visible (DRUV-vis) spectroscopy. M-BEA samples were mixed and finely ground with magnesium oxide (MgO, Sigma-Aldrich, 99.9995%) at a MgO:M-BEA mass ratio of 10:1. MgO was used as a background for measurements. The total reflectance sample spectra were obtained with a UV-vis spectrophotometer (Varian, Cary 5G) under ambient conditions. The band gap energies (**Table 5.1**) were determined by extrapolating the linear portion of the Tauc plots ($[F(R) \cdot hv]^{1/2}$) to the horizontal axis to determine the minimum energy of photons adsorbed (eV) (**Figure D2**). The band gap of ZrO₂ was measured in a similar manner as the M-BEA materials (**Figure D2**). Each Zr-BEA shows a greater band gap than ZrO₂, supporting that the Zr atoms are substituted within the framework at dispersed locations. Both Al-BEA materials and Al₂O₃ show very weak or no reflectance features, likely because the band gap of each material exceeds the scan range of the spectrophotometer. Nevertheless, the low weight loadings of each Al-BEA (Si:Al ~ 60-70) and the unfavorable nature of Al-O-Al pairs (Loewenstein's rule²⁹²) support that Al atoms are well dispersed within the *BEA framework in Al-BEA-OH and Al-BEA-F.

The coordination of metal atoms within M-BEA was examined using Raman spectroscopy. *Ex situ* Raman spectra were measured at ambient conditions on pressed catalyst pellets with a Raman spectrometer (Renishaw, InVia) equipped with a 532 nm laser. The accumulation time was

Catalyst	M wt% ^a	Si:M ^a	Si:Al ^a	Band Gap (eV) ^b	Φ_{IR} ^c	Active Metal (%) ^d
Al-BEA-OH	0.63	69	69	--	1.44	97 $\pm$ 4
Al-BEA-F	0.72	61	61	--	0.19	92 $\pm$ 3
Zr-BEA-OH	1.03	131	3980	5.8	1.41	104 $\pm$ 7
Zr-BEA-F	1.44	103	4090	5.7	0.21	96 $\pm$ 2

Table 5.1. Characterization of Synthesized M-BEA.

^aMeasured with ICP-OES. ^bExtracted from leading edge of Tauc plot from DRUV-vis. ^cCalculated from infrared transmission spectra of dehydrated M-BEA samples. ^dMeasured from *in situ* 1,2-diphenylethylenediamine site titrations.

20 s per scan, and each Raman spectra was calculated by averaging 10 scans. The power density at the sample was approximately 2 mW μm^{-2} (Gentec-EO, PRONTO-SI). The Raman spectra for each M-BEA-OH (**Figure D3**) and M-BEA-F (**Figure D4**) lack discernible features in the regions where the respective metal oxides show strong features, indicating the absence of M-O-M bonds. Together with the high band gap energies (**Table 5.1**), these spectra support that the M atoms in each material predominantly reside in tetrahedral positions within *BEA.

The relative density of (SiOH)_x groups within M-BEA was measured with infrared spectroscopy. A background spectrum was first taken with an empty transmission cell configured with CaF₂ windows. The cell was loaded into a Fourier-transform infrared spectrometer (Bruker, Vertex 70) equipped with a liquid N₂-cooled HgCdTe detector, as described previously.²¹⁶ The cell was connected to a temperature controller and gas manifold, then heated to 573 K (~5 K min⁻¹) and held for 2 h in flowing He (50 cm³ min⁻¹, 99.997%, Airgas) to desorb volatile compounds and H₂O. The background spectrum was then collected at 573 K (128 scans, 4 cm⁻¹). Each M-BEA was pressed into a pellet and loaded into the transmission cell. The cell was loaded into the spectrometer, and the spectra for M-BEA (**Figure D5**) were obtained in the same manner as the background measurement. The vibrational features on the FTIR spectra at 1800-2100 cm⁻¹ and 3300-3750 cm⁻¹ represent the Si-O-Si overtones¹⁵⁴ of the *BEA framework and $\nu(\text{O-H})$ of (SiOH)_x.

groups,¹⁵⁵⁻¹⁵⁶ respectively. The broad features from 3300-3700 cm⁻¹ arise from SiOH defects containing multiple hydroxyl moieties within (SiOH)_x groups. The sharper feature at ~3750 cm⁻¹ represents isolated SiOH defects that do not interact with other SiOH.¹⁵⁵⁻¹⁵⁶ The ratio of the areas for $\nu(\text{O-H})$ and $\nu(\text{Si-O-Si})$ at 1865 and 2000 cm⁻¹ gives a relative measure of SiOH density defined as Φ_{IR} (**Equation 5.1**) in each M-BEA. The isolated SiOH feature is excluded from $A_{\nu(\text{O-H})}$ in **Equation 5.1**. The $\nu(\text{O-H})$ region was deconvoluted into multiple peaks (see **Figure D6**), and the isolated SiOH peak area was subtracted from the combined area of the $\nu(\text{O-H})$ region.

$$\Phi_{IR} = \frac{A_{\nu(\text{O-H})}}{A_{\nu(\text{Si-O-Si})}} \quad (5.1)$$

Values of Φ_{IR} (**Table 5.1**) indicate that the M-BEA-OH materials contain greater densities of (SiOH)_x groups than M-BEA-F. Calculation estimates based on the quantity of Al removed and M incorporated indicate that the M-BEA-OH materials contain 2.1 – 2.6 (SiOH)_x (unit cell)⁻¹ (see **Section D1.5**). M-BEA-F were synthesized hydrothermally without Al present, so we cannot make the same calculation of (SiOH)_x (unit cell)⁻¹. However, previously established trends⁷³ between Φ_{IR} and (SiOH)_x suggest that the M-BEA-F samples synthesized for this work ($\Phi_{IR} \sim 0.20$, **Table 5.1**) contain fewer than 0.1 (SiOH)_x per unit cell.

The presence of Lewis and Brønsted acid sites in M-BEA was characterized by infrared spectra of adsorbed pyridine (C₅H₅N, Sigma-Aldrich, >99%) and deuterated acetonitrile (CD₃CN, Cambridge Isotope Laboratories, 99.8% D atom). The catalysts were pelletized, loaded into the spectrometer, and pre-treated at 573 K, as described above. The cell was then cooled to either 393 K (C₅H₅N) or 303 K (CD₃CN). A background spectrum was taken before flowing the adsorbates. C₅H₅N or CD₃CN were then introduced with a syringe pump (KD Scientific, Legato) and vaporized into a stream of flowing Ar (20 cm³ min⁻¹) within the heated gas-transfer lines. Reported

spectra were collected after the absorbance features had reached a steady state. The spectra and a detailed analysis of the results are provided in **Section D1.6**.

The structure of Al atoms within the Al-BEA materials was also examined with *ex situ* ^{27}Al NMR spectroscopy. The Al-BEA samples were loaded into a zirconia-based rotor (Bruker, 4 mm, kel-f cap). The rotor was then loaded into an NMR spectrometer (Bruker AVIII 400), where spectra were collected at ambient temperature. The spectra were referenced to aqueous Al^{3+} at 0 ppm. The reported spectra are an average of 1024 scans, with a 0.6 μs pulse time and 1 s relaxation time. **Figures D9 and D10** reports the ^{27}Al NMR spectra for the bare Al-BEA samples and Al-BEA impregnated with $\text{C}_5\text{H}_5\text{N}$. These spectra provide insight into the structure of Al atoms with and without adventitious H_2O present.

The morphology of the M-BEA materials was examined with scanning electron microscopy (SEM). The samples were dispersed on double-sided carbon tape attached to an SEM holder. A sputter coater (Emitech, K575) was then used to coat the materials with an Au-Pd alloy. Au-Pd provides a conductive surface layer that inhibits surface charging and improves the SEM signal quality. The sample holder was loaded into the microscope (Hitachi-S 4800) and degassed before taking images. The micrographs were obtained at a working distance of 10 mm with an accelerating voltage of 5 kV. The SEM images for all M-BEA materials are displayed in **Figure D11**.

Collectively, the characterization of the M-BEA materials gives strong evidence that each material possesses a crystalline *BEA framework containing similar densities of $(\text{SiOH})_x$. All M-BEA lack spectroscopically detectable quantities of the respective metal oxides and plausibly contain atomically dispersed metal atoms incorporated at framework positions.

5.2.3 Epoxide Ring-Opening Turnover Rate Measurements

Turnover rates for 1,2-epoxybutane ($\text{C}_4\text{H}_8\text{O}$, TCI Chemicals, >99.0%) ring-opening with methanol (CH_3OH , Sigma-Aldrich, $\geq 99.9\%$) in acetonitrile (CH_3CN , Fisher Chemical, HPLC Grade) solvent were measured in three-necked round-bottom flasks with magnetic stirring (700 rpm). Benzene (Sigma-Aldrich, thiophene-free, >99%) was included in the reaction mixture as an internal standard. The flasks were submerged in a temperature-controlled bath containing either H_2O (298 – 318 K) or silicone oil (Sigma-Aldrich, viscosity 100 cSt) (323 – 328 K) on a hot plate (Corning, PC-420D). The flasks were also connected to reflux condensers to prevent evaporative losses. The reaction mixture was stirred for 0.5 h at the reaction temperature before taking an initial aliquot ($\sim 0.5 \text{ cm}^3$) to determine the initial concentration of $\text{C}_4\text{H}_8\text{O}$ and the ring-opening products, 1-methoxy-2-butanol ($\text{C}_5\text{H}_{12}\text{O}_2$, 1M2B) and 2-methoxy-2-butanol ($\text{C}_5\text{H}_{12}\text{O}_2$, 2M1B). M-BEA ($\sim 15\text{-}60 \text{ mg}$) was then added to initiate the reaction, and aliquots were taken as a function of time with a syringe equipped with a polypropylene filter (Tisch Scientific, $0.22 \mu\text{m}$) to separate the sample solution from the catalyst. Elution times and sensitivity factors were determined using commercially obtained samples of $\text{C}_4\text{H}_8\text{O}$, CH_3OH , benzene, 1M2B (TCI Chemicals, >93.0%), and 2M1B (TCI Chemicals, >98.0%) (**Section D2**). The concentrations of $\text{C}_4\text{H}_8\text{O}$, benzene, and ring-opening products were quantified with a gas chromatograph (GC) (Agilent, 6850) equipped with a liquid autosampler, flame ionization detector, and polysiloxane column (HP-1, Agilent, 19091Z-115E).

Turnover rates were measured in CH_3CN co-solvent to allow for control of both $\text{C}_4\text{H}_8\text{O}$ and CH_3OH concentrations ($[\text{C}_4\text{H}_8\text{O}]$, $[\text{CH}_3\text{OH}]$, where $[x]$ denotes the concentration of species x). Measurements were also made in neat CH_3OH (24.7 M CH_3OH). The reaction yields two possible products, 1-methoxy-2-butanol (1M2B, a terminal ether) or 2-methoxy-1-butanol (2M1B,

a terminal alcohol) (see **Scheme 5.1** above). Initial turnover rate values were calculated by fitting turnover numbers (moles of product per moles of active metal) as a function of time to a second-order polynomial with the turnover rate fixed at zero at time equal to zero, then determining the derivative at time equal to zero. All reported turnover rates were measured at differential conversion (<10%) with an uncertainty of ~10%, as demonstrated with replicated measurements. The carbon balance closes within 90 – 110% for all reported measurements. Furthermore, the carbon selectivity to the desired 1M2B and 2M1B products exceeds 90% across all measurements. Two minor side products appear at similar GC retention times to the ring-opening products. While these products have not been identified, plausible structures include dimethoxybutane ($\text{C}_6\text{H}_{14}\text{O}_2$) from the reaction of either ring-opening product with CH_3OH , dibutyl ether from the reaction of two $\text{C}_4\text{H}_8\text{O}$ molecules, or 1,2-butylene carbonate from the reaction of $\text{C}_4\text{H}_8\text{O}$ with atmospheric CO_2 . Each ring-opening product may also react with a second epoxide molecule to form an oligomerization product, although we expect minimal contribution from these pathways at differential conversion.

Hot filtration experiments were conducted to determine if the metal atoms or catalytic protons leach from the *BEA framework during the batch reactions and form homogeneous complexes active for ring-opening. Briefly, a large aliquot (~4 cm^3) was taken ~600-900 s after adding the catalyst, filtered with a polypropylene filter (Tisch Scientific, 0.22 μm) to separate the catalyst, then transferred into a scintillation vial (20 cm^3 , Trident Technology). The vial was transferred to a hot plate, which was pre-heated to 308 K and stirred at 700 rpm. Aliquots (~0.5 cm^3) were taken from the vial as a function of time. **Figure D14** in **Appendix Section D3** shows that the product concentrations change negligibly after filtering out the solid catalyst but continue to increase in the presence of the catalyst. Furthermore, a dealuminated *BEA material (Si-BEA-

OH) shows product formation rates per gram of catalyst at least 13 times less than all M-BEA materials (**Table D5**), demonstrating that (SiOH)_x and Si-O-Si functions do not contribute significantly to the measured ring-opening turnover rates over M-BEA. These experiments provide strong evidence that the ring-opening of C₄H₈O with CH₃OH proceeds solely at active sites within the *BEA framework.

Mass transfer constraints prevent the measurement of intrinsic kinetic behavior, thus corrupting comparisons between catalysts and convoluting the interpretation of apparent rate measurements.²⁶³ Therefore, we conducted experimental measurements to detect these potential artifacts and select optimal reaction conditions using methods recently described.²⁹³ The conditions used for rate measurements here avoid internal and external mass transfer constraints because turnover rates do not depend on the loading of metal atoms for all materials within the range of loadings studied (**Figure D15** in **Section D3**). These measurements demonstrate that all M-BEA materials satisfy the Madon-Boudart criterion²⁶³ and are free of mass transfer artifacts. In addition, turnover rates exhibit combinations of first- and zero-order dependencies on the concentrations of C₄H₈O and CH₃OH at limiting conditions (**Section 5.3.1**).¹⁵⁹ A mass-transfer limited material would show a sub-linear dependence on reactant concentrations because the mean concentration of the reactants throughout the pores would not depend linearly on the fluid phase reactant concentrations for a zero-order reactant.

The percentage of active metal atoms within each M-BEA was probed using *in situ* site titration experiments with (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine (DPED, Sigma-Aldrich, 97%). Briefly, DPED was added to a mixture of CH₃CN, benzene, CH₃OH, and M-BEA at a ratio of DPED to metal atoms ranging from 0 to 1.5. The reaction flask was stirred for 0.5 h at 308 K to allow DPED to bind to the active sites before reaction. The reaction was then initiated by adding

C₄H₈O, after which an aliquot was quickly taken at ~0.004 h. Further aliquots were then taken as a function of time, as described above. The number of active sites in the materials was quantified by fitting a line to the linear portion of the titration curves shown in **Section D4**. All materials contain more than 90% active metal atoms, as shown in **Table 5.1**.

The DPED titration measurements for Zr-BEA-F suggest that a minor fraction (<5%) of Zr sites may be inactive for C₄H₈O ring-opening. While no extraframework Zr features (i.e., ZrO₂) are observed by Raman or DRUV-Vis, we cannot exclude the possibility that a small percentage of ZrO₂ may exist in Zr-BEA-F and do not catalyze C₄H₈O ring-opening. In contrast, the minor fraction of inactive Al sites observed in the titrations for Al-BEA-OH and Al-BEA-F aligns with octahedral Al features present in the ²⁷Al NMR spectra (**Figures D9 and D10**). Based on the peak area ratios of tetrahedral to octahedral Al in the presence of C₅H₅N, the ²⁷Al NMR spectra predict 4% and 10% of Al atoms exist as octahedral species in Al-BEA-OH and Al-BEA-F, respectively. Adding C₅H₅N removes residual H₂O that forms hydrated octahedral Al species, which provides a more accurate report of the structure of Al atoms than ²⁷Al NMR spectra of the bare zeolites (see **Section D1.7**). The greater intensity of the octahedral NMR feature and the presence of a Lewis acid Al feature in the CD₃CN FTIR spectra for Al-BEA-F also both agree with the lower active metal percentage in Al-BEA-F (92%) than Al-BEA-OH (97%). These three techniques provide strong evidence that each Al-BEA material contains a minor fraction of extraframework, octahedral, Lewis acidic Al species that do not catalyze C₄H₈O ring-opening. We do not believe the presence of these extraframework species convolutes the kinetics in this manuscript because they comprise < 10% of metal sites in all materials. Reported rates are normalized by the number of active metal atoms calculated from the DPED titrations for each material.

5.2.4 Liquid-Phase and Gas-Phase Adsorption Measurements

The mole fraction of CH₃OH in the pores of M-BEA was estimated via liquid-phase uptake measurements from CH₃CN. First, varying concentrations of CH₃OH were mixed with CH₃CN in a 5 cm³ solution, from which an initial aliquot was taken. ~100 mg of M-BEA was then added to the CH₃OH and CH₃CN solution, after which the solution was mixed for 2 h at a stir rate of 250 rpm and a temperature of 308 K. The catalyst and solution were left in contact for 2 h to ensure that the adsorption of CH₃CN and CH₃OH had reached equilibrium, after which a final aliquot was taken. The concentrations of CH₃CN and CH₃OH in the initial and final aliquots were quantified with GC. The intrapore solvent compositions, shown in **Figure 5.4a**, were estimated from the amount of solution absorbed by M-BEA and the difference in the liquid phase composition before and after mixing the solution with the catalyst.

The effect of (SiOH)_x density on gaseous CH₃OH (293 K) and CH₃CN (296 K) uptake was determined from gas-phase adsorption isotherms (Micromeritics, 3Flex). The M-BEA samples were pelletized and sieved to retain particles from 100 – 250 μm in diameter. The samples were degassed under dynamic vacuum prior to adsorption ($< 7 \times 10^{-4}$ Pa, 673 K, 3 h). The isotherms are presented below in **Figures 5b** and **5c**.

5.2.5 Liquid-Phase Adsorption Enthalpies for Reactants

The heat released upon adsorption of C₄H₈O and CH₃OH was measured with an isothermal titration calorimeter (ITC) (TA Instruments, NanoITC) equipped with sample and reference cells. A brief cleaning procedure was performed to prepare the sample and reference cells for each experiment. First, 500 cm³ of a cleaning solution consisting of 2 volume % detergent in DI H₂O (18.2 MΩ cm, Elga Purelab Flex 2) was flowed through the cell at room temperature. The sample cell was then rinsed with 1000 cm³ of DI H₂O. The sample cell and reference cell were then filled

with 350 μL of H_2O (maximum cell volumes are 500 μL). A 50 μL ITC syringe was filled with H_2O , then loaded into the instrument. A subsequent electrical calibration used sequential pulses to determine the heat released from a calibrated Pt resistor. Finally, pure DI H_2O was injected into DI H_2O to ensure the sample cell was clean enough to begin experiments. The cell was assumed to be clean when the H_2O - H_2O injection released negligible amounts of heat ($\pm 3 \mu\text{J}$ for each injection of 1 μL). The cleaning procedure was repeated if the H_2O - H_2O injection did not give sufficiently low heat rates.

In a typical experiment, a slurry of M-BEA (20-40 mg) in CH_3CN or CH_3OH was titrated by $\text{C}_4\text{H}_8\text{O}$ or CH_3OH (0.005 M) diluted in the same solvent used for the slurry. The mass of M-BEA in the sample cell was calculated by taking the difference between the mass added to the slurry and the mass remaining upon evaporation of the residual slurry after loading the cell. The titrations were carried out at 308 K with a stirring rate of 250 rpm. The sample cell was filled with 350 μL of M-BEA and solvent, while the reference cell was filled with 350 μL of solvent. The enthalpies of adsorption were calculated by averaging the integrated heats released upon adsorption of the titrant molecules to M-BEA sites from a 1 μL injection of titrant at low coverages ($< 0.25 \text{ mol titrant (mol M)}^{-1}$). The heat released in this low coverage regime remains approximately constant, suggesting that the calculated enthalpies represent the isosteric adsorption enthalpies for each titrant.⁷³

5.3 Results and Discussion

5.3.1 Brønsted and Lewis Acid Zeolites Show Distinct Ring-Opening Rate Dependences on Reactant Concentrations and $(\text{SiOH})_x$ Density

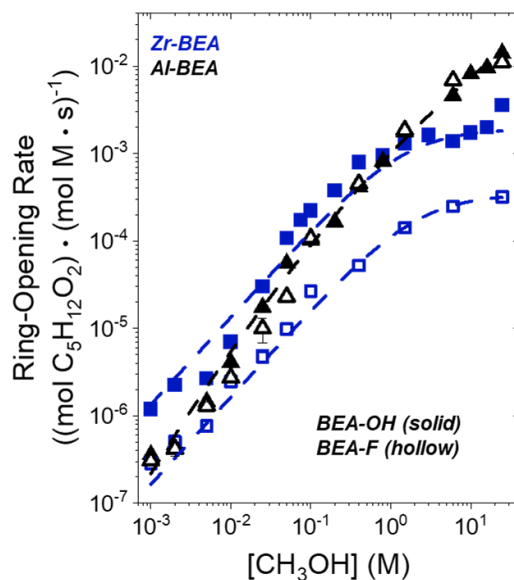


Figure 5.1. Turnover rates for $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH as functions of CH_3OH concentration over hydrophilic (solid points) and hydrophobic (hollow) Zr- (blue) and Al-BEA (black) materials (0.005 M $\text{C}_4\text{H}_8\text{O}$, CH_3CN solvent, 308 K).

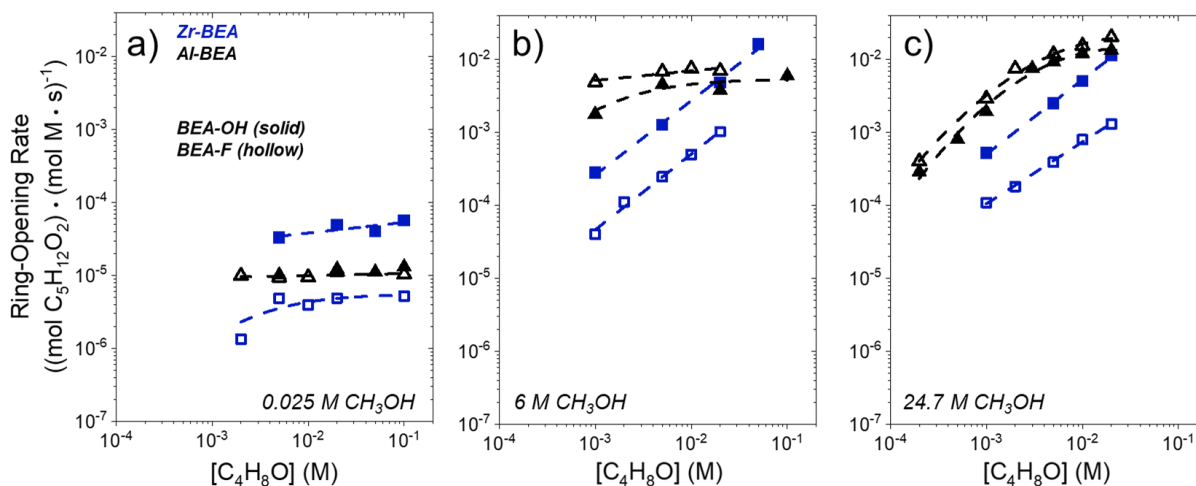
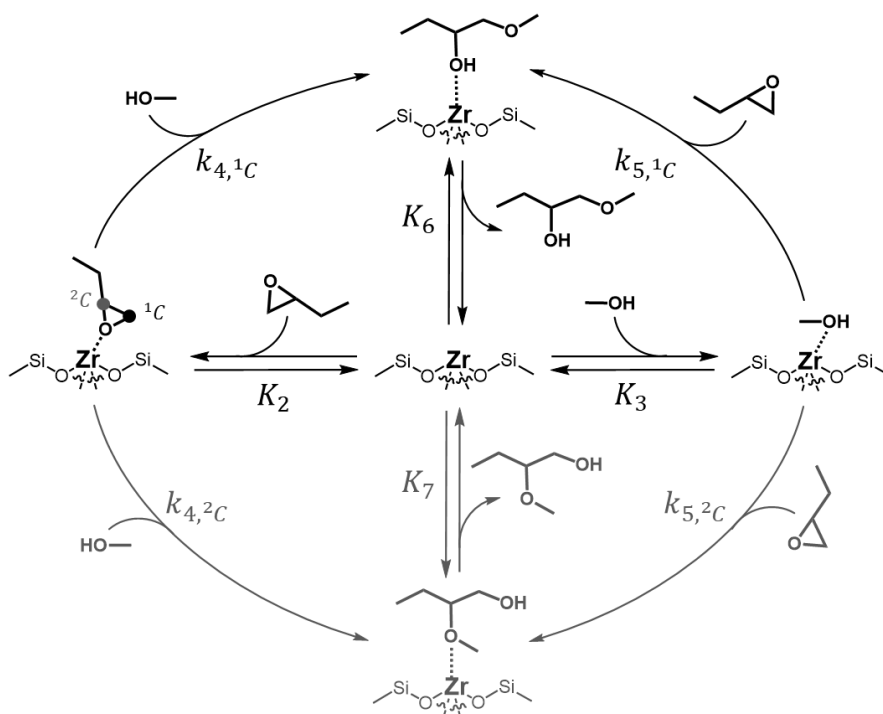


Figure 5.2. Turnover rates for $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH as functions of $\text{C}_4\text{H}_8\text{O}$ concentration at a) 0.025 M CH_3OH , b) 6 M CH_3OH , or c) neat (24.7 M) CH_3OH (CH_3CN solvent, 308 K) over hydrophilic (solid points) and hydrophobic (hollow) Zr- (blue) and Al-BEA (black) materials.

Turnover rates for C_4H_8O ring-opening depend on the concentrations of the reactants and products present, which determine the coverages of species on the active sites within M-BEA. **Figures 5.1** and **5.2** show that rates depend differently on $[CH_3OH]$, $[C_4H_8O]$, and $(SiOH)_x$ density between Al-BEA and Zr-BEA materials. The $(SiOH)_x$ -dense Brønsted acid (Al-BEA-OH) shows nearly identical turnover rates to the $(SiOH)_x$ -poor analog (Al-BEA-F) at all conditions. In contrast, ring-opening turnover rates over Zr-BEA-OH exceed rates over Zr-BEA-F by approximately an order of magnitude across the range of $[CH_3OH]$ and $[C_4H_8O]$ examined. Despite Zr-BEA and Al-BEA showing different rate dependences on $(SiOH)_x$ density, turnover rates over each acid type show nearly identical dependences on reactant concentrations among $(SiOH)_x$ -rich and $(SiOH)_x$ -poor materials. All M-BEA show linear rate dependences on $[CH_3OH]$ (**Figure 5.1**) and a nearly zero-order dependence on $[C_4H_8O]$ (**Figure 5.2**) at molar ratios of $[CH_3OH]$ to $[C_4H_8O]$ less than 50. These dependencies hold over Al-BEA catalysts up to ratios of $[CH_3OH]$ to $[C_4H_8O]$ around 1200. Turnover rates eventually reach a near zero-order dependence on $[CH_3OH]$ and linear dependence on $[C_4H_8O]$ when ratios of $[CH_3OH]$ to $[C_4H_8O]$ exceed 5000 over Al-BEA materials. However, rates transition to the regime of strong dependence on $[C_4H_8O]$ and weak dependence on $[CH_3OH]$ over the Zr-BEA materials at much lower ratios of $[CH_3OH]$ to $[C_4H_8O]$ (> 500). To summarize, the measurements in **Figures 5.1** and **5.2** demonstrate that the $(SiOH)_x$ density influences epoxide ring-opening rates over Lewis acid zeolites (Zr-BEA) but has a nearly negligible effect on rates over Brønsted acid zeolites (Al-BEA). The $(SiOH)_x$ density does not influence the dependence of rates on reactant concentrations over either class of materials, with either C_4H_8O - or CH_3OH -derived species saturating the active sites within $(SiOH)_x$ -rich and $(SiOH)_x$ -poor M-BEA materials during C_4H_8O ring-opening.



Scheme 5.2. Proposed catalytic cycle for C_4H_8O ring-opening with CH_3OH in CH_3CN solvent over Zr-BEA zeolites. We expect an identical set of steps over the Al-BEA materials, although the structure of the intermediates differs due to proton transfer to the reactive species. All adsorption steps are currently assumed as reversible. Steps to form 1M2B and 2M1B are denoted as ^1C or ^2C , to signify nucleophilic attack on the primary and secondary carbons in the epoxide ring, respectively. For brevity, we do not show the reversible adsorption of CH_3CN molecules (step 1) here. We portray only reactions with molecularly adsorbed CH_3OH and C_4H_8O and not dissociatively bound oxygenates, although we expect either scenario may occur.

Scheme 5.2 presents a plausible system of elementary steps that explain the rate dependencies in **Figures 5.1** and **5.2** over Zr-BEA materials (analogous set of steps for Al-BEA shown in **Scheme D1**). The cycle begins with the reversible adsorption of CH_3CN (step 1, not shown for clarity), C_4H_8O (step 2), or CH_3OH (step 3) to the active sites. The epoxide ring may open by the nucleophilic attack of bound C_4H_8O by CH_3OH (step 4) or the reaction of bound CH_3OH and a liquid phase C_4H_8O molecule (step 5). The distinct ring-opening products ($C_5H_{12}O_2$ – 1M2B and 2M1B) desorb to complete the catalytic cycle (steps 6 and 7). Here, steps with a ^1C subscript represent nucleophilic attack at the primary carbon in the C_4H_8O ring to form 1M2B, while a ^2C subscript signifies attack at the secondary carbon to form 2M1B. 1M2B and 2M1B may

form through either adsorbed intermediate by similar elementary steps that possess distinct rate constants (e.g., $k_{4,1C}$, $k_{4,2C}$) and transition state structures that drive changes in regioselectivity. The formation rates of 1M2B and 2M1B show very similar dependencies on $[CH_3OH]$ and $[C_4H_8O]$ (see **Section D5**), supporting that the products form from common intermediates.

Rates for ring-opening (r_{RO}) equal the sum of the rates of total product formation through bound C_4H_8O - (r_4) or CH_3OH -derived intermediates (r_5):

$$r_{RO} = r_4 + r_5 = k_4[C_4H_8O^*][CH_3OH] + k_5[C_4H_8O][CH_3OH^*] \quad (5.2)$$

where k_4 and k_5 represent the sum of the rate constants to form 1M2B and 2M1B in steps 4 ($k_{4,1C}$, $k_{4,2C}$) and 5 ($k_{5,1C}$, $k_{5,2C}$) in **Scheme 5.2**. $[C_4H_8O^*]$ and $[CH_3OH^*]$ represent the number of adsorbed C_4H_8O and CH_3OH intermediates, respectively. Applying the pseudo-steady state hypothesis to the bound intermediates and deriving a site balance yields a turnover rate expression that accounts for reactions through bound C_4H_8O or CH_3OH intermediates:

$$\frac{r_{RO}}{[L]} = \frac{\frac{k_2 k_4 [C_4H_8O][CH_3OH]}{k_{-2} + k_4 [CH_3OH]} + \frac{k_3 k_5 [C_4H_8O][CH_3OH]}{k_{-3} + k_5 [C_4H_8O]}}{1 + K_1 [CH_3CN] + \frac{k_2 [C_4H_8O]}{k_{-2} + k_4 [CH_3OH]} + \frac{k_3 [CH_3OH]}{k_{-3} + k_5 [C_4H_8O]} + \frac{k_4 [CH_3OH] + k_5 [C_4H_8O] + k_{-6} [1M2B]}{k_6} + \frac{k_4 [CH_3OH] + k_5 [C_4H_8O] + k_{-7} [2M1B]}{k_7}} \quad (5.3)$$

Section D6 provides a full derivation and discussion of the necessary assumptions to simplify the rate expression under conditions where C_4H_8O - or CH_3OH -derived species saturate active sites and act as the most abundant reactive intermediate (MARI). Briefly, we utilize adsorption enthalpy measurements of C_4H_8O and CH_3OH and the molar ratios of $[CH_3OH]$ to $[C_4H_8O]$ to simplify **Equation 5.3** to yield the following rate expressions under conditions of C_4H_8O - (**Equation 5.4**) and CH_3OH -derived (**Equation 5.5**) MARI species:

$$\frac{r_{RO}}{[L]} = k_4 [CH_3OH] \quad (5.4)$$

$$\frac{r_{RO}}{[L]} = k_5 [C_4H_8O] \quad (5.5)$$

Equation 5.4 describes the rate trends in **Figures 5.1** and **5.2** at lower molar ratios of [CH₃OH] to [C₄H₈O] (<50 over Zr-BEA, <1200 over Al-BEA), while **Equation 5.5** matches trends at higher [CH₃OH] to [C₄H₈O] ratios (>500 over Zr-BEA, >5000 over Al-BEA). The trends hold for both (SiOH)_x-rich and (SiOH)_x-poor materials, suggesting that each M-BEA material shares common reaction mechanisms and surface intermediates. Rate differences between materials instead likely stem from changes in the rate constants of the kinetically relevant nucleophilic attacks (k_4 and k_5).

Previous studies show that epoxide ring-opening rates and regioselectivities over zeolites depend strongly on the active metal and intrapore solvent structure. These variables likely drive the differences in k_4 and k_5 over Al-BEA and Zr-BEA materials through changes in the stability of reactive species. We postulate that turnover rate differences between Zr-BEA-OH and Zr-BEA-F reflect differences in non-covalent interactions with surrounding solvent molecules due to differences in (SiOH)_x density. Differences in k_4 and k_5 between Al-BEA and Zr-BEA may stem from the different charge transfer mechanisms of Lewis and Brønsted acid sites and the solvent environment surrounding these sites. The following section quantitatively examines the effect of these interactions on the stability of reactive species through activation barrier measurements.

5.3.2 Active Site Structure and Solvent Environment Drive Changes in Activation Barriers

The turnover rates for C₄H₈O ring-opening in **Figures 5.1** and **5.2** depend on both the (SiOH)_x density of the *BEA framework and the active metal substituted within *BEA, stemming from changes in the values of k_4 and k_5 from the kinetically relevant steps shown in **Scheme 5.2**. The rate constants depend on the activation free energies ($\Delta G^\ddagger$) and corresponding activation enthalpies ($\Delta H^\ddagger$) and entropies ($\Delta S^\ddagger$), according to transition state theory:

$$k_x = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} = \frac{k_B T}{h} e^{-\frac{\Delta H^\ddagger}{RT}} e^{\frac{\Delta S^\ddagger}{R}} \quad (5.6)$$

Scheme 5.3 depicts the proposed reaction coordinates for C₄H₈O ring-opening over (SiOH)_x-rich and (SiOH)_x-poor Zr-BEA and Al-BEA materials under a C₄H₈O-derived MARI. Values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ represent the difference between the energy of the transition state for nucleophilic attack and the sum of the energies of liquid-phase CH₃OH and the bound C₄H₈O intermediate (C₄H₈O*):

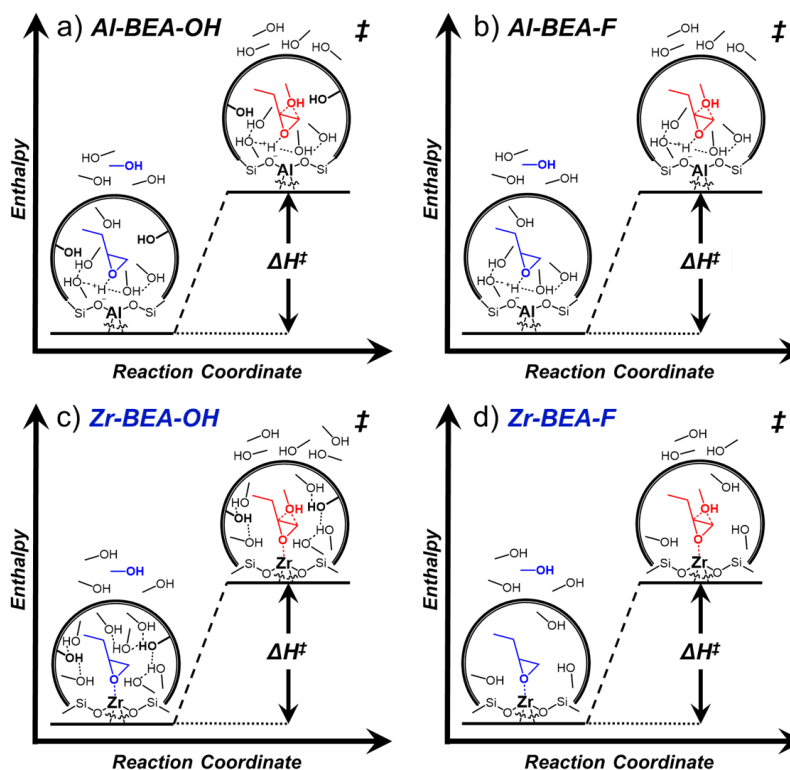
$$\Delta H^\ddagger = H^\ddagger - H_{CH_3OH} - H_{C_4H_8O^*} \quad (5.7)$$

$$\Delta S^\ddagger = S^\ddagger - S_{CH_3OH} - S_{C_4H_8O^*} \quad (5.8)$$

The activation parameters represent the total formation rate of both products. Both parameters consist of standard state (H^0 , S^0) and excess (H^ε , S^ε) contributions:

$$\Delta H^\ddagger = \Delta H^{\ddagger,0} + \Delta H^{\ddagger,\varepsilon} = (H^{\ddagger,0} + H^{\ddagger,\varepsilon}) - (H_{CH_3OH}^0 + H_{CH_3OH}^\varepsilon) - (H_{C_4H_8O^*}^0 + H_{C_4H_8O^*}^\varepsilon) \quad (5.9)$$

$$\Delta S^\ddagger = \Delta S^{\ddagger,0} + \Delta S^{\ddagger,\varepsilon} = (S^{\ddagger,0} + S^{\ddagger,\varepsilon}) - (S_{CH_3OH}^0 + S_{CH_3OH}^\varepsilon) - (S_{C_4H_8O^*}^0 + S_{C_4H_8O^*}^\varepsilon) \quad (5.10)$$



Scheme 5.3. Proposed reaction coordinate diagrams for C₄H₈O ring-opening with CH₃OH in CH₃CN solvent under conditions of a MARI species derived from C₄H₈O over a) Al-BEA-OH, b) Al-BEA-F, c) Zr-BEA-OH, d) Zr-BEA-F. CH₃OH adsorbs to react with C₄H₈O* and form the product, which then desorbs to complete the reaction.

H^0 and S^0 values represent the covalent interactions stemming from the coordinate covalent bonds between Lewis acidic Zr sites and reactive species and the ionic interactions between the zeolite anion and protonated intermediates and transition states in the Brønsted acid material. H^ε and S^ε values encompass non-covalent interactions of the transition state or reactive intermediates with surrounding solvent molecules and the pore walls of the zeolite.^{39, 124}

Figure 5.3 presents $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values as a function of $[\text{CH}_3\text{OH}]$ under conditions of a $\text{C}_4\text{H}_8\text{O}$ -derived MARI species, corresponding to the rate expression described in **Equation 5.4**. For all M-BEA, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values increase as a function of $[\text{CH}_3\text{OH}]$. $H_{\text{CH}_3\text{OH}}^0$ does not vary as a function of $[\text{CH}_3\text{OH}]$ over a given M-BEA material, while calculated $H_{\text{CH}_3\text{OH}}^\varepsilon$ values span a range of less than 3 kJ mol⁻¹ across the range of $[\text{CH}_3\text{OH}]$ (see **Section D7**). Therefore, changes in the stability of reactive species within the zeolite pores (i.e., $\text{C}_4\text{H}_8\text{O}^*$, transition state) drive the

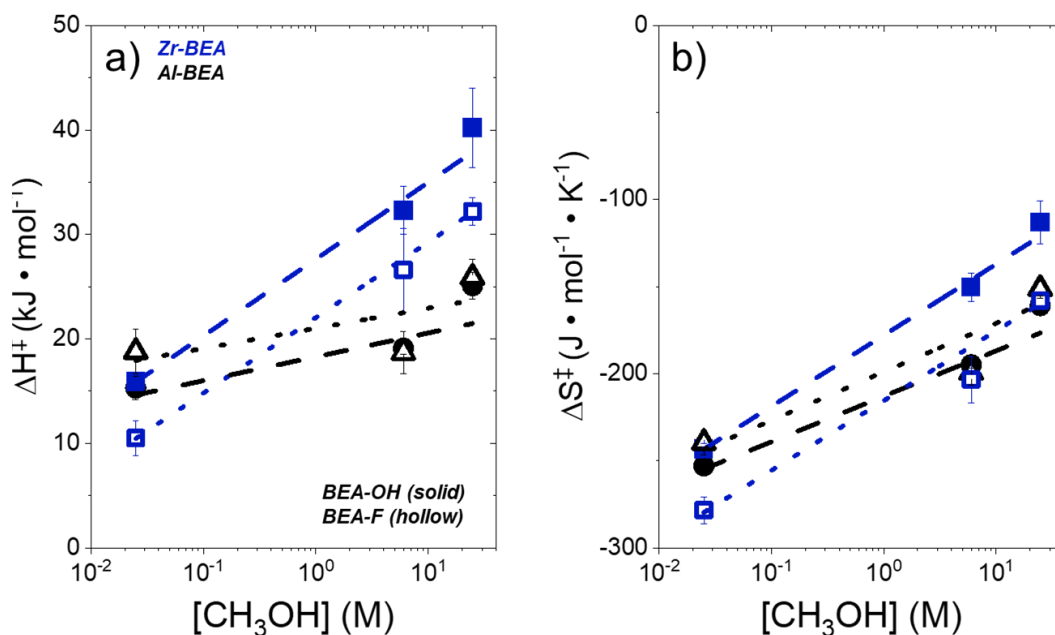


Figure 5.3. Activation a) enthalpies and b) entropies for $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH (solid points – 0.005 M $\text{C}_4\text{H}_8\text{O}$, 0.025 M CH_3OH in CH_3CN ; half solid points – 0.25 M $\text{C}_4\text{H}_8\text{O}$, 6 M CH_3OH in CH_3CN ; hollow points – 1 M $\text{C}_4\text{H}_8\text{O}$ in neat (24.7 M) CH_3OH), 298–323 K) over hydrophilic (solid points, dashed lines) and hydrophobic (hollow points, dotted lines) Zr- (blue) and Al-BEA (black) materials. Supplemental concentration dependence kinetics at 0.25 and 1 M $\text{C}_4\text{H}_8\text{O}$ are provided in **Section D9**.

activation barrier differences with $[\text{CH}_3\text{OH}]$ in **Figure 5.3**. Increasingly positive $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values at higher $[\text{CH}_3\text{OH}]$ suggest that the displacement of CH_3OH molecules from the *BEA pores during transition state formation leads to a greater enthalpic cost and corresponding entropic gain than the displacement of CH_3CN , consistent with our previous interpretations of epoxide ring-opening²⁹¹ and alkene epoxidation²⁵⁸ activation barriers over M-BEA materials.

From 0.025 M to 24.7 M CH_3OH , the Al-BEA materials show less significant increases in $\Delta H^\ddagger$ (7 – 10 kJ mol^{-1}) and $\Delta S^\ddagger$ (88 – 92 $\text{J mol}^{-1} \text{K}^{-1}$) than the Zr-BEA materials (22 – 25 kJ mol^{-1} , 120 – 130 $\text{J mol}^{-1} \text{K}^{-1}$). The different dependences of these energies on $[\text{CH}_3\text{OH}]$ may stem from both standard state and excess contributions. The protonation of the transition state and adsorbed $\text{C}_4\text{H}_8\text{O}$ in Al-BEA likely influences $\Delta H^{\ddagger,0}$ and $\Delta S^{\ddagger,0}$ values, leading to differences between Al- and Zr-BEA materials. Furthermore, the active site proton within Al-BEA likely delocalizes across clusters of CH_3OH molecules^{100, 273-274} at higher $[\text{CH}_3\text{OH}]$ values (24.7 M and possibly 6 M, illustrated in **Scheme 5.3**). The solvation of the active site may lower $\Delta H^\ddagger$ through either an enthalpic stabilization of the transition state (increasing $H^\ddagger$ in **Equation 5.7**) or an enthalpic destabilization of $\text{C}_4\text{H}_8\text{O}^*$ (increasing $H_{\text{C}_4\text{H}_8\text{O}^*}$). We hypothesize that the delocalization of the active site increases $H_{\text{C}_4\text{H}_8\text{O}^*}$ but leads to a corresponding increase in $S_{\text{C}_4\text{H}_8\text{O}^*}$ by increasing the mobility of this adsorbed intermediate, as supported by more endothermic $\text{C}_4\text{H}_8\text{O}$ adsorption enthalpies in CH_3OH than CH_3OH (see **Section 5.3.4**). These changes may arise from a combination of covalent and non-covalent interactions. Despite the convoluting effects of active site solvation in Al-BEA, the increasing trends of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ with $[\text{CH}_3\text{OH}]$ for all M-BEA shows the strong effect of non-covalent interactions through changes in $\Delta H^{\ddagger,\varepsilon}$ and $\Delta S^{\ddagger,\varepsilon}$.

The $(\text{SiOH})_x$ density of M-BEA can also influence $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for $\text{C}_4\text{H}_8\text{O}$ ring-opening. Al-BEA-OH and Al-BEA-F provide similar values of $\Delta H^\ddagger$ (within 1 – 4 kJ mol^{-1}) and

$\Delta S^\ddagger$ (within 5 – 10 J mol⁻¹ K⁻¹) at each [CH₃OH] value. The differences in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ largely compensate to provide very similar rates over Al-BEA-OH and Al-BEA-F (**Figures 5.1** and **5.2**), as $\Delta G^\ddagger$ values at 308 K fall within 1 kJ mol⁻¹ at each [CH₃OH] for these materials. In contrast, Zr-BEA-OH shows more positive $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values than Zr-BEA-F by 5 – 8 kJ mol⁻¹ and 35 – 55 J mol⁻¹ K⁻¹, respectively. Zr-BEA-OH provides $\Delta G^\ddagger$ values 5 – 6 kJ mol⁻¹ less than Zr-BEA-F (308 K), demonstrating that entropic gains lead to greater turnover rates in Zr-BEA-OH. The presence of (SiOH)_x groups plausibly alters $\Delta H^{\ddagger,\varepsilon}$ and $\Delta S^{\ddagger,\varepsilon}$ through changes in the solvent structure surrounding the active sites, as illustrated in **Scheme 5.3**. The active protons in the Al-BEA materials likely govern the solvent structure surrounding C₄H₈O* and the ring-opening transition state, leading to similar solvent configurations around the active sites in Al-BEA-OH (**Scheme 5.3a**) and Al-BEA-F (**Scheme 5.3b**). Therefore, the protons may lessen the effect of (SiOH)_x on the solvent environment near active sites, giving similar $\Delta H^\ddagger$ and $\Delta S^\ddagger$ between Al-BEA-OH and Al-BEA-F. In comparison, the stronger influence of (SiOH)_x on $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for Zr-BEA materials implies a more significant role of (SiOH)_x on the solvent structure surrounding the Zr sites. Zr-BEA-OH likely adsorbs greater quantities of CH₃OH and CH₃CN that form hydrogen bond networks within the pores (**Scheme 5.3c**), while the pores of Zr-BEA-F primarily contain weakly interacting CH₃OH and CH₃CN molecules (**Scheme 5.3d**). These hypotheses align with previous proposals for the structural differences of H₂O,^{134-135, 211} CH₃CN,^{211, 259} and alcohol^{132-133, 258} molecules within hydrophilic and hydrophobic Lewis acid zeolites. The formation of the ring-opening transition state likely requires the disruption of hydrogen bonds between solvent molecules within Zr-BEA-OH that leads to greater $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values compared to Zr-BEA-F at all [CH₃OH]. The entropic gains exceed the enthalpic penalty, leading to greater rates for ring-opening in Zr-BEA-OH than Zr-BEA-F. These trends align with previous observations for alkene

epoxidation with H₂O₂ in organic solvents (CH₃OH, CH₃CN) containing H₂O over Ti-BEA-OH and Ti-BEA-F,^{74, 76, 211, 258-259, 264} providing evidence that the intrapore solvent structure influences alkene epoxidation and the secondary epoxide ring-opening process in similar ways.

Figure 5.3 shows that differences in metal identity, solvent composition, and (SiOH)_x density lead to differences in rate constants for epoxide ring-opening through changes in $\Delta H^\ddagger$ and $\Delta S^\ddagger$, which stem from changes in the stability of reactive species in the zeolite pores. The distinct dependences of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ on (SiOH)_x density over Al-BEA and Zr-BEA materials imply that different contributions govern the intrapore solvent structure within these Brønsted and Lewis acid materials. The following section establishes the differences in solvent structure among M-BEA-OH and M-BEA-F that drive rate differences for ring-opening.

5.3.3 Solvent Structure Governed by Different Functions in Brønsted & Lewis Acid Zeolites

Recent studies show that the intrapore composition of binary liquid mixtures in zeolites depends on the liquid solvent composition,^{178, 225-226, 258} (SiOH)_x density within Lewis acid²⁵⁸ and siliceous zeolites,^{131, 227-228} and the active site density (H⁺) within Brønsted acids.^{99, 131, 199} We hypothesize that differences in the intrapore solvent composition will correlate strongly with observed trends in rates and activation barriers described above.

Figure 5.4 demonstrates that the solvent composition within M-BEA depends on the active metal identity, (SiOH)_x density, and mole fraction of CH₃OH within CH₃CN in the bulk solvent ($x_{CH_3OH,bulk}$). Here, χ represents the ratio of the estimated mole fractions of CH₃OH in the zeolite pores ($x_{CH_3OH,pore}$) and $x_{CH_3OH,bulk}$ at equilibrium (calculation details provided in **Section D10**):

$$\chi = \frac{x_{CH_3OH,pore}}{x_{CH_3OH,bulk}} \quad (5.11)$$

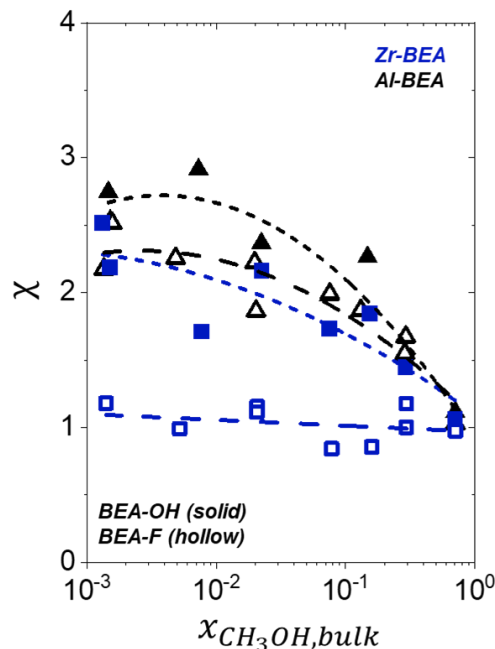


Figure 5.4. χ values as a function of $x_{CH_3OH,bulk}$ as a function of $x_{CH_3OH,pore}$ at 308 K in a mixture of CH_3OH and CH_3CN over hydrophilic (solid) and hydrophobic (hollow) Al- (black) and Zr-BEA (blue) materials.

The M-BEA-OH materials in **Figure 5.4** consistently show higher χ values than the corresponding M-BEA-F material, suggesting that $(SiOH)_x$ groups facilitate CH_3OH adsorption relative to CH_3CN . CH_3OH contains a greater sum of hydrogen bond donors and acceptors (3) than CH_3CN (1), meaning that CH_3CN molecules contain fewer functions to coordinate with $(SiOH)_x$ groups or form hydrogen-bonding networks with other molecules. χ values generally decrease with increasing $x_{CH_3OH,bulk}$ over each M-BEA material, with the M-BEA-OH and M-BEA-F materials collapsing to more similar values at higher $x_{CH_3OH,bulk}$. These trends suggest that $(SiOH)_x$ functions influence CH_3OH uptake more strongly at lower $x_{CH_3OH,bulk}$, when lower quantities of CH_3OH reside in the pores. This interpretation appears consistent with previous observations in which H_2O uptake within hydrophilic zeolites from mixtures with ethanol,²³⁰⁻²³¹ and acetic acid²³² depend more strongly on $x_{H_2O,bulk}$ at lower $x_{H_2O,bulk}$ values. At higher mole

fractions, CH₃OH molecules can likely associate with pre-adsorbed CH₃OH within the pores, leading to a weaker influence of the (SiOH)_x density or active site structure on CH₃OH adsorption.

Interestingly, Al-BEA-OH and Al-BEA-F show more similar χ values than Zr-BEA-OH and Zr-BEA-F across the range of $x_{CH_3OH,bulk}$. The greater dependence of χ values on (SiOH)_x density over Zr-BEA materials provides strong evidence that (SiOH)_x groups carry a greater influence on the intrapore solvent structure within Zr-BEA than Al-BEA materials. While Al-BEA-OH generally shows greater χ than Al-BEA-F, the similar trends and magnitudes of χ across $x_{CH_3OH,bulk}$ for these materials suggest that the H⁺ sites within Al-BEA impact the intrapore solvent structure more strongly than the framework Zr active sites in Zr-BEA. This explanation agrees with previous works that examined H₂O adsorption over Brønsted acid materials, which found that H₂O preferentially coordinates at H⁺ at lower coverages before binding to (SiOH)_x groups after saturating the H⁺ sites.^{99, 199, 294} CH₃OH molecules may show a similar binding preference to the H⁺ sites in Al-BEA materials here. The observations from **Figure 5.4** align with the interpretations of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values discussed in the previous section and the hypothesized differences in solvent structure among M-BEA illustrated in **Scheme 5.3** above. The active sites in Al-BEA-OH and Al-BEA-F likely promote similar surrounding configurations of solvent molecules, while the difference in (SiOH)_x density between Zr-BEA-OH and Zr-BEA-F leads to dissimilar solvent structures around the active sites. The distinct solvent structures within these materials likely drive the rate and activation barrier differences described in the previous sections.

While the χ values shown in **Figure 5.4** give insight into the intrapore solvent compositions within M-BEA during C₄H₈O ring-opening, they do not provide information about the intrapore solvent density. **Figure 5.5** present single-component vapor adsorption isotherms for CH₃OH and

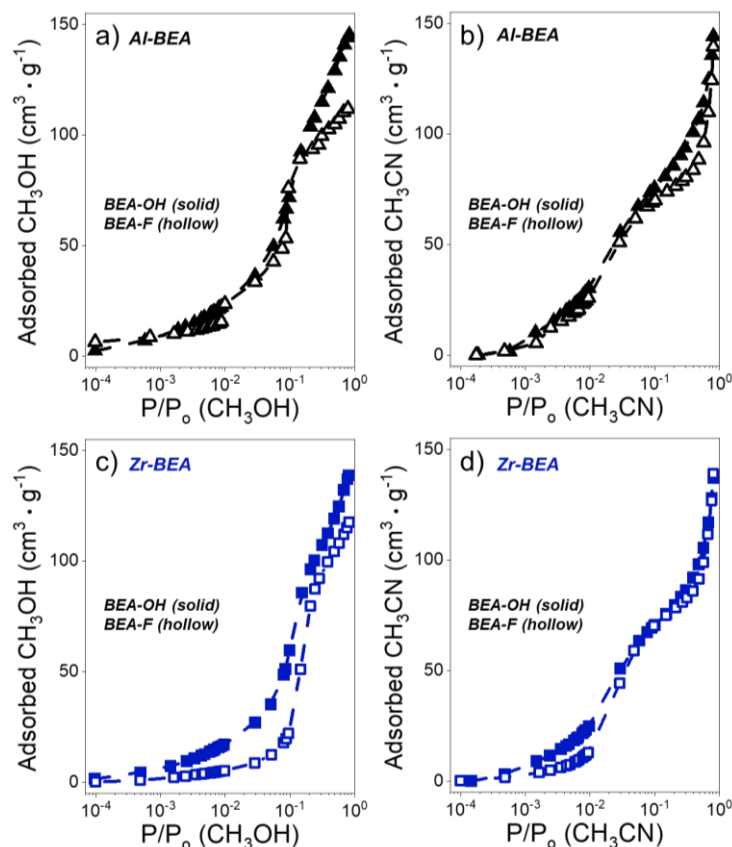


Figure 5.5. a) CH₃OH (293 K) and b) CH₃CN (296 K) adsorption isotherms over hydrophilic (solid) and hydrophilic (hollow) Al- (black) and Zr-BEA (blue) materials.

CH₃CN as a function of relative pressure (P/P_0) over M-BEA, revealing that the (SiOH)_x density and active site structure influence the number of solvent molecules within the M-BEA pores. At P/P_0 values < 0.05 , the ratio of adsorbed species between Al-BEA-OH and Al-BEA-F varies from 0.9 to 1.2 for CH₃CN and 1.0 to 1.5 for CH₃OH. In contrast, Zr-BEA-OH uptakes 1.5 to 2.4 times more CH₃CN and 2.7 to 5.1 more times CH₃OH than Zr-BEA-F at $P/P_0 < 0.05$. Within this low P/P_0 regime, CH₃CN and CH₃OH likely bind to the most favorable binding sites present within the M-BEA material. The similar uptakes of both adsorbates for the Al-BEA materials supports that CH₃CN and CH₃OH bind preferentially to H⁺ sites. The greater uptakes over Zr-BEA-OH than Zr-BEA-F indicate that the adsorbates coordinate to different framework locations; CH₃CN and

CH₃OH likely bind preferentially to the (SiOH)_x nests within Zr-BEA-OH, while the adsorbates should primarily bind to framework Zr atoms or Si-O-Si linkages within Zr-BEA-F.

As P/P_0 increases further, the M-BEA-OH and M-BEA-F materials reach more similar uptakes of both CH₃OH and CH₃CN regardless of acid type; at P/P_0 of 0.8, M-BEA-OH and M-BEA-F adsorb nearly identical quantities of CH₃CN while the M-BEA-OH materials adsorb 1.3 times more CH₃OH than M-BEA-F. Comparing across acid types, the total uptake at P/P_0 of 0.8 for Zr-BEA and Al-BEA materials of similar (SiOH)_x density differs by less than 10%. These similarities suggest that as the adsorbates coordinate to less favorable binding sites and begin to form extended networks within the pore, the M-BEA materials reach similar densities of CH₃OH and CH₃CN regardless of the intrapore (SiOH)_x density or active site character. Nevertheless, the differences in vapor uptake at $P/P_0 < 0.05$ in **Figure 5.5** provide additional evidence that the solvent environment surrounding the Brønsted acid sites depends weakly on nearby (SiOH)_x groups, while the (SiOH)_x nests within Zr-BEA-OH promote hydrogen-bonding structures of CH₃CN and CH₃OH near Zr active sites that do not appear within Zr-BEA-F pores. Furthermore, M-BEA-OH and M-BEA-F materials show greater differences in CH₃OH than CH₃CN uptake across the full range of P/P_0 , demonstrating that (SiOH)_x nests carry greater influence for the adsorption of CH₃OH and aligning with the interpretation of χ values in **Figure 5.4**. Overall, the comparisons of single-component vapor uptakes in **Figure 5.5** further supports that the H⁺ sites structure solvent similarly within Al-BEA-OH and Al-BEA-F, while the difference in (SiOH)_x density leads to differences in the solvent structure surrounding the catalytic active sites in Zr-BEA-OH and Zr-BEA-F.

Figures 5.4 and **5.5** give strong evidence that Lewis and Brønsted acid zeolites promote distinct intrapore solvent structures that depend differently on the (SiOH)_x density of the zeolite

pores. Tuning the liquid solvent composition, active site structure, and (SiOH)_x density provides opportunities to control the solvent composition and density within porous catalysts. The solvent environment within M-BEA significantly influences C₄H₈O ring-opening rates and likely impacts the thermodynamics and selectivities of the reaction, as highlighted in the following sections.

5.3.4 Enthalpy Correlations Show Intrapore Environment Affects Reactive Species Stability

The Brønsted-Evans-Polanyi model proposes that the enthalpy of reaction for an elementary step scales linearly with the intrinsic activation energy of the same step, therefore establishing a connection between the intrinsic kinetics and thermodynamics of a reaction.^{202, 234-235} Hammond later explained this connection by postulating that the transition state for a reaction resembles the stable state (i.e., reactant or product) most similar in energy.^{97, 198} Recent studies demonstrate that the liquid-phase adsorption enthalpies for epoxide molecules over *BEA zeolites correlate positively with $\Delta H^\ddagger$ values for alkene epoxidation as a function of the active metal,³⁰ (SiOH)_x density,^{73, 211} and solvent composition.²⁵⁸ More recently, we established linear correlations between epoxide adsorption enthalpies ($\Delta H_{ads,C_4H_8O}$) and $\Delta H^\ddagger$ values for C₄H₈O ring-opening over M-BEA materials, implicating a transition state for ring-opening that resembles the adsorbed C₄H₈O reactant.²⁹¹ The measurement of $\Delta H_{ads,C_4H_8O}$ can provide insight into the differences in ring-opening transition state stability over M-BEA-OH and M-BEA-F materials.

Figure 5.6 reveals that $\Delta H_{ads,C_4H_8O}$ measured by isothermal titration calorimetry (ITC) depends on the active metal identity, solvent choice, and density of (SiOH)_x groups within M-BEA. The Al-BEA materials show more exothermic $\Delta H_{ads,C_4H_8O}$ values than the Zr-BEA materials in a CH₃CN-rich solvent, suggesting that C₄H₈O adsorbs more strongly to the Brønsted acid sites than to Zr framework sites. This trend corresponds with the weaker dependence of rates on

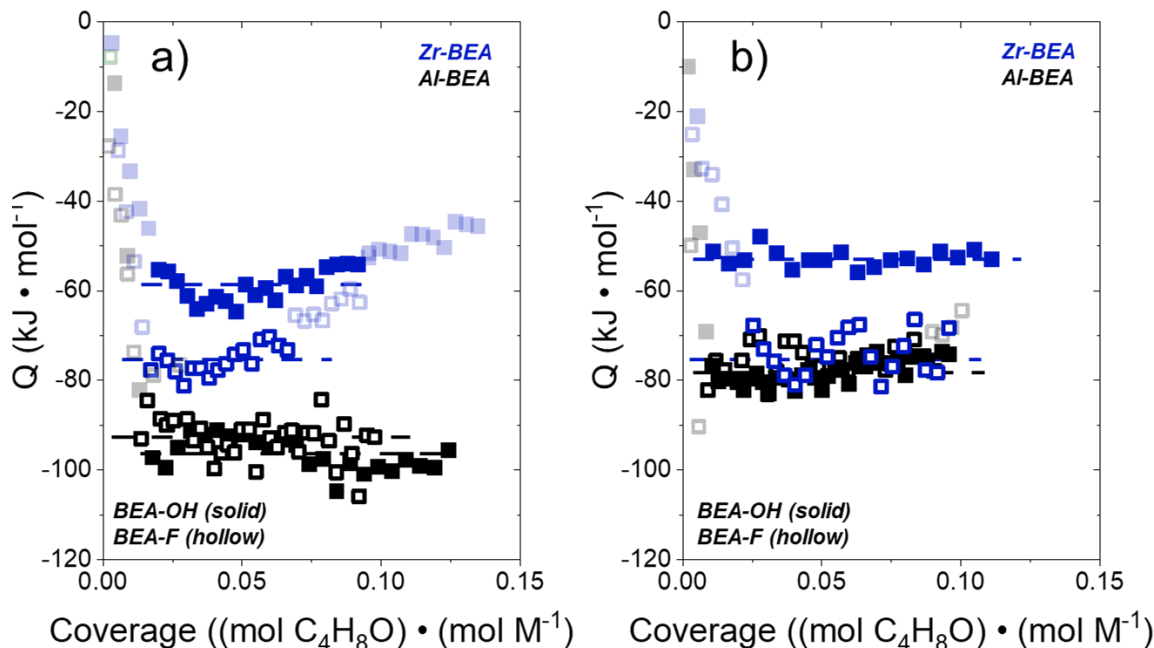


Figure 5.6. Heat released upon C_4H_8O adsorption in a) CH_3CN and b) CH_3OH as a function of C_4H_8O to metal ratio over hydrophilic (solid) and hydrophilic (hollow) Al- (black) and Zr-BEA (blue) materials (0.005 M C_4H_8O , 308 K). Transparent points are omitted from the adsorption enthalpy calculation, denoted by the dashed line. **Section D11** includes adsorption enthalpy calculation details, raw data for the ITC experiments from **Figure 5.6**, and further ITC measurements, including CH_3OH adsorption over each M-BEA.

$[C_4H_8O]$ in Al-BEA than Zr-BEA materials (**Figure 5.2**) and gives insight into why C_4H_8O saturates sites on Al-BEA across nearly all conditions examined. $\Delta H_{ads,C_4H_8O}$ values over Zr-BEA-OH and Zr-BEA-F change negligibly upon changing the solvent from CH_3CN and CH_3OH , while CH_3OH provides $\Delta H_{ads,C_4H_8O}$ values $\sim 15 \text{ kJ mol}^{-1}$ more endothermic than CH_3CN over both Al-BEA-OH and Al-BEA-F. The more endothermic $\Delta H_{ads,C_4H_8O}$ for Al-BEA in CH_3OH may stem from the solvation of H^+ by CH_3OH , which could influence the binding enthalpy of C_4H_8O to the H^+ sites. However, we also cannot exclude that the reaction of C_4H_8O and CH_3OH may contribute to the measured $\Delta H_{ads,C_4H_8O}$ in CH_3OH over both Zr-BEA and Al-BEA materials.

In both CH_3CN and CH_3OH , $\Delta H_{ads,C_4H_8O}$ values vary by less than 5 kJ mol^{-1} between Al-BEA-OH and Al-BEA-F. In contrast, Zr-BEA-OH shows a more endothermic $\Delta H_{ads,C_4H_8O}$ than Zr-

BEA-F by 17-21 kJ mol⁻¹ in both solvents. The similar $\Delta H_{ads,C_4H_8O}$ for the Al-BEA materials suggests that C₄H₈O similarly reorganizes the solvent surrounding the H⁺ sites in Al-BEA-OH and Al-BEA-F during adsorption. This observation provides strong evidence that the Al-BEA materials stabilize similar solvent structures around the H⁺ active sites, which leads to similar behavior between Al-BEA-OH and Al-BEA-F during C₄H₈O ring-opening, solvent adsorption, and C₄H₈O adsorption. The more endothermic $\Delta H_{ads,C_4H_8O}$ for Zr-BEA-OH compared to Zr-BEA-F likely originates from the disruption of hydrogen-bonded solvent molecules (CH₃OH or CH₃CN) by adsorbing C₄H₈O within the pores of Zr-BEA-OH. The displacement of weakly interacting solvent molecules within Zr-BEA-F requires a smaller enthalpic penalty and gives more exothermic $\Delta H_{ads,C_4H_8O}$ values.

Figure 5.7 shows that $\Delta H^\ddagger$ and $\Delta H_{ads,C_4H_8O}$ values correlate linearly for Al-BEA and Zr-BEA materials as a function of (SiOH)_x density at a given solvent composition. Interestingly, the Al-BEA and Zr-BEA materials do not fall on the same trendline. These differences likely originate from the proton transfer to the C₄H₈O* and ring-opening transition state or the delocalization of H⁺ by CH₃OH, which may convolute the comparisons between Brønsted and Lewis acids. Furthermore, changing the solvent from CH₃CN-rich to neat CH₃OH leads to a discontinuity in the trend for the Zr-BEA materials but not for the Al-BEA materials in **Figure 5.7**. While the reason for this discrepancy remains unclear, the enthalpy of reaction between C₄H₈O and CH₃OH may contribute to $\Delta H_{ads,C_4H_8O}$ and contribute to the discontinuity for the Zr-BEA materials. The solvation of H⁺ by CH₃OH in Al-BEA may offset this reaction contribution and lead to a consistent trend across all points. **Section D12** includes a “corrected” version of the enthalpy relationship from **Figure 5.7** that accounts for the possible contribution of the enthalpy of reaction to

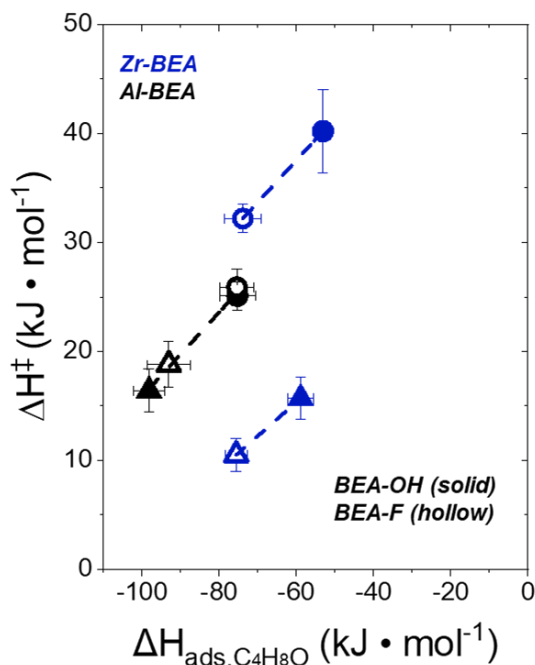


Figure 5.7. $\Delta H^\ddagger$ values for C_4H_8O ring-opening (from **Figure 5.3**, 0.025 M CH_3OH in CH_3CN (triangles) or 24.7 M CH_3OH (circles)) as a function of ΔH_{ads} for C_4H_8O over hydrophilic (solid) and hydrophilic (hollow) Al- (black) and Zr-BEA (blue) materials.

$\Delta H_{ads,C_4H_8O}$. Regardless of the reaction potentially convoluting $\Delta H_{ads,C_4H_8O}$ contributions between CH_3CN and CH_3OH , the linear correlations between $\Delta H^\ddagger$ and $\Delta H_{ads,C_4H_8O}$ over Zr-BEA and Al-BEA at a given solvent composition provide strong evidence that the adsorption of C_4H_8O and the formation of the C_4H_8O ring-opening transition state depend similarly on the surrounding solvent structure.

Al-BEA-OH and Al-BEA-F show very similar $\Delta H^\ddagger$ and $\Delta H_{ads,C_4H_8O}$ within both solvent compositions, giving further evidence that the difference in $(SiOH)_x$ density between these materials does not yield differences in the intrapore solvent structure that drive differences in catalysis or adsorption. The more endothermic values of each enthalpy at a higher $[CH_3OH]$ likely originate from a greater disruption of hydrogen-bonding solvent molecules during the formation of the ring-opening transition state and the adsorption of C_4H_8O within CH_3OH -rich solvents. $H_{C_4H_8O}^\varepsilon$ values vary by less than 3 kJ mol⁻¹ across the range of $[CH_3OH]$ studied (**Section D7**),

demonstrating that changes in $\Delta H_{ads,C_4H_8O}$ between solvents in **Figure 5.7** result from changes in the stability of $C_4H_8O^*$ rather than liquid-phase C_4H_8O . Significantly, the enthalpic penalty for forming the transition state in **Schemes 5.3a** and **5.3b** must exceed that for C_4H_8O adsorption to cause an increase in $\Delta H^\ddagger$ with $[CH_3OH]$; in other words, the excess enthalpy increases for the transition state ($H^{\ddagger,\varepsilon}$) must exceed that of the reference state for ring-opening ($H_{C_4H_8O^*}^\varepsilon$) (**Equation 5.9**). The transition state likely occupies more space than the $C_4H_8O^*$ intermediate and requires a more significant displacement of surrounding solvent molecules, which may yield a more significant excess enthalpic penalty.

The disruption of hydrogen-bonded solvent also appears to impart a greater enthalpic penalty to the larger transition state in the Zr-BEA materials. However, Zr-BEA-OH shows more endothermic $\Delta H^\ddagger$ and $\Delta H_{ads,C_4H_8O}$ values than Zr-BEA-F in both CH_3CN -rich and neat CH_3OH solvents. The inability of solvent molecules to form hydrogen-bonding networks in the pores of Zr-BEA-F likely lessens the enthalpic cost required to form the ring-opening transition state or adsorb C_4H_8O to the Zr sites. Notably, the slope of the correlation between Zr-BEA materials in **Figure 5.7** becomes more positive in neat CH_3OH compared to a CH_3CN -rich solvent. The steeper slope of the Zr-BEA correlations in neat CH_3OH likely occurs because $H^{\ddagger,\varepsilon}$ depends more strongly on the $(SiOH)_x$ density within Zr-BEA than $H_{C_4H_8O^*}^\varepsilon$ in the presence of CH_3OH than CH_3CN . Specifically, the difference in enthalpic penalties provided to the larger transition state and smaller $C_4H_8O^*$ becomes more significant when the pores of Zr-BEA-OH contain hydrogen-bonded CH_3OH compared to hydrogen-bonded CH_3CN . Overall, the different dependences of $\Delta H^\ddagger$ and $\Delta H_{ads,C_4H_8O}$ on $(SiOH)_x$ density between Al-BEA and Zr-BEA materials reinforces that the solvent structure within the *BEA pores depends on different functions within Brønsted and Lewis acid zeolites. The H^+ sites likely govern the solvent environment surrounding active sites within Al-

BEA-OH and Al-BEA-F, while the higher density of (SiOH)_x groups within Zr-BEA-OH likely leads to a significantly different solvent environment around the Zr active sites than in Zr-BEA-F.

The solvent structure within M-BEA pores appears to drive differences in ring-opening turnover rates and activation barriers through changes in the excess energies of reactive species, as described above. The following section examines the consequences of these excess interactions and the covalent interactions between the reactive species and active sites on the regioselectivities of C₄H₈O ring-opening.

5.3.5 Active Site Structure and Solvation Drive Changes in Ring-Opening Regioselectivity

The interactions between transition states and intermediates with active and interactions with surrounding solvent molecules within zeolites influence rates and barriers for epoxide ring-opening. The distribution of regioisomers for C₄H₈O ring-opening with CH₃OH over M-BEA (see **Scheme 5.1** above) also depends on these intrapore interactions, as shown in our previous work.²⁹¹ The regioselectivities are quantified with a rate ratio defined as β :

$$\beta = \frac{r_{1M2B}}{r_{2M1B}} \quad (5.12)$$

where r_{1M2B} and r_{2M1B} represent the formation rates of 1M2B and 2M1B, respectively. The formation rates depend on the reactant concentrations and product-specific rate constants for the kinetically relevant steps ($k_{4,1C}$, $k_{4,2C}$, $k_{5,1C}$, $k_{5,2C}$) (**Scheme 5.2**). The expression for β simplifies if we assume the products form from identical surface intermediates and fluid-phase reactants upon the same set of active sites and we consider only conditions of C₄H₈O*-covered active sites (full derivation and discussion of assumptions in **Section D6**). In this case, β solely depends on the difference between the free energies of the transition states for the individual products:

$$\beta = \frac{k_{4,1C}}{k_{4,2C}} = \exp\left(\frac{G_{2M1B}^{\ddagger} - G_{1M2B}^{\ddagger}}{RT}\right) \quad (5.13)$$

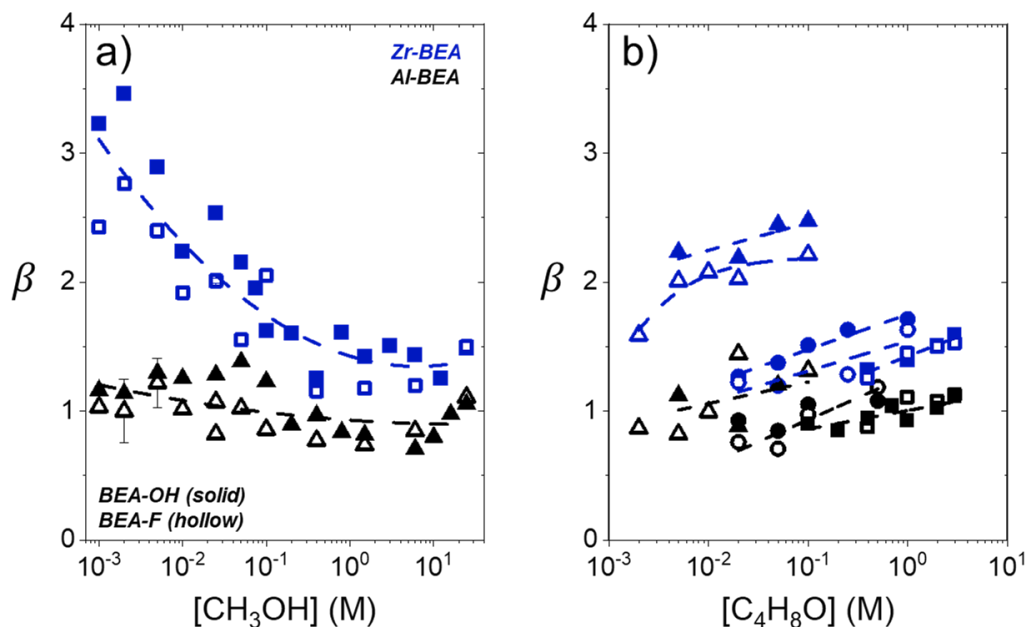


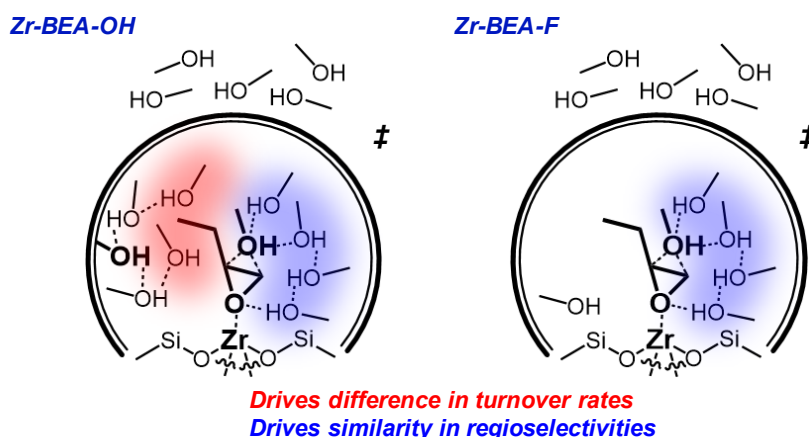
Figure 5.8. β values for C_4H_8O ring-opening with CH_3OH as a function of a) CH_3OH concentration ($0.005 - 1$ M C_4H_8O , $[CH_3OH]:[CH_3CN] = 0.2 - 100$, CH_3CN solvent, 308 K) and b) C_4H_8O concentration at 0.025 M (triangles), 6 M (circles), or 24.7 M CH_3OH (squares) (CH_3CN , 308 K) over hydrophilic (solid) and hydrophilic (hollow) Al- (black) and Zr-BEA (blue). All measurements were made under $C_4H_8O^*$ -covered active sites.

Figure 5.8 presents β values as a function of reactant concentrations under conditions of $C_4H_8O^*$ -covered active sites, which depend on the liquid solvent composition and the active metal and $(SiOH)_x$ density within the $^*BEA$ pores. β values decrease at greater $[CH_3OH]$ for the Zr-BEA materials (**Figure 5.8a**), with β values approaching $3 - 3.5$ at the lowest $[CH_3OH]$ (< 0.1 M CH_3OH) and β values of $1 - 1.5$ in CH_3OH -rich solvents. The β values over Al-BEA-OH and Al-BEA-F change less strongly with $[CH_3OH]$, with values between 0.75 and 1.5 across the range of $[CH_3OH]$. **Figure 5.8b** shows that β values increase slightly with increasing $[C_4H_8O]$ across each M-BEA at several values of $[CH_3OH]$ (0.025 M, 6 M, and 24.7 M). The generally greater regioselectivities to the terminal ether (1M2B) compared to the terminal alcohol (2M1B) in **Figure 5.8** aligns with prior studies, which commonly attribute the difficulty of forming the terminal alcohol to the steric hindrance for nucleophilic attack at the more substituted C-atom of the oxirane

ring.^{63, 104-106} However, **Figure 5.8** also reveals that increasing the number of hydrogen bond donors and acceptors within the solvent by increasing [CH₃OH] leads to a greater preference to form 2M1B, which agrees with a recent report showing that intentionally adding hydrogen-bonding acceptors to the system (e.g., diols) leads to greater selectivity to terminal alcohols during epoxide ring-opening with alcohols over homogeneous borane catalysts.⁸¹ Over M-BEA, CH₃OH molecules may preferentially stabilize the 2M1B transition state relative to 1M2B through hydrogen-bonding interactions.

The weaker dependence of β values on reaction composition over Al-BEA compared to Zr-BEA materials in **Figure 5.8** suggests that the intrapore solvent environment plays a lesser role in regioselectivity trends over the Brønsted acids. Instead, the covalent interactions between the H⁺ sites and reactive species appear to drive the distribution of regioisomers over Al-BEA. At an equivalent reaction composition, the Al-BEA materials consistently show lower β values than the Zr-BEA materials. Recent quantum chemical calculations reveal that protonation of the epoxide causes elongation of the weaker C-O bond between the more substituted carbon and epoxide oxygen atom,²⁷⁰ thereby facilitating the nucleophilic attack at this carbon to form the terminal alcohol.^{268, 270, 279-280} These interactions between the epoxide ring, H⁺ site, and the attacking CH₃OH molecule likely lead to β values near unity in all conditions. A previous study reported β values from 0.8 to 1.3 for C₄H₈O ring-opening in neat CH₃OH catalyzed by sulfuric acid and Brønsted acid zeolites of varying pore, agreeing with the span of values for Al-BEA in **Figure 5.8**.²⁶⁷ Homogeneous (i.e., aluminum triflate)^{57, 278} and heterogeneous Lewis acids (i.e., Hf-, Sn-, Zr-BEA)⁶³ previously achieved β values between 1.2 and 1.4 for C₄H₈O ring-opening in neat CH₃OH. **Figure 5.8** demonstrates that introducing an organic co-solvent (i.e., CH₃CN) provides opportunities to extend to higher β values over Lewis acidic materials.

The (SiOH)_x density of the M-BEA materials only slightly affects β values, in contrast to the strong effect of the active metal choice and solvent composition. The weak influence of (SiOH)_x on regioselectivity aligns with previous observations for 1,2-epoxyhexane ring-opening over Sn-BEA catalysts.¹⁰⁷ While this trend corresponds with the weak dependence of rates, activation barriers, and intrapore solvent composition on the (SiOH)_x density of Al-BEA (*vide supra*), it diverges from the consistent differences shown between the Zr-BEA materials in previous sections. The explanation for this dissimilarity also remains unclear, but we postulate that the differences in solvent structure between Zr-BEA-OH and Zr-BEA-F do not influence β values as strongly as rates or activation barriers. The solvent environment surrounding the epoxide ring, where the nucleophilic attack occurs (i.e., near the active site), may feel the influence of (SiOH)_x groups less significantly than the extended solvent structure near the hydrophobic alkyl tail of the transition state (i.e., further from the active site) (see **Scheme 5.4**). In other words, the disruption of hydrogen-bonded solvent molecules by the alkyl tail of the transition state likely facilitates greater rates in Zr-BEA-OH over Zr-BEA-F but does not contribute significantly to regioselectivity trends. To summarize, **Figure 5.8** indicates that changing the active metal and



Scheme 5.4. Proposed origins of differences between Zr-BEA-OH and Zr-BEA-F. The disruption of hydrogen bonded-solvent by the alkyl tail of the transition state drives greater rates in Zr-BEA-OH, while the similar solvent structure surrounding the epoxide ring leads to similar regioselectivities among the materials.

solvent composition leads to differences in regioselectivities by altering the stability of transition states to form the ring-opening products, with a weak contribution of $(\text{SiOH})_x$ density to the regioselectivity trends.

Industrial liquid-phase epoxide ring-opening processes commonly utilize homogeneous catalysts²⁹⁵⁻²⁹⁸ and ion-exchange resins,²⁹⁹⁻³⁰¹ which provide high rates but suffer from issues with deactivation, regeneration, and separation. Microporous silicates (i.e., zeolites) offer a more stable and sustainable alternative that allow for precise control of the density and structure of intrapore liquids through changes in the active site character and $(\text{SiOH})_x$ density. While shown here for epoxide ring-opening, manipulating the properties of zeolite catalysts provides opportunities to control rates and selectivities of liquid-phase processes in general.

5.4 Conclusions

Rates and regioselectivities for epoxide ring-opening reactions depend intimately on the structure of solvent molecules, type of acid site (Lewis or Brønsted), and quantity of $(\text{SiOH})_x$ groups confined within zeolite pores. Introducing a high density of $(\text{SiOH})_x$ defects to the Lewis acidic zeolite (i.e., Zr-BEA-OH) facilitates $\text{C}_4\text{H}_8\text{O}$ ring-opening rates by ~ 10 times compared to the low density $(\text{SiOH})_x$ counterpart (i.e., Zr-BEA-F). Measurements of activation barriers, $\text{C}_4\text{H}_8\text{O}$ adsorption enthalpies, and intrapore solvent compositions provide evidence that the disruption of networked solvent molecules within Zr-BEA-OH confers entropic gains to the transition state for ring-opening. This strong effect of $(\text{SiOH})_x$ nests on turnover rates over Lewis acidic zeolites corresponds to previous reports for alkene epoxidation^{72, 74-76, 78, 258, 264} and glucose isomerization,^{132, 135-137, 289} where $(\text{SiOH})_x$ groups stabilize hydrogen-bonded solvent structures that increase and decrease rates, respectively.

In contrast to the Lewis acids, Al-BEA-OH and Al-BEA-F show similar ring-opening rates (within a factor of 2), activation barriers, and solvent compositions across all conditions examined. These trends align with previous studies that Brønsted acid zeolites of different $(\text{SiOH})_x$ density provide rate constants for ethanol dehydration⁹⁹ and rates for glucose acetalization³⁰² within a factor of 2 in a condensed phase. Taking this work together with previous studies, the interactions between solvent molecules and $(\text{SiOH})_x$ nests in zeolites can strongly influence the kinetics of a variety of liquid phase catalytic reactions over Lewis acid sites but generally have a weak effect on kinetics over Brønsted acid sites. The Brønsted acid protons likely lessen the effect of $(\text{SiOH})_x$ on the solvent environment near active sites, while the density of $(\text{SiOH})_x$ groups likely governs differences in solvent structure among the Zr-BEA materials. Interestingly, regioselectivities depend weakly on $(\text{SiOH})_x$ density for Al- and Zr-BEA, instead showing strong dependences on the acid type and reaction solvent composition. Therefore, different combinations of variables drive changes in rates and regioselectivities for ring-opening, providing opportunities to control these important reaction parameters independently. Evidently, the choices of zeolite acid type, intrapore $(\text{SiOH})_x$ density, and solvent carry strong consequences and warrant consideration during the design of catalysis and adsorption processes at zeolite-liquid interfaces.

CHAPTER 6

CONCLUSIONS AND FUTURE DIRECTIONS

6.1 Introduction

Alkene epoxidation and epoxide ring-opening reactions work in tandem to produce important intermediates for many fine and commodity chemicals. These reactions depend sensitively on the covalent and non-covalent interactions between reactive species, active sites, and solvent molecules at solid-liquid interfaces. Altering the alkyl chain length of the alkene reactant demonstrates that the displacement of hydrogen-bonded solvent molecules drives greater epoxidation rates with H_2O_2 within hydrophilic, $(\text{SiOH})_x$ -rich titanium-incorporated zeolites compared to their hydrophobic counterparts. In particular, the disruption of confined water molecules during transition state formation provides an entropic gain that overwhelms the corresponding enthalpic penalty. Increasing the concentration of water further facilitates selective alkene epoxidation processes by increasing epoxidation rates while simultaneously decreasing rates of the undesired H_2O_2 decomposition pathway. The subsequent epoxide ring-opening reaction also depends sensitively on the intrapore environment in zeolites. The rates and regioselectivities of epoxide ring-opening with alcohols depend on the active metal, acid type, solvent composition, and $(\text{SiOH})_x$ density. Rates in Lewis acid zeolites increase with the $(\text{SiOH})_x$ density of the zeolite pores and the electronegativity of the active metal atoms. Compared to Lewis acids, Brønsted acid zeolites show consistently greater regioselectivities to terminal alcohol products over terminal ethers, likely due to the formation of protonated epoxide intermediates that facilitate nucleophilic attack at the more substituted epoxide carbon. Manipulating the properties of the zeolite and reaction mixture alters the intrapore environment during liquid-phase catalysis,

thereby providing opportunities to control rates and selectivities for alkene epoxidation and epoxide ring-opening.

Chapter 2 utilized experimental kinetic measurements, adsorption enthalpies, and solvent adsorption together with grand canonical molecular dynamics (GCMD) simulations to demonstrate the significance of excess contributions originating from solvent displacement during the epoxidation of alkenes of varying size with H_2O_2 . Despite apparently identical reaction mechanisms for all cases, hydrophilic Ti-BEA-OH provides rates 40-450 times greater than hydrophobic Ti-BEA-F across the range of alkenes in the presence of 200 mM H_2O . Apparent barriers ($\Delta H_{app}^\ddagger$, $\Delta S_{app}^\ddagger$) increase with the carbon number of the alkene, density of $(\text{SiOH})_x$ groups, and quantity of intrapore hydrogen-bonding solvent molecules (CH_3CN and H_2O). Epoxide adsorption enthalpies correlate linearly with $\Delta H_{app}^\ddagger$, suggesting that longer alkyl chains disrupt more solvent molecules (H_2O or CH_3CN). Radial distribution functions of solvent molecules and Born-Haber analysis of adsorption enthalpy contributions from GCMD show that the observed enthalpy differences primarily stem from the displacement of hydrogen-bonded solvent molecules from the Ti-BEA pores to the liquid-phase. These conclusions suggest that the free energy changes from solvent displacement drive greater rates in Ti-BEA-OH through entropic gains provided to the transition state.

Chapter 3 reveals the strong role of the organic solvent choice and H_2O fraction on the rates and selectivities of C_6H_{12} epoxidation in Ti-BEA zeolites of varying $(\text{SiOH})_x$ density. Greater mole fractions of H_2O lead to increases in epoxidation turnover rates while H_2O_2 decomposition rates decrease within acetonitrile, methanol, and gamma-butyrolactone co-solvents, leading to greater selectivities of H_2O_2 toward epoxidation at higher H_2O fractions. The reversibility of H_2O_2 activation changes with the choice of organic solvent identity and H_2O fraction. However, the

mechanism and rate-determining step for alkene epoxidation or H_2O_2 decomposition do not change among solvents or catalysts. The normalization of rates by reactant activities and the measurement of activation barriers show that the change in rates and selectivities instead originate from the H_2O fraction altering the $G^\ddagger$ values of reactive species for C_6H_{12} epoxidation and H_2O_2 decomposition in different ways. Greater rates of C_6H_{12} epoxidation at higher H_2O fractions originate from the destabilization of liquid-phase C_6H_{12} and the entropic stabilization of the hydrophobic epoxidation transition state. On the other hand, the decreased rates of H_2O_2 decomposition at higher H_2O fractions suggest that H_2O stabilizes fluid phase H_2O_2 and the Ti-OOH intermediate to a greater degree than the hydrophilic decomposition transition state.

Chapter 4 explores the influence of the active metal within zeolites and intrapore solvent environment on rates and regioselectivities for epoxide ring-opening reactions. Rate dependences on reactant concentrations suggest that both Lewis and Brønsted acids can catalyze ring-opening through a CH_3OH - or $\text{C}_4\text{H}_8\text{O}$ -derived intermediate species, although reaction through a $\text{C}_4\text{H}_8\text{O}$ -derived intermediate species dominates over the Brønsted acid. Rates among Lewis acids increase with the functional Lewis acidity of the metal active sites, correlating with decreases in activation enthalpies and increases in reactant adsorption enthalpies that suggest an increased stabilization of the ring-opening transition state. Greater quantities of $[\text{CH}_3\text{OH}]$ lead to increases in both activation enthalpies and entropies, demonstrating that the disruption of CH_3OH molecules provides entropy increases to the transition state. Regioselectivities toward the terminal ether product exceed 50% under most conditions, although changes in the solvent composition provide opportunities to alter regioselectivity. Selectivity towards the terminal ether generally decreases with increasing $[\text{CH}_3\text{OH}]$ over each M-BEA. Al-BEA consistently gives lower regioselectivities to the terminal

ether than the Lewis acids. Activation barrier differences between products demonstrate an increased enthalpic preference to form the terminal alcohol in CH₃OH-rich environments.

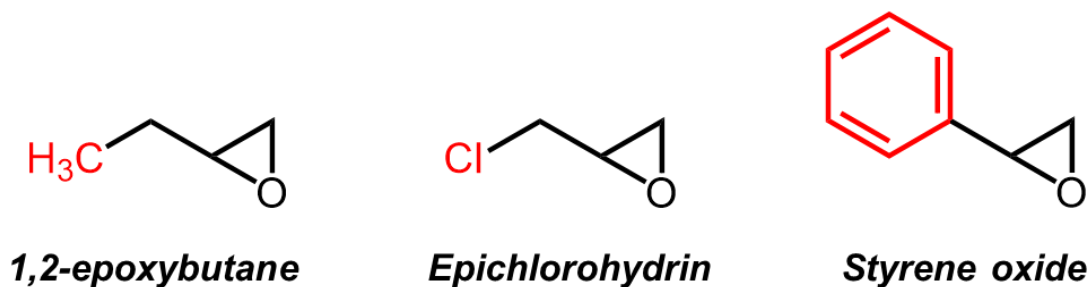
Chapter 5 explores how the interplay of solvent molecules, acid sites (Lewis or Brønsted), and (SiOH)_x groups within zeolite pores affect epoxide ring-opening. Hydrophilic (Al-BEA-OH) and hydrophobic (Al-BEA-F) Brønsted acids show rates within a factor of two that appear to originate from similar activation barriers and intrapore solvent compositions. In contrast, hydrophilic Lewis acid zeolites (Zr-BEA-OH) show ring-opening rates ~10 times greater than hydrophobic Lewis acid (Zr-BEA-F). Zr-BEA-OH adsorbs greater quantities of hydrogen-bonded solvent molecules, which are disrupted by the ring-opening transition state and provide entropy increases that overwhelm the accompanying enthalpic penalty. The different trends between acid types suggest that the density of (SiOH)_x groups leads to significant differences in the solvent environment within Lewis acid zeolites, while the Brønsted acid protons negate the effect of nearby (SiOH)_x on the solvent structure near active sites. The regioselectivity shows strong dependences on the acid type and solvent composition but varies weakly with (SiOH)_x density, demonstrating that altering the properties of the catalyst and reaction system can allow for independent control of the ring-opening rate and product distribution.

To summarize, the work in this dissertation utilizes a suite of kinetic, spectroscopic, calorimetric, and synthesis techniques to demonstrate how to manipulate covalent and non-covalent interactions within liquid-filled zeolite pores to facilitate desired reaction pathways during both alkene epoxidation and epoxide ring-opening. The lessons learned in these chapters inform the design of more sustainable and selective chemical reactions at solid-liquid interfaces.

6.2 Future Directions

6.2.1 Mechanistic Origins of Regioselectivity Differences for Epichlorohydrin Ring-Opening

Conventional organic chemistry principles suggest that the intrinsic structure and functional groups of the participating epoxides and nucleophiles limit the range of possible regioselectivities for epoxide ring-opening reactions.^{280, 303} Unfunctionalized terminal aliphatic epoxides (e.g., 1,2-epoxybutane in **Scheme 6.1**) give selectivities of 50-60% toward the terminal ether during reactions with alcohol nucleophiles,^{57, 63, 267, 278} and the slight preference to form the terminal ether purportedly originates from the steric hindrance that affects nucleophilic attack at the internal epoxide carbon. Manipulations to the catalyst structure and solvation environment extend the selectivity range for terminal aliphatic epoxides to 20-80% for the terminal ether, as demonstrated for 1,2-epoxyoctane ring-opening over fluorinated aryl borane catalysts⁸¹⁻⁸² and 1,2-epoxybutane over zeolites (**Chapters 4 and 5**). In contrast, the ring-opening of styrene oxide with alcohols predominantly gives >90% selectivity to the terminal alcohol product because the electron-donating phenyl group stabilizes positive charge on the internal epoxide carbon during nucleophilic attack.^{103, 304-306} Similar logic proposes that epichlorohydrin (C_3H_5ClO) undergoes nucleophilic ring-opening to give >90% selectivity toward the terminal ether because the electron-withdrawing chlorine atom destabilizes positive charge at the transition state.^{63, 307-309} Brønsted and Lewis acid catalysts provide similar regioselectivities for the ring-opening of epichlorohydrin



Scheme 6.1. Structures for 1,2-epoxybutane (a representative aliphatic epoxide with terminal methyl group), epichlorohydrin, and styrene oxide.

and styrene oxide, but the functional groups on these epoxides largely restrict the possible distribution of regioisomers. Based on our prior work with this chemistry, we anticipate that differences between free energies of ring-opening transition states for the terminal alcohol and terminal ether product cause these trends. However, tests of this hypothesis require knowledge of the reaction mechanism, insight into reaction intermediates within the pores, and quantitative measures of turnover rates, apparent barriers, and regioselectivities following systematic variations in catalyst and solvent properties. Here, we propose to examine C_3H_5ClO ring-opening with CH_3OH over Brønsted (Al-BEA-OH) and Lewis acid (Sn-BEA-OH) zeolites to develop design principles for how to control regioselectivities regardless of epoxide structure and functionality.

Figure 6.1 demonstrates that the formation rates of the terminal ether (TE) and terminal alcohol (TA) depend on the reactant concentrations and active metal within *BEA during C_3H_5ClO ring-opening. Rates over Sn-BEA-OH exceed those over Al-BEA-OH at nearly all conditions,

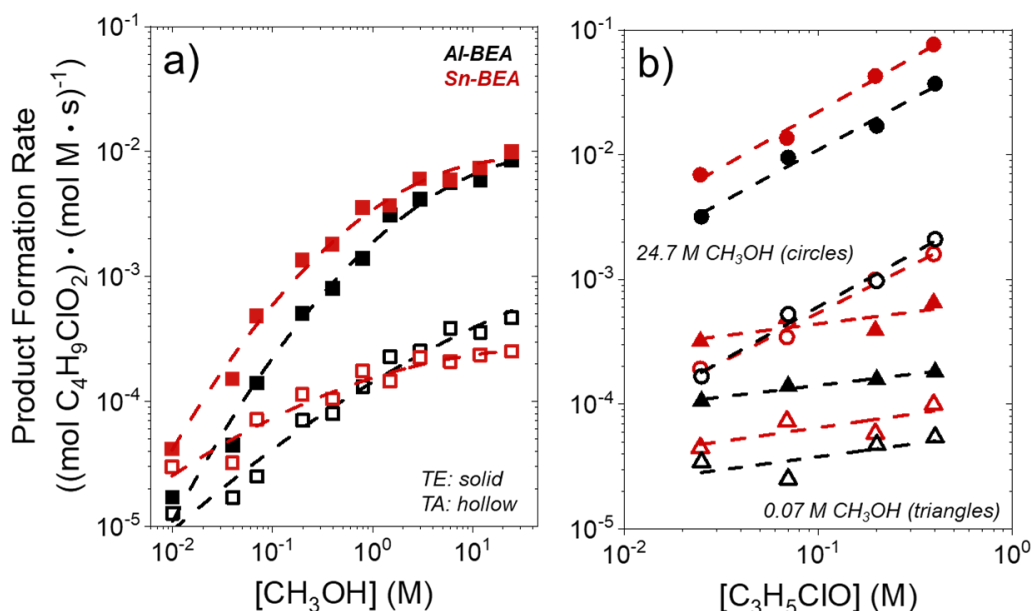


Figure 6.1. Formation rates of the terminal ether (solid points) and terminal alcohol (hollow) products for C_3H_5ClO ring-opening with CH_3OH as a function of a) CH_3OH concentration (0.07 M C_3H_5ClO , CH_3CN , 308 K) and b) C_3H_5ClO concentration (triangles – 0.07 M CH_3OH , circles – 24.7 M CH_3OH , CH_3CN , 308 K) over Al- (black) and Sn-BEA (red).

Catalyst	[CH ₃ OH]:[C ₃ H ₅ ClO] < 15		[CH ₃ OH]:[C ₃ H ₅ ClO] > 30	
	TE	TA	TE	TA
Al-BEA	[CH ₃ OH] ^{1.05}	[CH ₃ OH] ^{0.58}	[CH ₃ OH] ^{0.29}	[CH ₃ OH] ^{0.24}
	[C ₃ H ₅ ClO] ^{0.14}	[C ₃ H ₅ ClO] ^{0.19}	[C ₃ H ₅ ClO] ^{0.77}	[C ₃ H ₅ ClO] ^{0.83}
Sn-BEA	[CH ₃ OH] ^{0.99}	[CH ₃ OH] ^{0.45}	[CH ₃ OH] ^{0.19}	[CH ₃ OH] ^{0.10}
	[C ₃ H ₅ ClO] ^{0.16}	[C ₃ H ₅ ClO] ^{0.22}	[C ₃ H ₅ ClO] ^{0.83}	[C ₃ H ₅ ClO] ^{0.80}

Table 6.1. Formation Rate Orders of TE and TA for C₃H₅ClO ring-opening from **Figure 6.1**.

with a maximum difference of 5 times in the regime of low [CH₃OH]. The greater rates over Sn-BEA-OH align with the observed trends for C₄H₈O ring-opening, where Sn-BEA also showed greater rates than Al-BEA at nearly all conditions (**Chapter 4**). Both materials show similar product formation rate dependencies on reactant concentrations, with rate trends that suggest both materials feature kinetic regimes with C₃H₅ClO- or CH₃OH-derived species saturating active sites.

Table 6.1 reveals that the TE formation rate depends more strongly on [CH₃OH] than TA, and the largest difference between the dependence of TE and TA rates (0.5 – 0.6) appears at lower ratios of [CH₃OH] to [C₃H₅ClO] (values < 15). The reaction order behavior starkly contrasts with that for C₄H₈O ring-opening, where the formation rates of the TE and TA products exhibit very similar dependence on [CH₃OH] (**Appendix C6**). Formation rates of TE and TA products show nearly identical dependence on [C₃H₅ClO], which agrees with the observed dependence of rates for TE and TA on [C₄H₈O] during ring-opening of 1,2-epoxybutane. The differences in the TE and TA formation rates on [CH₃OH] for C₃H₅ClO ring-opening suggests that the two products may form by distinct mechanisms or *via* uniquely structured reactive intermediates, which leads to significant differences in reaction regioselectivity as [CH₃OH] changes. The ratio of the formation rates of the terminal ether to terminal alcohol (β) predicts these regioselectivity changes at both low (< 15, **Equation 6.1**) and high (> 30, **Equation 6.2**) [CH₃OH]:[C₃H₅ClO] values:

$$\beta = \frac{r_{TE}}{r_{TA}} = \frac{k_{4,1C} [CH_3OH]^1 [C_3H_5ClO]^{0.15}}{k_{4,2C} [CH_3OH]^{0.5} [C_3H_5ClO]^{0.2}} \quad (6.1)$$

$$\beta = \frac{r_{TE}}{r_{TA}} = \frac{k_{5,1C} [CH_3OH]^{0.25} [C_3H_5ClO]^{0.8}}{k_{5,2C} [CH_3OH]^{0.15} [C_3H_5ClO]^{0.8}} \quad (6.2)$$

where k_x values represent rate constants from the rate-determining steps shown in **Scheme 5.2**.

Figure 6.2a presents the ratio of the formation rates of the terminal ether to terminal alcohol (β) as a function of $[CH_3OH]$ for C_3H_5ClO ring-opening, revealing that the preference to form the TE product increases strongly with increasing $[CH_3OH]$. In the absence of the CH_3CN co-solvent (24.7 M CH_3OH), Sn-BEA-OH and Al-BEA-OH show β values of 40 and 18, respectively. These values align with previously achieved regioselectivities for C_3H_5ClO ring-opening with CH_3OH in the absence of a co-solvent over Al- and Sn-BEA zeolites.⁶³ Values of β decrease steadily with decreasing $[CH_3OH]$ (i.e., larger fraction of CH_3CN co-solvent) and give nearly identical β values for Sn-BEA-OH (1.4) and Al-BEA-OH (1.2), corresponding to similar

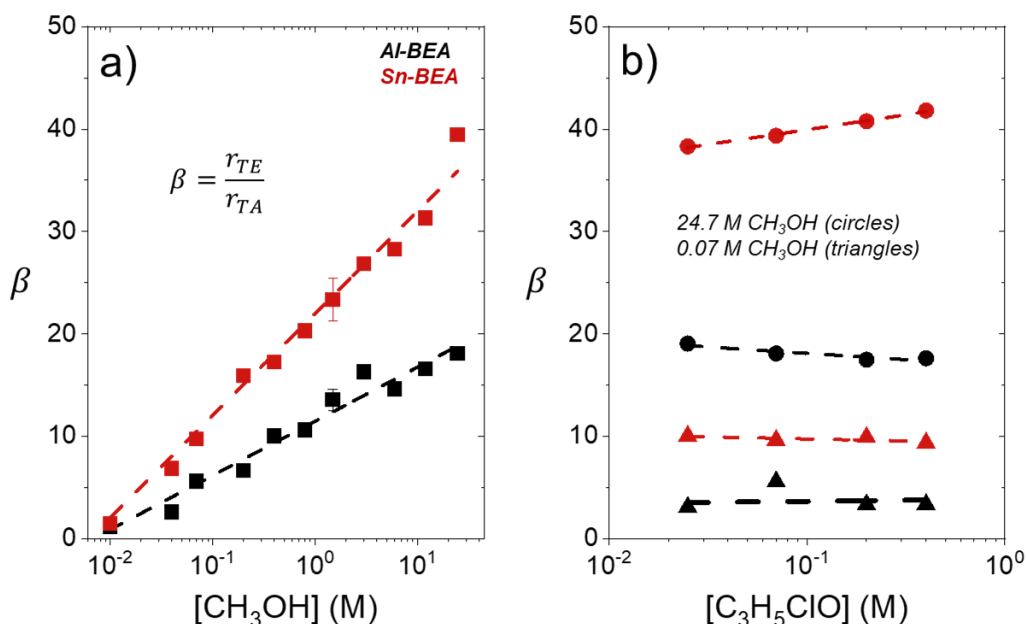


Figure 6.2. Values of β for C_3H_5ClO ring-opening with CH_3OH as a function of a) CH_3OH concentration (0.07 M C_3H_5ClO , CH_3CN , 308 K) and b) C_3H_5ClO concentration (triangles – 0.07 M CH_3OH , circles – 24.7 M CH_3OH , CH_3CN , 308 K) over Al- (black) and Sn-BEA (red).

likelihood to form either TE or TA, at the lowest $[\text{CH}_3\text{OH}]$ studied (0.01 M CH_3OH). In contrast to the strong effect of $[\text{CH}_3\text{OH}]$, β changes negligibly with $[\text{C}_3\text{H}_5\text{ClO}]$ when ratios of $[\text{CH}_3\text{OH}]$ to $[\text{C}_3\text{H}_5\text{ClO}]$ fall below two on either Sn-BEA-OH or Al-BEA-OH. Yet, β yields a weak positive dependence on $[\text{C}_3\text{H}_5\text{ClO}]$ over Sn-BEA-OH and weak negative dependence with $[\text{C}_3\text{H}_5\text{ClO}]$ over Al-BEA-OH at higher $[\text{CH}_3\text{OH}]$ to $[\text{C}_3\text{H}_5\text{ClO}]$ ratio (> 60). Overall, β depends much more strongly on values of $[\text{CH}_3\text{OH}]$ than $[\text{C}_3\text{H}_5\text{ClO}]$. These trends indicate that the regioselectivity of $\text{C}_3\text{H}_5\text{ClO}$ ring-opening responds to either selective solvation of transition states for distinct regioisomers or that the regioisomers form through distinct mechanisms or differently structured intermediates.

Figure 6.3 presents *in situ*, solid-state ^1H -enhanced cross-polarization (CP) ^{13}C NMR spectra that reveal the adsorption structures of CH_3OH and $\text{C}_3\text{H}_5\text{ClO}$ on the surface of Al-BEA-OH. **Figure 6.3a** shows that $^{13}\text{CH}_3\text{OH}$ adsorbed to Al-BEA-OH gives peak locations that align with previous proposals³¹⁰⁻³¹² for CH_3OH -derived structures: physisorbed to Si-O features (green, 49.9 ppm), chemisorbed CH_3OH at Brønsted acid sites (yellow, 51.7 ppm), and protonated CH_3OH at Brønsted acid sites (60.6 ppm). Physisorbed CH_3OH likely does not act as a reactive intermediate because purely siliceous *BEA materials provide much lower epoxide ring-opening rates than Lewis or Brønsted acid *BEA zeolites (see **Table D5**). The protonation of CH_3OH reduces its nucleophilicity, making protonated CH_3OH an unlikely reactive intermediate for ring-opening as well. With the other options ruled out, chemisorbed CH_3OH may represent the reactive surface intermediate for the ring-opening of $\text{C}_3\text{H}_5\text{ClO}$.

Figure 6.3b reveals that $^{13}\text{C}_3\text{H}_5\text{ClO}$ forms ring-opened carbocations upon adsorption to the Brønsted acid sites. DFT-predicted chemical shifts (Amsterdam Density Functional³¹³) agree with the observed peak locations for both the primary (~ 45 ppm, 69-75 ppm) and secondary (~ 44 ,

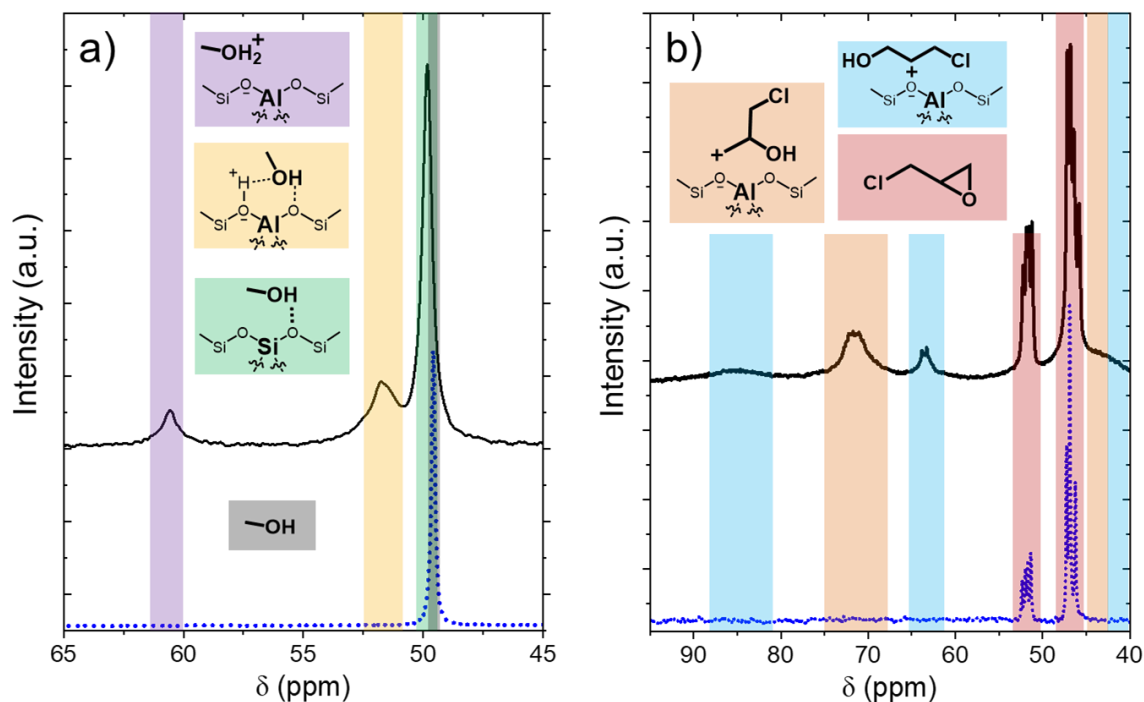


Figure 6.3. ^{13}C NMR cross-polarization spectra (black lines) of a) $^{13}\text{CH}_3\text{OH}$ on Al-BEA-OH (0.2 M $^{13}\text{CH}_3\text{OH}$, CH_3CN , 298 K, 5.5 hr), and b) $^{13}\text{C}_3\text{H}_5\text{ClO}$ on Al-BEA-OH (0.2 M $^{13}\text{C}_3\text{H}_5\text{ClO}$, CH_3CN , 298 K, 4 hr). Times report the span between acquisition of the NMR spectra and the initial contact between the liquid solution and the Al-BEA-OH material. Blue dotted lines show the single-pulse spectra for $^{13}\text{CH}_3\text{OH}$ and $^{13}\text{C}_3\text{H}_5\text{ClO}$ in the absence of Al-BEA-OH.

63, 85 ppm) carbocation bound at Brønsted acid sites. While the CP spectra predominantly reveal chemically bound surface species, the appearance of sharp features, such as those at 45-48 ppm and 51-52 ppm, indicate a liquid-phase $\text{C}_3\text{H}_5\text{ClO}$ near the surface. The same features (45-48 ppm and 51-52 ppm) also appear on the single-pulse (SP) ^{13}C -NMR spectra shown with the dotted blue line, which show liquid-phase and surface species with equal sensitivity. Upon contacting the solution mixture with Al-BEA-OH, the features representing the liquid-phase $\text{C}_3\text{H}_5\text{ClO}$ do not broaden in the CP (**Figure 6.3b**) nor SP spectra (**Figure E1b**). The lack of broadening or peak-shifting of the $\text{C}_3\text{H}_5\text{ClO}$ features suggests that $\text{C}_3\text{H}_5\text{ClO}$ does not adsorb to the zeolite surface as an intact molecule.³¹⁴ Instead, $\text{C}_3\text{H}_5\text{ClO}$ readily forms ring-opened carbocations upon adsorption to the Brønsted acid sites, with no other forms of adsorbed $\text{C}_3\text{H}_5\text{ClO}$ apparent from the NMR

spectra. Based on the areas of the terminal ether (69-75 ppm) and terminal alcohol (63, 85 ppm) peaks not convoluted with $\text{C}_3\text{H}_5\text{ClO}$ features, the ratio of primary to secondary carbocations on the surface equals ~ 1.3 .

Figure 6.4 presents changes in concentrations of reactants, products, and surface intermediates during the ring-opening of $^{13}\text{C}_3\text{H}_5\text{ClO}$ with CH_3OH over Al-BEA-OH at low $[\text{CH}_3\text{OH}]$ (0.2 M CH_3OH) derived from ^{13}C NMR single-pulse spectra (see **Figure E1**). **Figure 6.4a** shows the growth of activated CH_3OH species (chemisorbed and protonated CH_3OH) on the surface before adding $\text{C}_3\text{H}_5\text{ClO}$. After adding $\text{C}_3\text{H}_5\text{ClO}$ to initiate the reaction, the concentration of $\text{C}_3\text{H}_5\text{ClO}$ steadily decreases while the concentrations of the ring-opened carbocations and products increase. While the epoxide features prevent tracking the concentration of the chemisorbed CH_3OH species (gold points) after adding the epoxide, the concentration of protonated CH_3OH decreases over time. The decrease in CH_3OH -derived surface intermediate

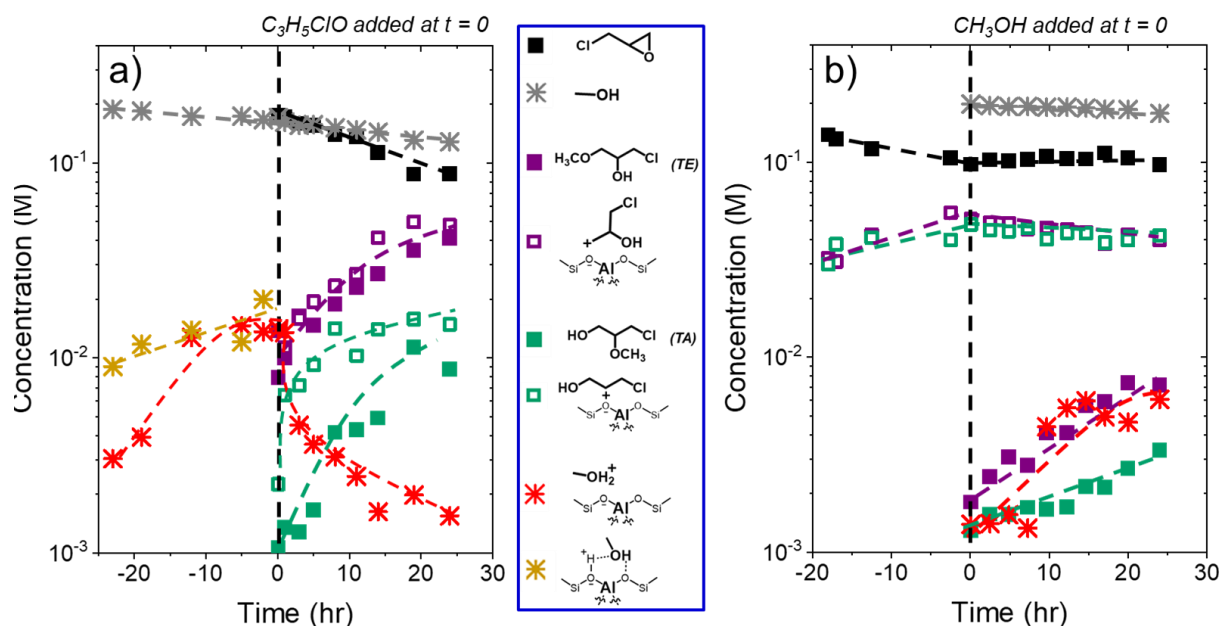


Figure 6.4. Concentration-time profiles derived from ^{13}C NMR single-pulse spectra during ring-opening of $\text{C}_3\text{H}_5\text{ClO}$ with CH_3OH (0.2 M ^{13}C - $\text{C}_3\text{H}_5\text{ClO}$, 0.2 M ^{13}C - CH_3OH , CH_3CN , Al-BEA-OH, 298 K), where reaction was initiated by adding a) ^{13}C - $\text{C}_3\text{H}_5\text{ClO}$ or b) ^{13}C - CH_3OH to the NMR rotor after pre-mixing all other components. Epoxide features convolute chemisorbed CH_3OH (gold points), preventing those features from being tracked in presence of the epoxide.

concentration with time may indicate that these species react with $\text{C}_3\text{H}_5\text{ClO}$ to form ring-opening products, or that the CH_3OH desorbs from the surface to allow $\text{C}_3\text{H}_5\text{ClO}$ to coordinate to the surface. $\text{C}_3\text{H}_5\text{ClO}$ adsorbs much more strongly to the surface than CH_3OH (see **Appendix Section E3**), suggesting that the slow decrease in the concentration of CH_3OH -derived surface species does not simply originate from CH_3OH desorbing to accommodate $\text{C}_3\text{H}_5\text{ClO}$ adsorption. Instead, these CH_3OH -derived species likely react with liquid-phase $\text{C}_3\text{H}_5\text{ClO}$ to form ring-opened products, with the chemisorbed CH_3OH species acting as the primary reactive intermediate during ring-opening (*vide supra*). Interestingly, the concentrations of TE and the primary ring-opened carbocation increase simultaneously, while TA concentrations do not increase significantly until the secondary ring-opened carbocation begins to accumulate on the surface. This distinction may simply indicate that the more stable secondary carbocation reacts less readily with CH_3OH -derived species than primary carbocations. Alternatively, the more rapid initial accumulation of TE may suggest that TE formation does not require formation of the primary carbocation as a pre-requisite.

Figure 6.4b reveals that initiating the reaction by adding CH_3OH reduces the rate of product formation by an order of magnitude compared to **Figure 6.4a**. Prior to the addition of CH_3OH , $\text{C}_3\text{H}_5\text{ClO}$ ring opens to form both primary and secondary carbocations on the surface. The TE and TA products appear in tandem with the formation of protonated CH_3OH on the surface. These data provide evidence that the formation of ring-opened carbocations after $\text{C}_3\text{H}_5\text{ClO}$ adsorption at the Brønsted acid sites hinders the adsorption of CH_3OH , suppressing the reaction rate. The reaction can likely still proceed with intact CH_3OH as the nucleophile but will proceed at a slower rate than with adsorbed or activated CH_3OH . The formation of ring-opened carbocations on the surface hinders the adsorption of CH_3OH , suppressing the reaction rate.

Organic chemistry literature proposes that epoxide ring-opening reactions proceed either through a concerted bimolecular substitution (S_N2) pathway where the nucleophile attacks the intact epoxide or through a stepwise monomolecular (S_N1) pathway in which protonation of the epoxide either forms partial positive charges or fully opens the epoxide ring before nucleophile attack.^{268, 280, 315} An S_N2 pathway yields the following rate expressions under conditions where C_3H_5ClO -derived (**Equation 6.3**) or CH_3OH -derived (**Equation 6.4**) species saturate the active sites in Al-BEA-OH.

$$r_{RO,S_N2} = k[CH_3OH]^1[C_3H_5ClO]^0 \quad (6.3)$$

$$r_{RO,S_N2} = k[CH_3OH]^0[C_3H_5ClO]^1 \quad (6.4)$$

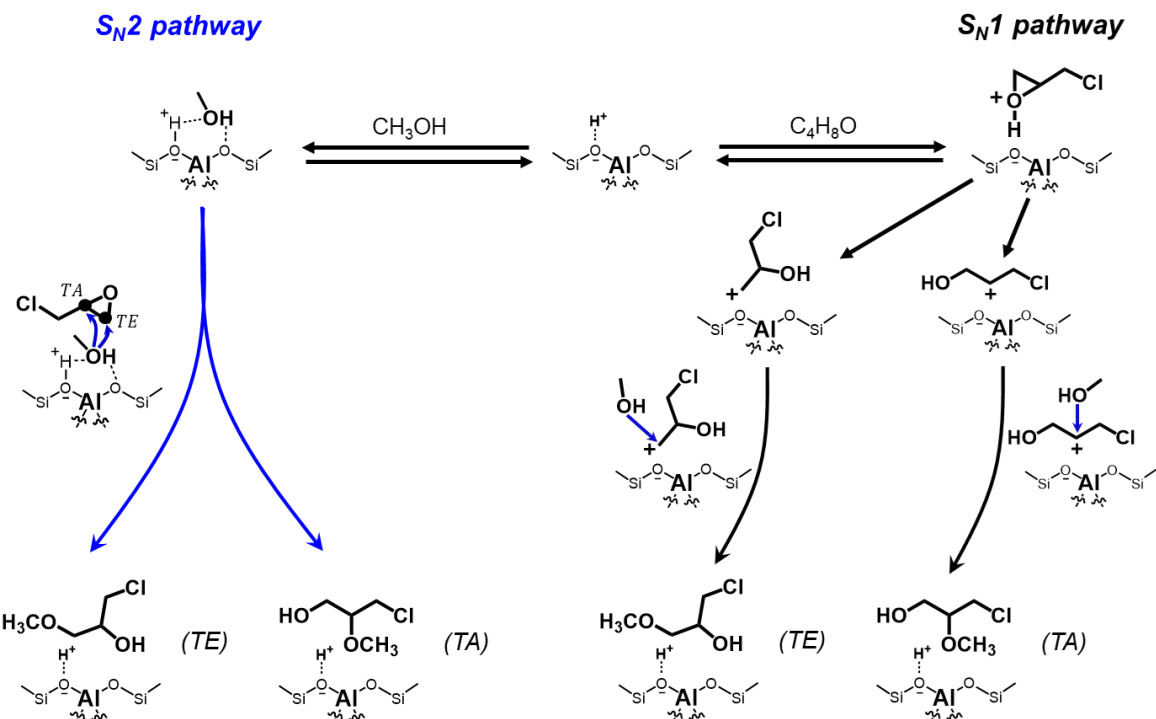
On the other hand, an S_N1 pathway does not show a rate dependence on $[CH_3OH]$ regardless of whether intermediates originating from C_3H_5ClO (**Equation 6.5**) or CH_3OH (**Equation 6.6**) saturate the surface:

$$r_{RO,S_N1} = k[CH_3OH]^0[C_3H_5ClO]^0 \quad (6.5)$$

$$r_{RO,S_N1} = k[CH_3OH]^0[C_3H_5ClO]^1 \quad (6.6)$$

The reaction orders from **Table 6.1** do not directly match the expectation from S_N1 or S_N2 pathways, suggesting that the reaction does not strictly proceed through a single pathway. Al-BEA-OH may catalyze ring-opening through S_N1 or S_N2 pathways, with the dominant pathway depending on what intermediates saturate active sites.

Motivated by the past mechanistic proposals and the evidence from kinetics (**Figures 6.1** and **6.2**) and the ^{13}C NMR spectra (**Figures 6.3** and **6.4**), **Scheme 6.2** presents speculative steps for the ring-opening of C_3H_5ClO with CH_3OH over Al-BEA-OH. C_3H_5ClO may adsorb to form a protonated complex at the Brønsted acid sites, which readily ring-open to form primary and



Scheme 6.2. Plausible product-forming steps for ring-opening of C_3H_5ClO with CH_3OH over Al-BEA-OH. Reaction may proceed through a concerted S_N2 pathway with an activated CH_3OH intermediate (blue) or a stepwise S_N1 pathway in which the epoxide ring-opens to form carbocations, followed by adsorption and activation of CH_3OH (black).

secondary carbocations. CH_3OH then adsorbs to react with the carbocations and form the products. These steps mirror typical proposals for an S_N1 ring-opening pathway.^{268, 280, 315} Alternatively, CH_3OH may activate to form a chemisorbed or protonated complex at the Brønsted acid sites. These intermediates may then attack an intact C_3H_5ClO molecule to form the products through an S_N2 mechanism. The S_N2 pathway matches literature proposals for ring-opening under basic or neutral conditions, but proposals under acidic conditions (i.e., H^+ present) that suggest the reaction must proceed through an S_N1 pathway with a protonated epoxide intermediate.^{268, 280, 315} The kinetic and spectroscopic data from **Figures 6.1 to 6.4** give evidence that Brønsted acids may catalyze ring-opening through either the expected C_3H_5ClO -derived intermediate or a CH_3OH -derived species.

The regioselectivity of S_N1 reaction pathways depends primarily on the ring-opened carbocation that forms.^{63, 268, 270} The S_N1 pathway for C₃H₅ClO ring-opening (**Scheme 6.2**) likely dominates at low [C₃H₅ClO]:[CH₃OH] ratios, in which C₃H₅ClO can saturate the Brønsted acid sites. The distribution of cations in **Figures 6.3** and **6.4** suggest that TE and TA form at similar rates through the S_N1 pathway, which aligns with β values near one at the lowest [CH₃OH] studied (**Figure 6.2**). Of note, the β value predicted from the ratio of carbocations (~1.3) falls below the β value (~2.7) from the product formation rate in **Figure 6.4b**. This distinction may suggest that the greater stability of the secondary ring-opened carbocation lowers its reactivity to form TA, meaning that β depends on both the abundance and reactivity of the ring-opened carbocations. Nevertheless, the kinetic and spectroscopic data suggest that the ratio of primary to secondary ring-opened carbocations at Brønsted acid sites drives β differences at low [C₃H₅ClO]:[CH₃OH] ratios.

The regioselectivity of S_N2 pathways depends on the steric hindrance during the rate-determining nucleophilic attack step.^{63, 268, 270} The S_N2 pathway in **Scheme 6.2** likely prevails at greater [C₃H₅ClO]:[CH₃OH] ratios, where CH₃OH-derived intermediates form at the Brønsted acid sites. An S_N2 reaction should, therefore, prefer to form TE because of the greater steric hindrance associated with the nucleophilic attack at the interior epoxide carbon to form TA. This interpretation aligns with the increasing β values as [CH₃OH] increases in **Figure 6.2**. While we hypothesize that steric effects govern the significant preference for TE, we do not rule out that differences in solvation and hydrogen bonding preferentially stabilize the transition state to form TE over TA at higher [CH₃OH] values. Nevertheless, the data from **Figures 6.1** to **6.4** supports that adding greater fractions of CH₃OH increases the quantity of activated CH₃OH intermediates on the Al-BEA-OH surface, which promotes the S_N2 pathway that favors TE formation.

Overall, the kinetic and spectroscopic data provide strong evidence for the mechanistic origins of regioselectivity differences for $\text{C}_3\text{H}_5\text{ClO}$ ring-opening over Al-BEA-OH. Ongoing work in this study aims to establish similar connections for Sn-BEA-OH, utilize NMR spectra at greater $[\text{CH}_3\text{OH}]$ to validate the mechanistic proposals and prevalence of pathways with $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ character, and measure activation barriers to gain further mechanistic understanding.

6.2.2 Effect of Organic Solvent Structure and Polarity on $\text{C}_4\text{H}_8\text{O}$ Ring-Opening with CH_3OH

The results presented in **Chapters 4 and 5** show that differences in the intrapore solvent structure, induced by changes in the fraction of CH_3CN co-solvent and zeolite $(\text{SiOH})_x$ density, lead to significant differences in rates and regioselectivities for $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH . The choice of organic solvent can also influence the kinetics of reactions at solid-liquid interfaces by altering the stability of reactive species, as previously demonstrated for alkene epoxidation,^{258, 264, 316} hydrogenation of carbonyl compounds,³¹⁷⁻³¹⁹ and aldol condensation reactions.³²⁰⁻³²¹ Past studies also investigated different organic co-solvents for epoxide ring-opening with azides,⁷⁹ amines,³²²⁻³²³ and water⁶⁴ over solid catalysts, finding that the choice of co-solvent can lead to differences in rates^{64, 79, 322-323} and regioselectivities.⁷⁹ While these studies demonstrate an evident impact of adding a co-solvent for ring-opening reactions, the literature lacks clear connections to explain how differences in reaction performance correspond to the properties and the composition of the co-solvent present. Here, we propose to strengthen those connections by investigating $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH over Sn-BEA zeolite in the presence of co-solvents with distinct polarities and structures: a short-chain nitrile (acetonitrile, ACN, CH_3CN), longer-chain ether (1,2-dimethoxyethane, DME, $\text{C}_4\text{H}_{10}\text{O}_2$), and cyclic ether (1,4-dioxane, DIOX, $\text{C}_4\text{H}_8\text{O}_2$).

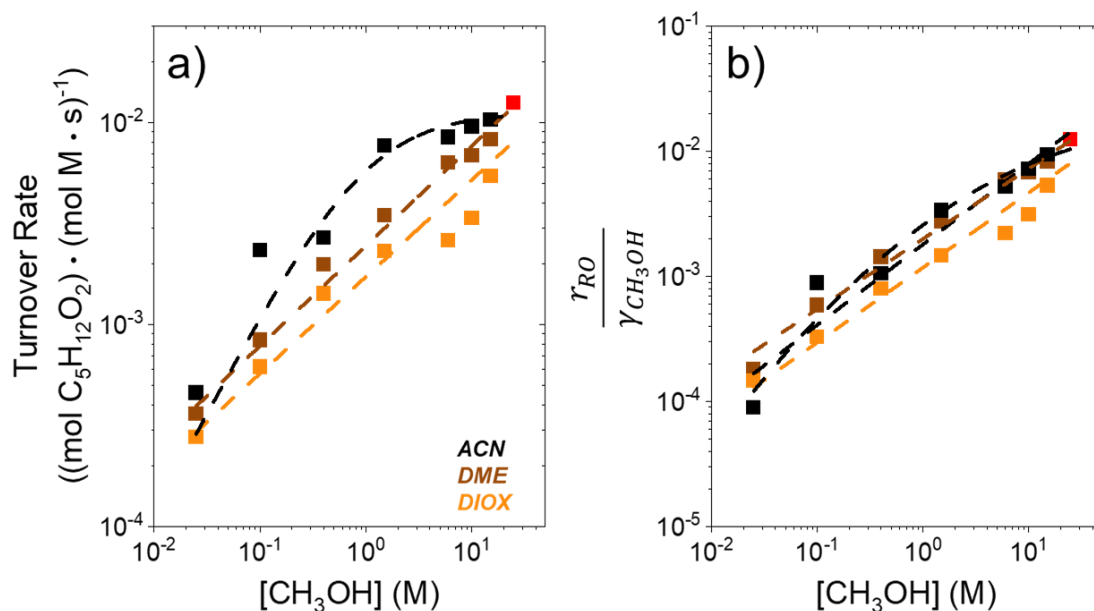


Figure 6.5. a) Turnover rates and b) turnover rates normalized by the activity coefficient of CH_3OH for $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH as a function of CH_3OH concentration (0.005 M $\text{C}_4\text{H}_8\text{O}$, 308 K) with CH_3CN (black), $\text{C}_4\text{H}_{10}\text{O}_2$ (brown), and $\text{C}_4\text{H}_8\text{O}_2$ (orange) co-solvents. Red data points represent neat CH_3OH (24.7 M). Activity coefficients were calculated with the NRTL method on ChemCAD.

Figure 6.5a presents turnover rates for $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH over Sn-BEA in the presence of the different co-solvents. At a given $[\text{CH}_3\text{OH}]$, ACN provides the greatest ring-opening rates, while DIOX provides the lowest rates. Rates fall within a factor of two for all co-solvents when normalized by the activity coefficient of CH_3OH (**Figure 6.5b**), suggesting that nucleophile stability plays a significant role in rate differences between co-solvents. The remaining differences in rates may stem from changes in the stability of adsorbed $\text{C}_4\text{H}_8\text{O}$ or the ring-opening transition states. In ACN co-solvent, rates depend linearly on $[\text{CH}_3\text{OH}]$ at lower $[\text{CH}_3\text{OH}]$ and transition to a zero-order dependence at higher concentrations, implying the transition from a $\text{C}_4\text{H}_8\text{O}$ -covered surface to CH_3OH -covered surface shown over Lewis acids in **Chapters 4** and **5**. In contrast, rates show a linear dependence on $[\text{CH}_3\text{OH}]$ at all concentrations with DME and DIOX as co-solvents, suggesting that $\text{C}_4\text{H}_8\text{O}$ -covered surfaces dominate at all conditions examined. DME

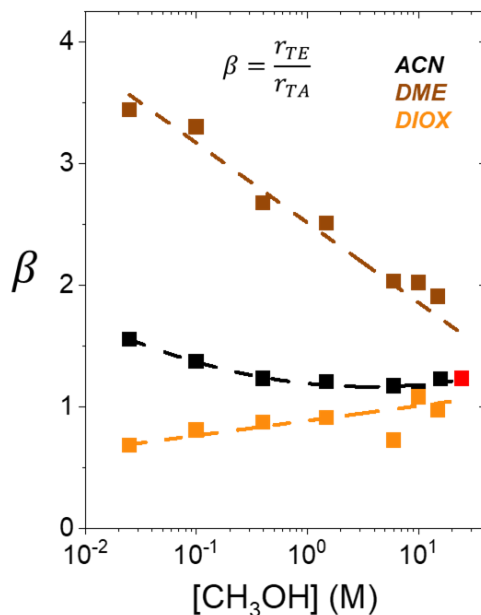
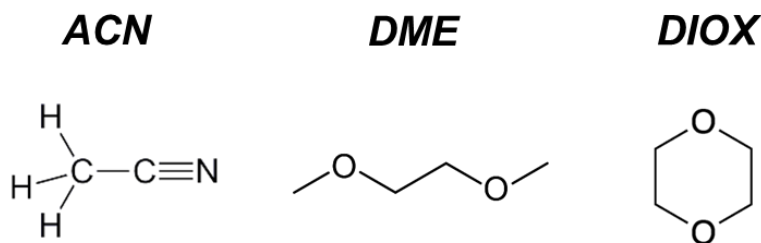


Figure 6.6. Values of β for $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH as a function of CH_3OH concentration (0.005 M $\text{C}_4\text{H}_8\text{O}$, 308 K) with CH_3CN (black, ACN), $\text{C}_4\text{H}_{10}\text{O}_2$ (brown, DME), and $\text{C}_4\text{H}_8\text{O}_2$ (orange, DIOX) co-solvents. Red data points represent neat CH_3OH (24.7 M).

and DIOX may stabilize adsorbed $\text{C}_4\text{H}_8\text{O}$ or destabilize adsorbed CH_3OH relative to ACN, leading to the absence of a CH_3OH -saturated surface regime.

Figure 6.6 reveals that the choice of co-solvent influences both the magnitude and dependence of β values on $[\text{CH}_3\text{OH}]$. In neat CH_3OH , Sn-BEA shows a slight preference for the terminal ether product, 1M2B ($\beta = 1.25$). Adding greater fractions of CAN increases this preference, with a maximum β value of 1.5 at 0.025 M CH_3OH . Replacing CH_3OH with fractions of DME facilitates terminal ether formation to a much greater degree (maximum $\beta = 3.5$ at 0.025 M CH_3OH). In contrast, DIOX co-solvent favors the terminal alcohol product, 2M1B, and lowers β to a minimum of 0.7 at 0.025 M CH_3OH . We propose that these co-solvents lead to different trends of regioselectivities because they stabilize the transition states for the terminal ether and terminal alcohol products to different degrees. **Scheme 6.3** shows that DME possesses terminal ether functional groups and structurally resembles 1M2B, which may promote its formation



Scheme 6.3. Chemical structures of acetonitrile (ACN), 1,2-dimethoxyethane (DME), and 1,4-dioxane (DIOX).

through favorable van der Waals interactions between DME molecules and the 1M2B transition state. In contrast, ACN and DIOX do not structurally resemble either ring-opening product. ACN may promote 1M2B due to the entropic penalty associated with the attack at the hindered interior epoxide carbon during 2M1B formation, as shown in **Chapter 4**. The bulky and nonpolar nature of DIOX may prevent these molecules from forming hydrogen-bonding networks with CH₃OH. Previous homogeneous alcohol dehydration studies found that adding fractions of organic solvents (including DIOX) to water promotes greater local water concentrations around the alcohol reactants than in pure water, leading to increased stabilization of the dehydration transition state and greater reaction rates.²⁰³⁻²⁰⁴ DIOX may similarly promote greater concentrations of CH₃OH self-clustered around the active sites within the pores. A greater concentration of CH₃OH near ring-opening transition states with increasing [DIOX] may decrease β for similar reasons as simply increasing [CH₃OH] within ACN or DME.

Figures 6.5 and 6.6 demonstrate that varying the organic co-solvent provides further opportunities to increase ring-opening rates and regioselectivities towards a desired product. Ongoing work seeks to explain the observed trends with activation barrier and reactant adsorption enthalpy measurements. Furthermore, we aim to extend to Brønsted acid zeolites and investigate organic co-solvents with a wider range of structures and polarities to establish design principles for how the organic solvent environment influences epoxide ring-opening within zeolites.

6.2.3 Understanding the Role of the Nucleophile on C₄H₈O Ring-Opening Regioselectivities

Chapters 4 – 5 and Sections 6.2.1 – 6.2.2 provide insight into how to influence epoxide ring-opening reactions with alcohol nucleophiles. However, many classes of nucleophiles can participate in ring-opening reactions, including water, amines, thiols, and carboxylic acids.^{280, 324} The products from the reactions of epoxides with these varying nucleophiles have wide-ranging applications, underscoring the importance of understanding how to control rates and regioselectivities across different nucleophiles. Previous studies demonstrate that the nucleophile identity can lead to significant differences in the regioselectivity for epoxide ring-opening over heterogeneous catalysts. When reacting with alcohol nucleophiles, epichlorohydrin, terminal aliphatic epoxides, and styrene oxide all show different product distributions. Epichlorohydrin^{63, 103, 308} and styrene oxide^{103, 305-306} show high selectivities to the terminal ether and terminal alcohol products, respectively, while terminal aliphatic epoxides typically give a nearly even product distribution.^{63, 267, 291} In contrast, amine^{65, 325-326} and thiol³²⁷⁻³²⁸ nucleophiles lead to dominant formation of terminal alcohol and terminal ether products, respectively, regardless of the epoxide structure and functional groups. While the reason for the different reported trends among nucleophiles remains unclear, the nucleophile strength and structure have a significant effect on ring-opening regioselectivities. Here, we aim to establish connections between nucleophile properties and trends in zeolite-catalyzed C₄H₈O ring-opening rates and selectivities by comparing alcohol (1-butanol), amine (butylamine), and thiol (butanethiol) nucleophiles.

Figure 6.7 demonstrates that changing the nucleophilic functional group leads to significant differences in the rate and regioselectivity of C₄H₈O ring-opening. Turnover rates with butanol and butanethiol fall within 15% of each other, while butylamine gives rates ~10 times lower than the other nucleophiles. Conventional wisdom suggests that alcohols would show the

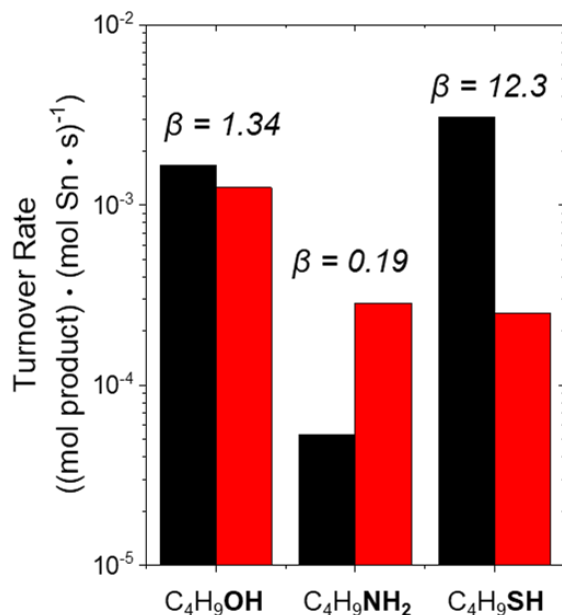


Figure 6.7. Secondary alcohol (black bars) and terminal alcohol (red bars) formation rates and β values for C_4H_8O ring-opening with butanol, butylamine, and butanethiol over Sn-BEA-OH zeolite (0.02 M C_4H_8O , 0.4 M nucleophile, CH_3CN , 308 K). Here, β values equal the formation rate of the secondary alcohol to the terminal alcohol (see **Scheme 1.2**).

lowest reaction rates of these nucleophiles, as the nucleophilicity of amines and thiols exceeds that of alcohols.³²⁹ Despite this contradiction, the low rates with butylamine in **Figure 6.7** align with previous reports for epoxide ring-opening over Lewis acid zeolites, which the authors attribute to the high basicity of amine nucleophiles.^{65, 325} The basicity of amines significantly exceeds alcohols and thiols, suggesting that amines may hinder the ring-opening reaction by binding to the Lewis acid sites more strongly than the other nucleophiles.

The regioselectivities align with the expected ranges achieved with alcohol, amine, and thiol nucleophiles from previous reports. The β values achieved for butanethiol and butylamine in **Figure 6.7** fall well outside the range of β achieved with alcohols reported in the earlier chapters of this thesis, demonstrating the significant role of the nucleophile on the product distribution. Interestingly, the trend of β values with nucleophile basicity opposes the expectation from organic chemistry intuition. More basic nucleophiles promote an S_N2 -type reaction where the nucleophile

prefers to attack the less-substituted carbon to form the secondary alcohol. In contrast, less acidic nucleophiles prefer an S_N1-type reaction where nucleophilic attack occurs more significantly at the more substituted carbon to form the terminal alcohol.^{268, 270} One would expect β values to proceed in the order butylamine > butanol > butanethiol based on this logic, but the β values in **Figure 6.7** show the exact opposite trend. Evidently, the interactions between nucleophile, epoxide, co-solvent molecules, and Sn sites lead to complex trends of rates and regioselectivities of epoxide ring-opening that challenge conventional expectations.

Future work will investigate how the identity of the active metal and the concentration of the nucleophile relative to the epoxide and acetonitrile co-solvent influence rates and regioselectivities of epoxide ring-opening. We aim to develop structure-function relationships that can guide the preferential formation of the terminal and secondary alcohol products for each class of nucleophiles.

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APPENDIX A
SUPPLEMENTAL DATA AND ANALYSIS FOR CHAPTER 2

A1. Characterization of Ti-BEA Zeolites

A1.1 X-Ray Diffractograms of Ti-BEA

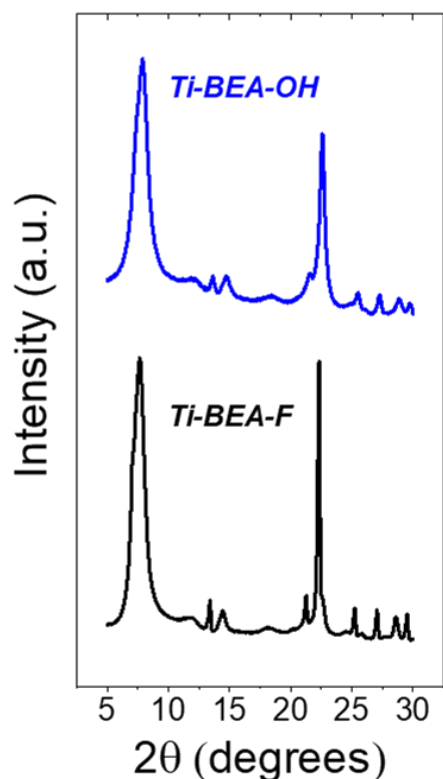


Figure A1. Powder X-ray diffractograms obtained with Cu K α radiation (0.15418 nm) under ambient conditions for Ti-BEA-OH (blue) and Ti-BEA-F (black). Spectra are vertically offset for clarity.

The crystallographic features for each Ti-BEA material are indicative of the BEA framework. The sharper feature at ~ 22.5 degrees for Ti-BEA-F suggests a high degree of crystallinity, as expected for zeolites synthesized in fluoride media.³³⁰ The broader feature for Ti-BEA-OH indicates a smaller crystallite size¹³⁸ and the presence of internal defects formed by dealumination of the Al-BEA-OH (Si:Al = 20) parent zeolite.

A1.2 Diffuse Reflectance UV-Vis Spectra

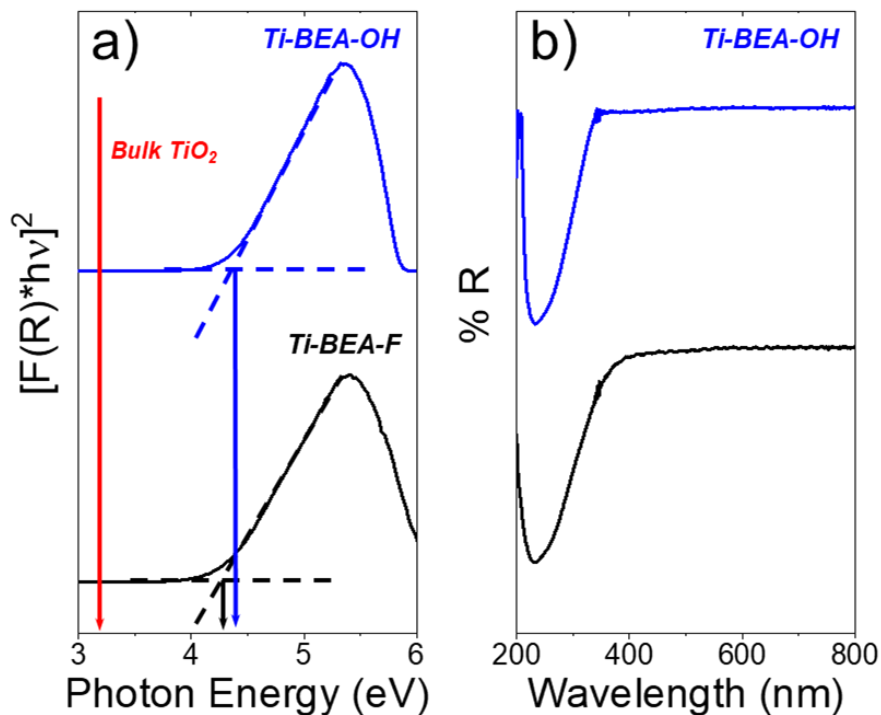


Figure A2. a) Tauc plots and b) DR-UV-Vis spectra obtained with a UV-Vis spectrophotometer at ambient conditions for Ti-BEA-OH (blue) and Ti-BEA-F (black). Spectra were normalized to the most intense feature around 5.5 eV and 225 nm and are vertically offset for clarity.

The band gaps for Ti-BEA-OH (4.32 eV) and Ti-BEA-F (4.27 eV) were obtained by extrapolating the linear absorbance region of the Tauc plot to the baseline. The intersection of the baseline and linear region represents the band gap photon energy, as illustrated in **Figure A2a**. The band gaps for both Ti-BEA are much greater than the band gap for bulk titania (TiO_2 , 3.2 eV),³³¹ suggesting that the titanium atoms are well dispersed within the *BEA framework. The photon energy was obtained from the wavelength as follows:

$$\text{Photon Energy (eV)} = \frac{3 \times 10^8 \frac{\text{m}}{\text{s}}}{\text{Wavelength (nm)} \times \frac{1 \text{ m}}{10^9 \text{ nm}}} \times h \times \left(6.242 \times 10^{18} \frac{\text{eV}}{\text{J}} \right)$$

where h equals the Planck constant. The ordinate from **Figure A2a** was obtained from the ordinate of the raw spectra in **Figure A2b**. The Kubelka-Munk function was calculated from % R:

$$F(R) = \frac{\left(1 - \frac{\%R}{100}\right)^2}{2 * \left(\frac{\%R}{100}\right)}$$

$F(R)$ was then multiplied by the photon energy, and the resulting quantity was squared to yield the ordinate for **Figure A2a**.

A1.3 Infrared Spectra of Ti-BEA Materials

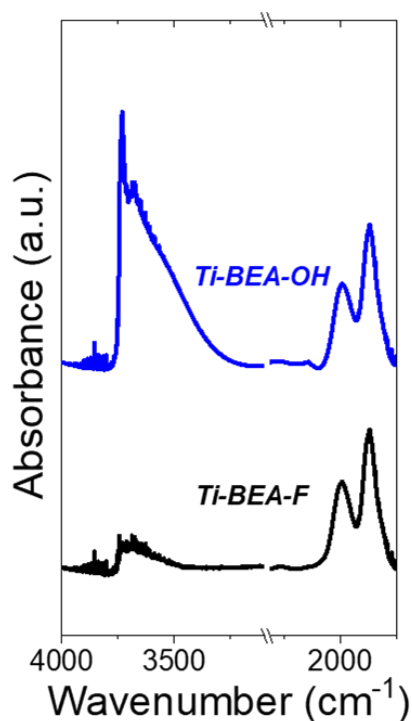


Figure A3. Infrared spectra of dehydrated samples of Ti-BEA-OH (blue) and Ti-BEA-F (black). The samples were dehydrated under flowing He ($50 \text{ cm}^3 \text{ min}^{-1}$) at 573 K prior to measurement. Spectra are vertically offset for clarity.

The significant difference in the -OH stretching region area ($3300\text{-}3750 \text{ cm}^{-1}$) between the zeolites relative to the unchanging Si-O-Si region ($1800\text{-}2100 \text{ cm}^{-1}$) indicates that Ti-BEA-OH contains a much greater density of Si-OH groups than Ti-BEA-F (i.e., more hydrophilic), as

quantified by the Φ_{IR} values shown in **Table 2.1**. Φ_{IR} values were calculated by peak fitting on Origin 2021 (OriginLab Corporation). The peak areas for the -OH and Si-O-Si are shown in **Table A1** and were calculated with Gaussian fits, as illustrated in **Figures A4** and **A5**. During peak fitting, the peak centers were fixed at the values shown in **Table A1**.

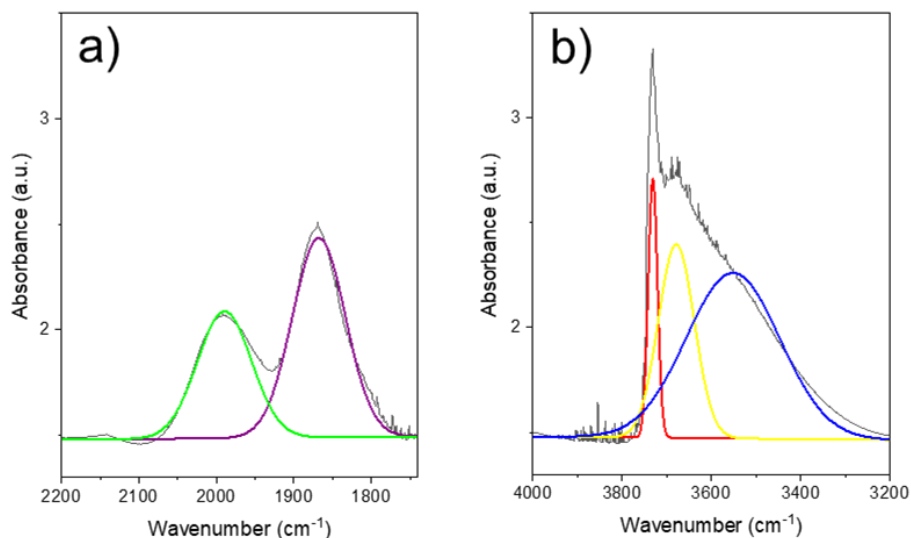


Figure A4. Fitted peaks for the a) Si-O-Si overtones at 1865 (purple) and 2000 cm⁻¹ (green) and b) isolated (red) and networked (blue, yellow) Si-OH regions for Ti-BEA-OH.

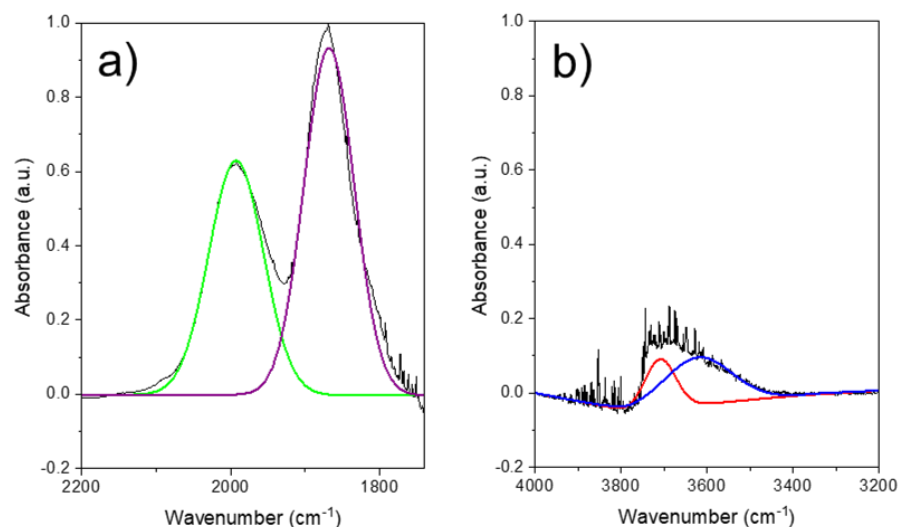


Figure A5. Fitted peaks for the a) Si-O-Si overtones at 1865 (purple) and 2000 cm⁻¹ (green) and b) isolated (red) and networked (blue) Si-OH regions for Ti-BEA-F.

Ti-BEA-OH		Ti-BEA-F	
Peak Center (cm ⁻¹)	Integrated Area	Peak Center (cm ⁻¹)	Integrated Area
3731	32.1	3709	11.7
3679	93.4	3620	24.8
3551	207.5	1993	57.9
1990	52.8	1868	79.0
1868	81.2		

Table A1. Peak areas for fitted peaks from IR spectra of Ti-BEA samples.

As shown in **Equation 2.1**, the equation to calculate Φ_{IR} is:

$$\Phi_{IR} = \frac{A_{v(O-H)}}{A_{v(Si-O-Si)}} \quad (A1)$$

The red peaks in the -OH stretch represent isolated SiOH features, so these peak areas were excluded from the Φ_{IR} calculations. The blue and yellow peaks represent networked (SiOH)_x features which are summed to get $A_{v(O-H)}$ for Ti-BEA-OH; only the blue peak was used in $A_{v(O-H)}$ for Ti-BEA-F. The green and purple peaks in the Si-O-Si region were summed together to get $A_{v(Si-O-Si)}$. Substituting these areas to **Equation A1** gives Φ_{IR} values of 2.25 and 0.27 for Ti-BEA-OH and Ti-BEA-F, respectively.

A1.4 Ex situ Raman Spectra of Ti-BEA Materials

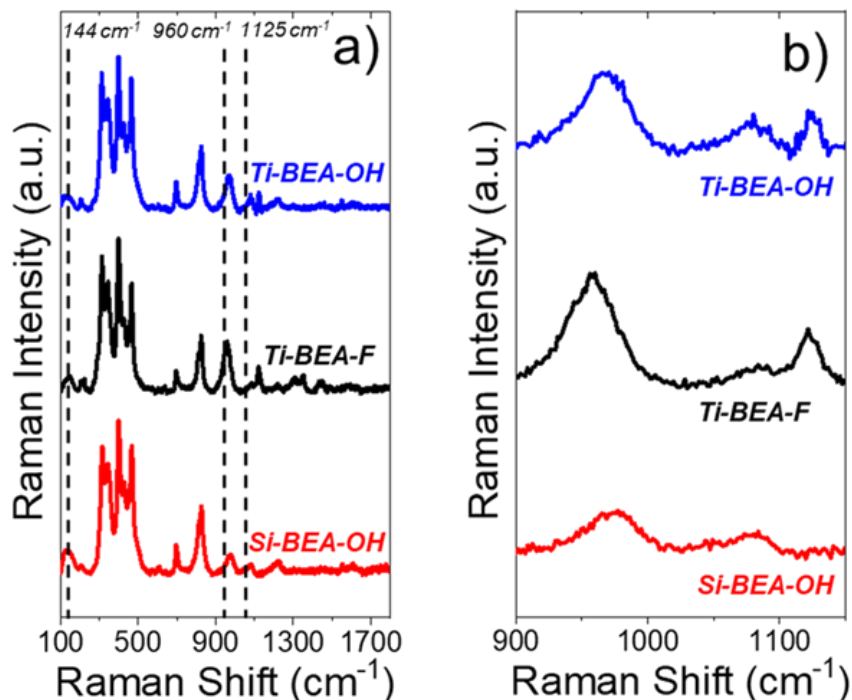


Figure A6. a) *Ex situ* Raman spectra of Ti-BEA-OH (blue), Ti-BEA-F (black), and Si-BEA-OH (red), and b) the *ex situ* spectra zoomed into the 900-1150 cm^{-1} region. The spectra are an average of 10 scans with an exposure time of 20 s. Spectra are normalized by the maximum feature at $\sim 400 \text{ cm}^{-1}$ and are vertically offset for clarity. The spectra were taken at ambient conditions with a Raman spectrometer (Renishaw, InVia) equipped with a 532 nm laser that delivered a power density of $\sim 2 \text{ mW } \mu\text{m}^{-2}$.

Bulk anatase TiO_2 shows an intense E_g vibration peak at 144 cm^{-1} ,^{254, 332} which is hardly observable in the Raman spectra of each Ti-BEA. The area of this feature is also slightly more intense in Si-BEA-OH, which suggests the feature results from a mode inherent to the *BEA framework instead of TiO_2 . The intense peaks between 250 and 550 cm^{-1} represent features of the *BEA framework: the peaks at 315 and 345 cm^{-1} are assigned to six-membered rings, the peaks at 400 and 425 cm^{-1} are assigned to five-membered rings, and the peak at 465 cm^{-1} represents four-membered rings characteristic of the *BEA framework.³³³⁻³³⁴ The peak at $\sim 695 \text{ cm}^{-1}$ has previously been reported on Raman spectra of crystalline *BEA zeolites, suggesting the feature may be

characteristic of the *BEA framework.³³⁵⁻³³⁶ The peak at $\sim 820\text{ cm}^{-1}$ represents a symmetric skeletal mode of microporous silicates.³³⁷⁻³³⁸

The feature at $\sim 960\text{ cm}^{-1}$ has been commonly attributed to silanol defects^{150, 333, 339} and Ti atoms incorporated at tetrahedral positions in zeolite frameworks.^{150, 254, 339-343} The peak at $\sim 1125\text{ cm}^{-1}$ represents an additional feature of Ti atoms within the framework; previous studies assign the ~ 960 and $\sim 1125\text{ cm}^{-1}$ peaks to antisymmetric and symmetric Ti-O-Si vibrations, respectively.^{254, 342-344} **Figure A6b** shows that each Ti-BEA zeolite contains features at ~ 960 and 1125 cm^{-1} , consistent with the proposal that Ti atoms reside in the *BEA framework. Si-BEA-OH also contains a feature at $\sim 960\text{ cm}^{-1}$, likely resulting from contributions of silanol defects as reported in literature. Collectively, the Raman spectra suggest that Ti atoms predominately reside at tetrahedral framework positions within the *BEA zeolite framework.

A1.5 N₂ and Ar Adsorption Isotherms over Ti-BEA Materials

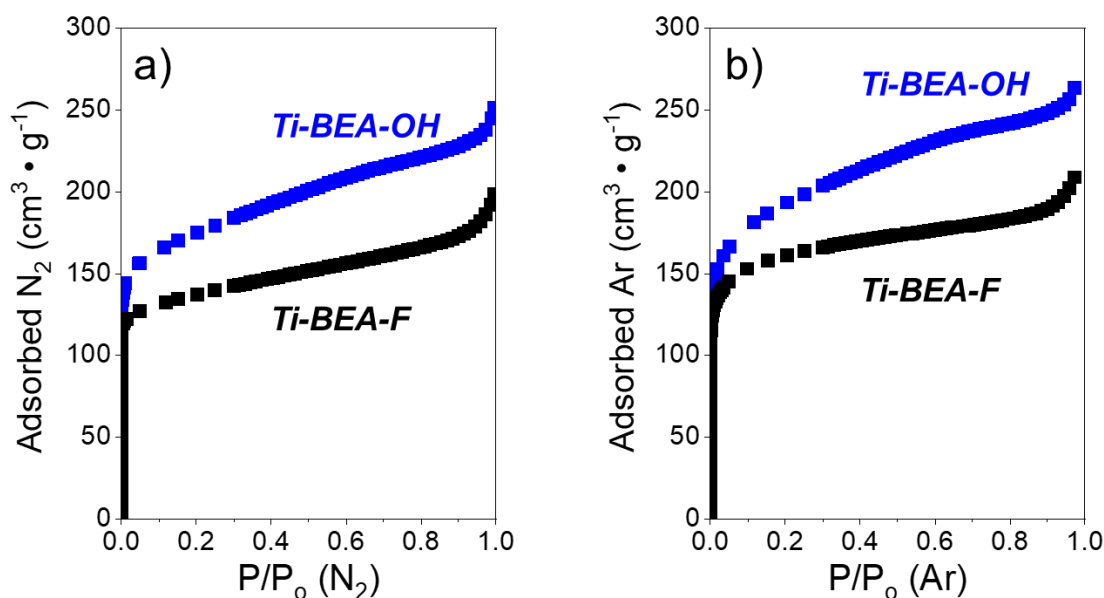


Figure A7. a) N₂ (77 K) and b) Ar (87 K) adsorption isotherms over Ti-BEA-OH (blue) and Ti-BEA-F (black). The samples were degassed at 673 K under vacuum ($<0.0007\text{ kPa}$) before adsorption.

The BET surface areas and micropore volumes reported in **Table 2.1** were calculated from the adsorption isotherms in **Figure A7**. The values in **Table 2.1** are consistent with previous reports of surface areas^{64, 85, 345} and micropore volumes^{64, 76, 132-133, 136} of *BEA zeolites, supporting that Ti-BEA-OH and Ti-BEA-F possess the *BEA framework.

The BET surface area of Ti-BEA-OH exceeds Ti-BEA-F by ~1.2 times for each method, while the micropore volume is ~1.1 times greater in Ti-BEA-OH for N₂ adsorption and nearly identical between the zeolites for Ar adsorption. While the external surface areas of Ti-BEA-OH are ~2 times greater than Ti-BEA-F, the total pore volumes (micropore + mesopore) differ by < 1.25 times between zeolites for each adsorption measurement (**Table A2**). Notably, the differences in micropore volumes are less significant than differences in CH₃CN (~1.5 times) or H₂O uptake (~30 times) between Ti-BEA-OH and Ti-BEA-F (**Section 2.3.3**), suggesting that differences in available pore volume are not primarily responsible for solvent uptake differences.

Catalyst	External Surface Area (N ₂) (m ² g ⁻¹)	External Surface Area (Ar) (m ² g ⁻¹)	Total Pore Volume (N ₂) (cm ³ g ⁻¹)	Total Pore Volume (Ar) (cm ³ g ⁻¹)
Ti-BEA-OH	200	177	0.389	0.521
Ti-BEA-F	109	79	0.307	0.583

Table A2. External surface areas and mesopore volumes of Ti-BEA materials, obtained from N₂ and Ar physisorption isotherms.

A1.6 Calculation of (SiOH)₄ (unit cell)⁻¹ in Ti-BEA-OH

The density of silanol nests per unit cell in Ti-BEA-OH was estimated based on the initial quantity of Al present in the commercial zeolite (Si:Al = 20). A *BEA unit cell contains 64 heteroatoms (i.e., Si, Al, or Ti), so the initial quantity of Al per unit cell equals 3.1:

$$Al + Si = 64$$

$$Al + 20Al = 64$$

$$Al = 3.1$$

Assuming that all Al atoms are removed, the dealumination produces 3.1 (SiOH)₄ (unit cell)⁻¹. The Ti weight loading was measured as 0.355% from EDXRF, which gives a Si/Ti ratio of 219. This can be used to calculate the number of Ti atoms per unit cell incorporated into the formed (SiOH)₄:

$$Ti + Si = 64 \qquad Ti + 219Ti = 64 \qquad \mathbf{Ti = 0.3}$$

The final (SiOH)₄ (unit cell)⁻¹ is equal to the quantity of removed Al subtracted by the added Ti:

$$(SiOH)_4 = removed\ Al - added\ Ti = \mathbf{2.75\ (SiOH)_4\ per\ unit\ cell}$$

Ti-BEA-F was synthesized hydrothermally without Al present, so we cannot make the same calculation of (SiOH)₄ (unit cell)⁻¹.

A2. ¹H NMR Spectroscopy to Measure H₂O Uptake – Calculation Procedure

The ratio of the peak areas for H₂O and CH₃CN was calculated for each sample, and the known initial concentration of H₂O and peak area ratios before and after contact with Ti-BEA were used to calculate the final H₂O concentration:

$$[H_2O]_{final} = [H_2O]_{initial} * \frac{final\ H_2O:CH_3CN\ peak\ area}{initial\ H_2O:CH_3CN\ peak\ area} \qquad (A2)$$

The H₂O uptake was then measured by taking the difference between H₂O concentrations in bulk solvent and multiplying by the total volume of solvent used for the experiment:

$$H_2O\ uptake\ (mol) = V_{solvent} * ([H_2O]_{initial} - [H_2O]_{final}) \qquad (A3)$$

The uptake of H₂O molecules per unit cell was then computed with the mass of zeolite added to the solvent and the molecular weight of each *BEA unit cell. The unit cell consists of 64 heteroatoms (Si or Ti) and 128 O atoms. For example, each unit cell in Ti-BEA-F contains approximately 0.22 Ti atoms (as calculated by the same method for Ti-BEA-OH in **Section A1.6**), so the unit cell molecular weight can be calculated as follows:

$$0.25MW_{Ti} + 63.75MW_{Si} + 128MW_O = 0.22 \left(47.867 \frac{g}{mol} \right) + 63.78 \left(28.0855 \frac{g}{mol} \right) + 128 \left(15.999 \frac{g}{mol} \right) = 3850 \frac{g}{mol \cdot unit\ cell} \quad (A4)$$

From there, the uptake of H₂O molecules per unit cell of Ti-BEA-F was calculated as:

$$\frac{H_2O\ uptake\ (molecules)}{unit\ cell} = \frac{H_2O\ uptake\ (mol)}{mass\ zeolite\ added\ to\ solvent\ (g)} * 3850 \frac{g}{mol \cdot unit\ cell} \quad (A5)$$

Note: Each data point in **Figure 2.4** showed a decrease in bulk H₂O concentration after contacting the solvent with the zeolite, which leads to a positive uptake value of H₂O in **Equation A3**, indicating preferential uptake of H₂O relative to CH₃CN.

A3. FT-Infrared Spectroscopy to Measure CH₃CN Uptake – Calculation Procedure

CH₃CN uptakes were measured at varying CH₃CN pressure using the area of the ν(C≡N) infrared absorbance features, as depicted in **Figure A8**. First, the extinction coefficient of CH₃CN was calculated by measuring gaseous CH₃CN adsorption in an empty infrared cell (i.e., no catalyst present). The moles of CH₃CN at a given feed pressure was calculated with the ideal gas law (PV = nRT), where P is the feed pressure, V represents the volume of the IR cell, and T is the temperature (313 K). Beer's law can be used to measure the extinction coefficient:

$$A = \varepsilon * l_{cell} * [CH_3CN] \quad (A6)$$

where A represents the absorbance in the empty cell (ν(C≡N) area), ε defines the extinction coefficient of CH₃CN, l_{cell} is the path length of the IR cell, and [CH₃CN] represents CH₃CN concentration (moles of CH₃CN per unit volume of catalyst disk). Beer's law must be modified slightly to isolate the moles of CH₃CN. The path length and volume of the catalyst disk terms can be merged to yield an area term:

The ν(C≡N) area was plotted against $l_{cell} * [CH_3CN]$, and the slope of this line equals the CH₃CN extinction coefficient of 9.06 mm M⁻¹. (**Figure A9**). The extinction coefficient from this

empty cell measurement was then used to calculate the concentration of adsorbed CH₃CN when a catalyst pellet was added to the infrared cell:

$$[CH_3CN]_{ads} = \frac{\nu(C\equiv N) \text{ area}}{\varepsilon * l_{pellet}} \quad (A7)$$

where l_{pellet} is the thickness of the catalyst pellet. $[CH_3CN]_{ads}$ was then converted to moles of CH₃CN per unit cell (n_{CH_3CN}) using the mass of the Ti-BEA catalyst pellet (m_{pellet}) and the mass per *BEA unit cell (as calculated in **Equation A4**):

$$n_{CH_3CN} = [CH_3CN]_{ads} * \frac{3850 \frac{g}{mol * unit \ cell}}{6.022 * 10^{23} \frac{1}{mol}} * \frac{V_{pellet}}{m_{pellet}} \quad (A8)$$

The pellet volume (V_{pellet}) was calculated from l_{pellet} and the pellet diameter (d_{pellet}):

$$V_{pellet} = \pi * (0.5 * d_{pellet})^2 * l_{pellet} \quad (A9)$$

From there, the molecules of CH₃CN adsorbed per unit cell ($CH_3CN_{unit \ cell}$) was calculated:

$$CH_3CN_{unit \ cell} = n_{CH_3CN} * 6.022 * 10^{23} \frac{molecules}{mol} \quad (A10)$$

The intensity of the Si-O-Si overtone features for each Ti-BEA sample scales linearly with m_{pellet} , demonstrating that the pellets have a uniform and reproducible thickness that reflect the total amount of catalyst loaded into the IR cell.

It is important to note that the range of $\nu(C\equiv N)$ areas for the extinction coefficients (0.01 – 0.08 a.u.) falls at the lowest end of areas from the measurements with catalyst present (0.05 – 8.5 a.u.). It was not possible to get the area ranges to overlap because of the mismatch between uptakes and pellet thickness, and the limitation of the accessible range of partial pressures for CH₃CN. Therefore, we use the full range of empty cell calibration data to determine the extinction coefficient of CH₃CN.

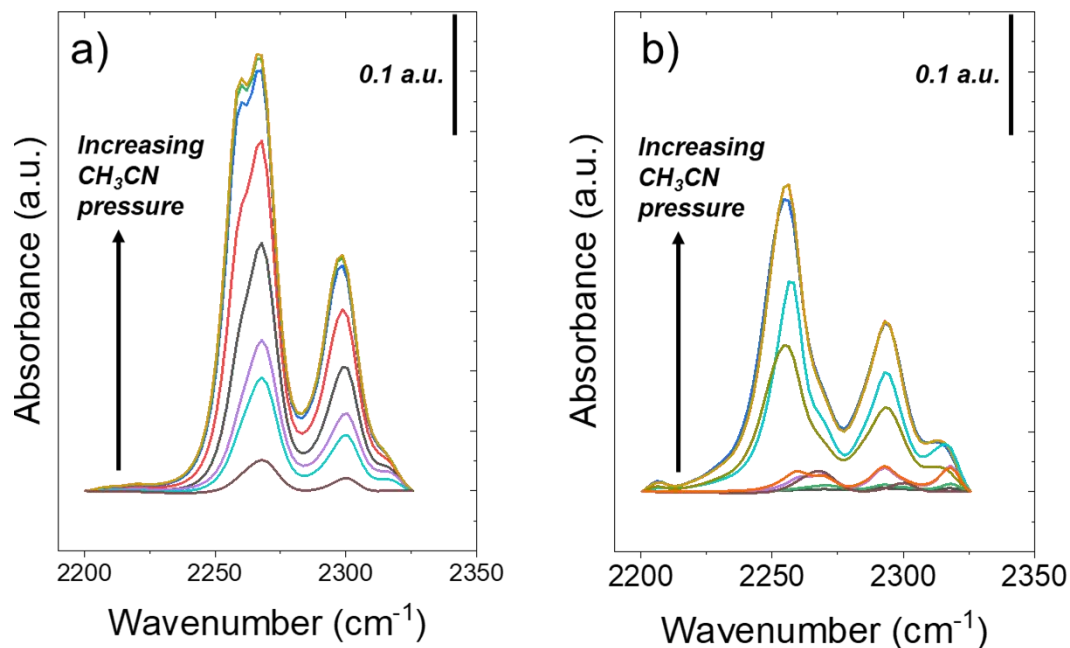


Figure A8. $\nu(\text{C}\equiv\text{N})$ infrared absorbance features over a) Ti-BEA-OH and b) Ti-BEA-F, where greater feed pressures of CH₃CN lead to greater peak areas (0.008 – 20 kPa CH₃CN, 313 K).

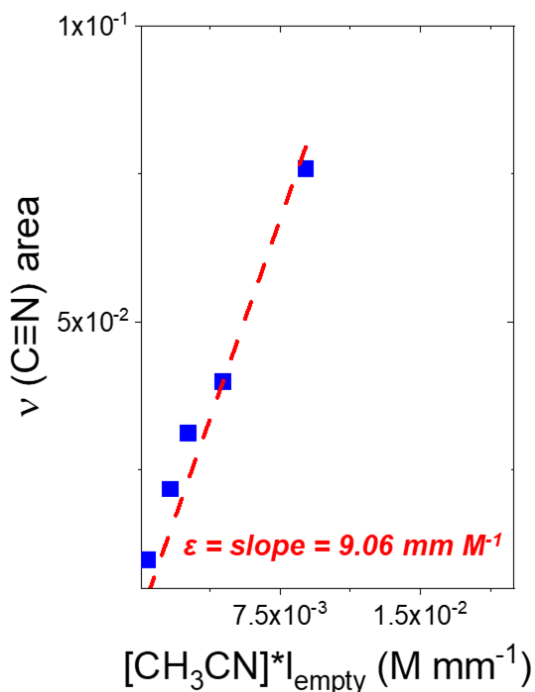


Figure A9. $\nu(\text{C}\equiv\text{N})$ infrared absorbance area in an empty infrared cell (0.5 – 20 kPa CH₃CN, 313 K) plotted against the CH₃CN concentration times path length. The slope with the intercept set as 0 equals the extinction coefficient for CH₃CN.

A4. Comparison of CH₃CN Adsorption with FTIR Spectroscopy to Previous Literature

The CH₃CN uptake values in Ti-BEA from **Figure 2.6** show an opposite trend on (SiOH)_x density than alcohol molecules within Sn-BEA zeolites (i.e., 2-butanol, methanol).¹³²⁻¹³³ Di Iorio et al. used infrared spectroscopy to show that 2-butanol forms dimeric, tightly ordered networks in hydrophobic Sn-BEA and oligomeric, extended networks in hydrophilic Sn-BEA.¹³³ Vega Vila and Gounder performed similar experiments with methanol and correlated infrared spectra with methanol physisorption data to demonstrate that methanol packs at greater densities within hydrophobic Sn-BEA pores.¹³² Hydrophobic zeolites may adsorb alcohols more readily than aprotic molecules (e.g., CH₃CN) because alcohol molecules can hydrogen-bond together and CH₃CN molecules do not, meaning that (SiOH)_x groups provide the only hydrogen-bonding function for adsorbing CH₃CN. While these studies utilize infrared spectroscopy to measure alcohol adsorption isotherms with an identical procedure as used for CH₃CN in this work, they do not report alcohol uptake per unit cell. Other works examine CH₃CN interactions and adsorption in zeolites experimentally³⁴⁶⁻³⁴⁸ and computationally^{347, 349-351}, but do not report molecular uptakes. To our knowledge, the method utilized here to determine CH₃CN per unit cell is novel, although similar infrared measurements have been carried out with deuterated acetonitrile (CD₃CN). Previous studies calculated extinction coefficients for CD₃CN onto SiOH,¹³⁶⁻¹³⁷ Sn,¹³⁷ and Ti¹⁰⁹ sites from adsorption isotherms to quantify the number of Lewis acid sites or SiOH defects present in *BEA zeolites. Additionally, works from our group measured adsorption isobars to calculate the adsorption enthalpy of CD₃CN to Lewis acid metal atoms within *BEA (i.e., Ti, Nb, Ta, Zr, Hf).^{31, 74} Overall, calculating CH₃CN per unit cell with infrared spectroscopy builds on previous methods with similar probe molecules and provides a novel method to gain additional information from infrared spectra of molecules adsorbed into zeolites.

A5. CH₃CN and H₂O₂ Drying Procedure

CH₃CN and H₂O₂ diluted in CH₃CN were dried over sulfates in a multi-step procedure. For CH₃CN, 50 mL were first contacted with 3 g of magnesium sulfate (MgSO₄). The mixture of CH₃CN and MgSO₄ was left in the fridge overnight, then centrifuged the next day to separate the components. The CH₃CN recovered from centrifuging was then contacted with 300 mg of CaSO₄. This mixture was again left in the fridge overnight and centrifuged the next day to recover the dried CH₃CN. For the H₂O₂ solution, 10 mL of H₂O₂ was first mixed with 20 mL of CH₃CN. The same sequential procedure with MgSO₄ (7 g) and CaSO₄ (750 mg) as outlined above was then performed to produce a dried solution with H₂O₂ concentrations between 4.1 and 4.4 M. The CH₃CN and H₂O₂ solutions were left in the fridge over CaSO₄ until used for kinetics or ITC experiments. The H₂O₂ solution was used within a week of completing the drying procedure to avoid significant build-up of H₂O from H₂O₂ decomposition.

The masses of MgSO₄ and CaSO₄ used for drying were estimated from reported values of the maximum number of moles of water that the sulfate can bind and the amount of water remaining in the solution after drying. The quantity of MgSO₄ used was in 5% excess of the value needed to bind all the moles of H₂O present. A large excess of CaSO₄ (factor of 100) was then used to ensure that all H₂O remaining after the MgSO₄ drying was bound by the CaSO₄.

A6. Rate Dependences on Reactant Concentration Over Ti-BEA-F

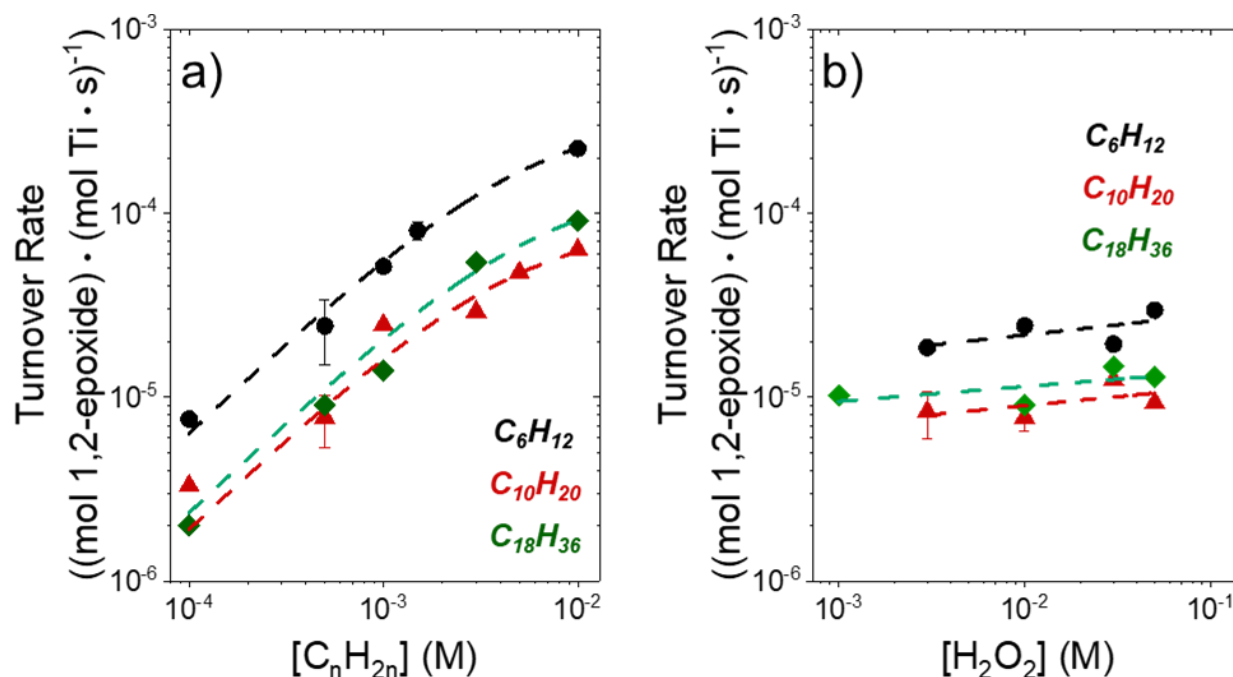


Figure A10. Turnover rates for epoxide formation as a function of a) alkene concentration (10 mM H₂O₂, 200 mM H₂O) and b) H₂O₂ concentration (0.5 mM C_nH_{2n}, 200 mM H₂O) for primary n-alkenes (C₆H₁₂ (●), C₁₀H₂₀ (▲), C₁₈H₃₆ (◆)) over Ti-BEA-F in CH₃CN solvent at 313 K.

Figure A10a shows that epoxidation turnover rates over Ti-BEA-F show a linear dependency on alkene concentration ($[C_nH_{2n}]$) at low ratios of $[C_nH_{2n}]$ to $[H_2O_2]$. The linear dependency suggests that mass transfer limitations are not an issue across the range of alkenes.¹⁵⁹ Rates shift to a sub-linear dependency on $[C_nH_{2n}]$ at higher ratios of $[C_nH_{2n}]$ to $[H_2O_2]$. **Figure A10b** shows that epoxidation rates feature a nearly zero-order dependence on $[H_2O_2]$ at low ratios of $[C_nH_{2n}]$ to $[H_2O_2]$. The rate dependences are similar among each alkene and resemble those shown for Ti-BEA-OH in **Figure 2.2**, indicating that differences in rates between alkenes and Ti-BEA zeolites do not result from a change in the reaction mechanism.

A7. Derivation of Rate Expression for Alkene Epoxidation over Ti-BEA Materials

Scheme 2.1 shows the elementary steps for alkene (C_nH_{2n}) epoxidation and H_2O_2 decomposition.³⁰ Epoxidation rates can be modeled by adapting **Equation 2.2**:

$$r_E = k_4[Ti - OOH][C_nH_{2n}] \quad (A11)$$

where r_E is the epoxidation rate, k_4 is the rate constant for step 4 in **Scheme 2.1**, and $[Ti-OOH]$ and $[C_nH_{2n}]$ represent the number of H_2O_2 -activated metal sites and alkene molecules in the liquid-phase. Applying the pseudo-steady state hypothesis to the Ti-OOH intermediate gives:

$$r_E = \frac{k_3 k_4 K_2 [C_nH_{2n}] [H_2O_2] [CH_3CN*]}{k_4 [C_nH_{2n}] + k_6 [H_2O_2]} \quad (A12)$$

The total number of Ti active sites ($[L]$) can be written as:

$$[L] = [CH_3CN*] + [C_nH_{2n}*] + [H_2O_2*] + [OOH*] + [C_nH_{2n}O*] \quad (A13)$$

where $[CH_3CN*]$ is the number of active sites, which are assumed to be occupied by an acetonitrile molecule. The active sites are unlikely to be unoccupied because epoxidation takes place in a basic solvent (acetonitrile) with a moderate heat of adsorption to bind to the Lewis acidic Ti active sites. $[C_nH_{2n}*]$, $[H_2O_2*]$, $[OOH*]$, and $[C_nH_{2n}O*]$ represent the concentrations of alkene, hydrogen peroxide, hydroperoxo intermediate, and epoxide product molecules adsorbed to the active site. Substituting rate constants, equilibrium constants, and reactant and product concentrations gives:

$$[L] = 1 + K_1 [C_nH_{2n}] + K_2 [H_2O_2] + \frac{k_3 K_2 [H_2O_2]}{k_4 [C_nH_{2n}] + k_6 [H_2O_2]} + \frac{[C_nH_{2n}O]}{K_5} \quad (A14)$$

Combining **Equations A11** and **A13** gives an expression for epoxidation turnover rates:

$$\frac{r_E}{[L]} = \frac{\frac{k_3 k_4 K_2 [C_nH_{2n}] [H_2O_2] [*]}{k_4 [C_nH_{2n}] + k_6 [H_2O_2]}}{1 + K_1 [C_nH_{2n}] + K_2 [H_2O_2] + \frac{k_3 K_2 [H_2O_2]}{k_4 [C_nH_{2n}] + k_6 [H_2O_2]} + \frac{[C_nH_{2n}O]}{K_5}} \quad (A15)$$

Ti-OOH saturates the Ti-BEA surface at the low ratios of $[C_nH_{2n}]:[H_2O_2]$ used when measuring activation barriers ($[C_nH_{2n}]:[H_2O_2] < 1$), so the $[OOH*]$ term dominates in the MARI, and all other terms can be canceled out. **Equation A15** then simplifies to the same form as **Equation 2.2**:

$$\frac{r_E}{[L]} = k_4[C_nH_{2n}] \quad (A16)$$

Under conditions in which the active sites are saturated with the epoxide product, the $[C_nH_{2n}O^*]$ is dominant in the MARI and **Equation A15** simplifies to:

$$\frac{r_E}{[L]} = \frac{k_3k_4K_2K_5[C_nH_{2n}][H_2O_2][*]}{[C_nH_{2n}O](k_4[C_nH_{2n}]+k_6[H_2O_2])} \quad (A17)$$

H_2O_2 decomposition rates can be modeled as follows:

$$r_D = k_6[Ti - OOH][H_2O_2] \quad (A18)$$

Substituting terms for $[Ti-OOH]$ and using the site balance for $[L]$ gives an expression for H_2O_2 decomposition turnover rates:

$$\frac{r_D}{[L]} = \frac{\frac{k_3k_6K_2[H_2O_2]^2}{k_4[C_nH_{2n}]+k_6[H_2O_2]}}{1+K_1[C_nH_{2n}]+K_2[H_2O_2]+\frac{k_3K_2[H_2O_2]}{k_4[C_nH_{2n}]+k_6[H_2O_2]}+\frac{[C_nH_{2n}O]}{K_5}} \quad (A19)$$

When $Ti-OOH$ is the MARI ($[C_nH_{2n}]:[H_2O_2] < 1$), we can simplify **Equation A19** to:

$$\frac{r_D}{[L]} = k_6[H_2O_2] \quad (A20)$$

H_2O_2 decomposition rates thus increase linearly with $[H_2O_2]$ in this regime.³¹

A8. Rates and Activation Barriers for H₂O₂ Decomposition

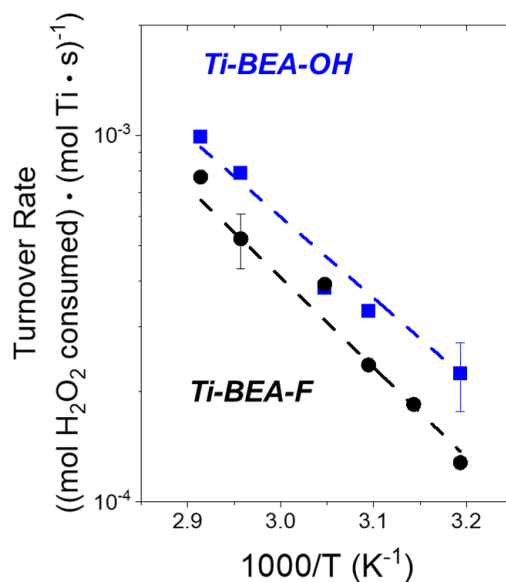


Figure A11. Turnover rates for H₂O₂ consumption (1 mM H₂O₂, CH₃CN + 200 mM H₂O) as a function of inverse temperature (313 – 343 K) for Ti-BEA-OH (blue) and Ti-BEA-F (black).

Catalyst	$\Delta H_{app\ (decomp)}^{\ddagger}$ (kJ mol ⁻¹)	$\Delta S_{app\ (decomp)}^{\ddagger}$ (J mol ⁻¹ K ⁻¹)
Ti-BEA-OH	43 ± 5	-121 ± 14
Ti-BEA-F	47 ± 5	-107 ± 15

Table A3. Activation enthalpies and entropies for H₂O₂ decomposition (1 mM H₂O₂, CH₃CN + 200 mM H₂O, 313 – 343 K) for Ti-BEA-OH and Ti-BEA-F.

Figure A11 shows that H₂O₂ decomposition rates vary negligibly (i.e., less than a factor of 2) between Ti-BEA-OH and Ti-BEA-F. This difference is negligible relative to the differences in epoxidation rates between Ti-BEA-OH and Ti-BEA-F, which falls between a factor of 40 and 450 across the range of alkenes studied here.

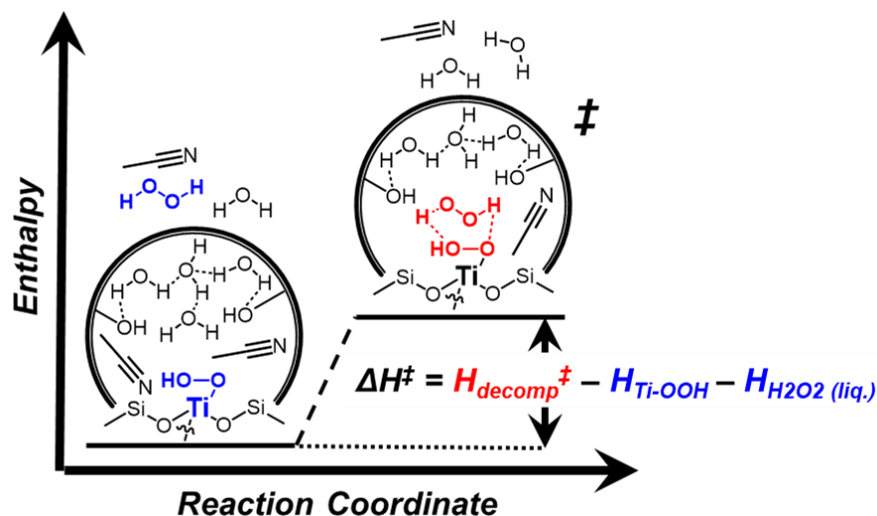
Since decomposition rates were measured at equal [H₂O₂], the rate differences reflect a difference in the rate constant for step 6 in **Scheme 2.1** (k_6) (**Equation A20**). k_6 is defined as:

$$k_6 = \frac{k_B T}{h} \cdot \exp\left(-\frac{\Delta G_{app\ (decomp)}^{\ddagger}}{RT}\right) \quad (\text{A21})$$

where the apparent free energy barrier ($\Delta G_{app(decomp)}^\ddagger$) is equal to the difference between the stability of the Ti-OOH intermediate, liquid-phase H_2O_2 , and H_2O_2 decomposition transition state:

$$\Delta G_{app(decomp)}^\ddagger = (G_{decomp}^{\ddagger,0} + G_{decomp}^{\ddagger,\epsilon}) - (G_{Ti-OOH}^0 + G_{Ti-OOH}^\epsilon) - (G_{H_2O_2,liq.}^0 + G_{H_2O_2,liq.}^\epsilon) \quad (A22)$$

Activation enthalpies ($\Delta H_{app(decomp)}^\ddagger$) and entropies ($\Delta S_{app(decomp)}^\ddagger$) for decomposition vary between Ti-BEA-OH and Ti-BEA-F by 4.2 kJ mol⁻¹ and 14.5 J mol⁻¹ K⁻¹, respectively (**Table A3**). The differences in decomposition barriers may result from changes in the stability of the H_2O_2 decomposition transition state or the Ti-OOH intermediate, which is common to alkene epoxidation and H_2O_2 decomposition. The differences in $\Delta H_{app(decomp)}^\ddagger$ and $\Delta S_{app(decomp)}^\ddagger$ between Ti-BEA-OH and Ti-BEA-F mostly compensate, causing H_2O_2 decomposition rates to vary by less than a factor of 2 at all temperatures examined. Therefore, any differences in the stability of Ti-OOH likely have a weak effect on differences in epoxidation rates, which show much larger differences between Ti-BEA-OH and Ti-BEA-F than H_2O_2 decomposition.



Scheme A1. Proposed rate-determining step of H_2O_2 decomposition over Ti-BEA.

It is also intuitive that the stability of the H_2O_2 decomposition transition state may depend more strongly on interactions with surrounding solvent molecules than Ti-OOH, because the

transition state is likely larger than Ti-OOH. **Scheme A1** shows the proposed rate-determining step of H₂O₂ decomposition. Previous studies suggest that H₂O₂ decomposition proceeds through a bimolecular mechanism in which an H₂O₂ molecule reacts with an activated H₂O₂ intermediate over Ti-,^{181, 219} Nb-,²²⁰ and Ta-incorporated¹⁴⁹ microporous and mesoporous catalysts. The larger transition state likely interacts with a greater number of surrounding solvent molecules. Overall, the rates and activation barriers for H₂O₂ decomposition show that solvent molecules influence decomposition much less significantly than alkene epoxidation and weakly affect the stability of the Ti-OOH intermediate shared between the epoxidation and decomposition pathways.

Catalyst + Alkene	H ₂ O ₂ Consumption Rate (mol H ₂ O ₂)* (mol Ti*s) ⁻¹	Epoxidation Rate (mol epoxide)* (mol Ti*s) ⁻¹	H ₂ O ₂ Decomposition Rate (mol H ₂ O ₂)* (mol Ti*s) ⁻¹	Selectivity (%)
Ti-BEA-OH + C ₆ H ₁₂	1.20 x 10 ⁻³	1.01 x 10 ⁻³	1.90 x 10 ⁻⁴	84.2
Ti-BEA-OH + C ₁₈ H ₃₆	8.98 x 10 ⁻⁴	3.27 x 10 ⁻⁴	5.71 x 10 ⁻⁴	36.4
Ti-BEA-F + C ₆ H ₁₂	2.49 x 10 ⁻⁴	1.66 x 10 ⁻⁵	2.32 x 10 ⁻⁴	6.7
Ti-BEA-F + C ₁₈ H ₃₆	3.73 x 10 ⁻⁴	9.02 x 10 ⁻⁶	3.64 x 10 ⁻⁴	2.4

Table A4. H₂O₂ decomposition rates and selectivities with C₆H₁₂ and C₁₈H₃₆ present (0.5 mM C_nH_{2n}, 1 mM H₂O₂, 200 mM H₂O, CH₃CN, 313 K) for Ti-BEA-OH and Ti-BEA-F.

To further examine if changes in Ti-OOH stability may affect epoxidation rates, rates of H₂O₂ consumption were measured with C₆H₁₂ and C₁₈H₃₆ present. We hypothesized that the identity of the alkene might affect Ti-OOH stability by leading to differences in the solvent environment in the pores of Ti-BEA. **Table A4** shows rates of H₂O₂ consumption, alkene epoxidation, H₂O₂ decomposition, and epoxidation selectivities. H₂O₂ decomposition rates were calculated by subtracting the alkene epoxidation rate from the overall H₂O₂ consumption rate:

$$H_2O_2 \text{ Decomposition Rate} = H_2O_2 \text{ Consumption Rate} - \text{Epoxidation Rate} \quad (\text{A23})$$

Epoxidation selectivities equal the ratio of epoxidation rate to overall H₂O₂ consumption rate:

$$Selectivity = \frac{Epoxidation\ Rate}{H_2O_2\ Consumption\ Rate} \quad (A24)$$

Rates of H₂O₂ decomposition are greater with C₁₈H₃₆ present than C₆H₁₂ over both Ti-BEA-OH (by a factor of 3) and Ti-BEA-F (by a factor of 1.6). The rate differences may partially result from competition between the epoxidation and decomposition pathways. C₆H₁₂ gives greater epoxidation rates and lower H₂O₂ decomposition rates for both Ti-BEA-OH and Ti-BEA-F. Alkenes of different carbon numbers may also lead to differences in the solvent environment in Ti-BEA, which could affect decomposition rates. The presence of C₁₈H₃₆ in Ti-BEA may lead to lower densities of solvent in the pores. This could reduce the enthalpic penalty of solvent disruption as H₂O₂ adsorbs to form the transition state for H₂O₂ decomposition, leading to greater rates. Alternatively, the longer alkyl chain may promote a less polar solvent environment that favors hydrogen bonding between Ti-OOH and H₂O₂ molecules, increasing selectivity towards the decomposition pathway. Collectively, the data presented in this section demonstrate that rates of H₂O₂ decomposition depend weakly on the zeolite and alkene identity in comparison to rates of alkene epoxidation, indicating that differences in Ti-OOH stability likely do not contribute significantly to differences in rates of alkene epoxidation.

A9. Alkene Excess Energy Calculations from Activity Coefficients to Probe Changes in

Alkene Stability in the Bulk Solvent

Alkene	H ^ε (kJ mol ⁻¹)	G ^ε (kJ mol ⁻¹)
C ₆ H ₁₂	8	6
C ₁₂ H ₂₄	17	12
C ₁₈ H ₃₆	26	18

Table A5. Excess energies for select alkenes (CH₃CN, 200 mM H₂O, 313 K).

Table A5 shows excess energies for three alkenes across the range studied. The excess energies were computed using activity coefficients from ChemCAD using the Volume-Translated Peng-Robinson (VTPR) method. Activity coefficients were also computed with the UNIFAC LLE and Modified UNFAC (Dortmund) models, which showed similar magnitudes and trends for the activity coefficients as VTPR. The equations to compute the excess energies are as follows:

$$G_j^\varepsilon = RT * \ln(\gamma_j) \quad (\text{A25})$$

$$H_j^\varepsilon = -RT^2 * \frac{d \ln(\gamma_j)}{dT} \quad (\text{A26})$$

The differential term ($\frac{d \ln(\gamma_j)}{dT}$) was obtained by calculating activity coefficients between 308-333 K by increments of 5 K. As shown in **Figure A12**, the natural log of the activity coefficients was plotted against the temperature, and the slope of this line equaled the differential term.

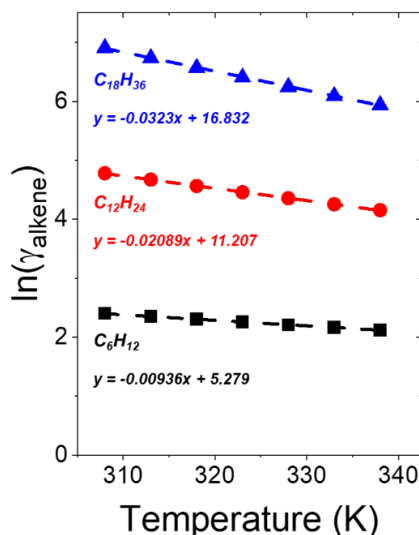


Figure A12. Natural logs of activity coefficients for 1-hexene (black), 1-dodecene (red), and 1-octadecene (blue) computed with ChemCAD using the Volume-Translated Peng-Robinson (VTPR) method at temperatures from 308-338 K, CH₃CN solvent + 200 mM H₂O.

If the increases in H^ε and G^ε for longer chain alkenes were primarily responsible for differences in epoxidation rates and activation barriers, $\Delta H_{app}^\ddagger$ and $\Delta G_{app}^\ddagger$ for epoxidation would decrease with increasing carbon number, and epoxidation rates would systematically increase with

carbon number. **Figures 2.2** and **Figure 2.4** show that rates and barriers do not follow those trends, so changes in alkene stability are not responsible for kinetic differences.

A10. Enthalpy, Entropy, and Free Energy of Alkene Formation

Alkene	H _f (kJ mol ⁻¹)	S _f (J mol ⁻¹ K ⁻¹)	G _f (kJ mol ⁻¹)
C ₆ H ₁₂	-42	-433	87
C ₈ H ₁₆	-83	-628	104
C ₁₀ H ₂₀	-124	-822	121
C ₁₂ H ₂₄	-165	-1017	138
C ₁₄ H ₂₈	-207	-1212	155
C ₁₆ H ₃₂	-248	-1406	171
C ₁₈ H ₃₆	-289	-1601	188

Table A6. Formation energies for alkenes at 298 K.

The enthalpies and entropies were obtained from Yaws Chemical Property Handbook.¹⁹⁴ The enthalpies, entropies, and free energies of formation scale nearly linearly with increasing numbers of methylene units from C₆ to C₁₈ (per -CH₂ unit: approximately 41.2 kJ mol⁻¹ decrease in H_f, 195.6 J mol⁻¹ K⁻¹ decrease in S_f, 16.8 kJ mol⁻¹ increase in G_f). The formation energies reported in **Table A6** provide insight into how the standard state energies of the alkenes trend with alkene carbon number. We anticipate that the corresponding epoxide products will show similar energy changes with increases in the number of -CH₂ units, based on Benson's group additivity theory.³⁵² In this case, the free energy for the epoxidation reaction would remain nearly constant across the range of alkenes and rules out changes in the standard state free energies of alkenes contributing to differences in $\Delta H_{app}^\ddagger$ and $\Delta S_{app}^\ddagger$ between alkenes.

A11. Isothermal Titration Calorimetry

A11.1 Cleaning and Calibration Procedures

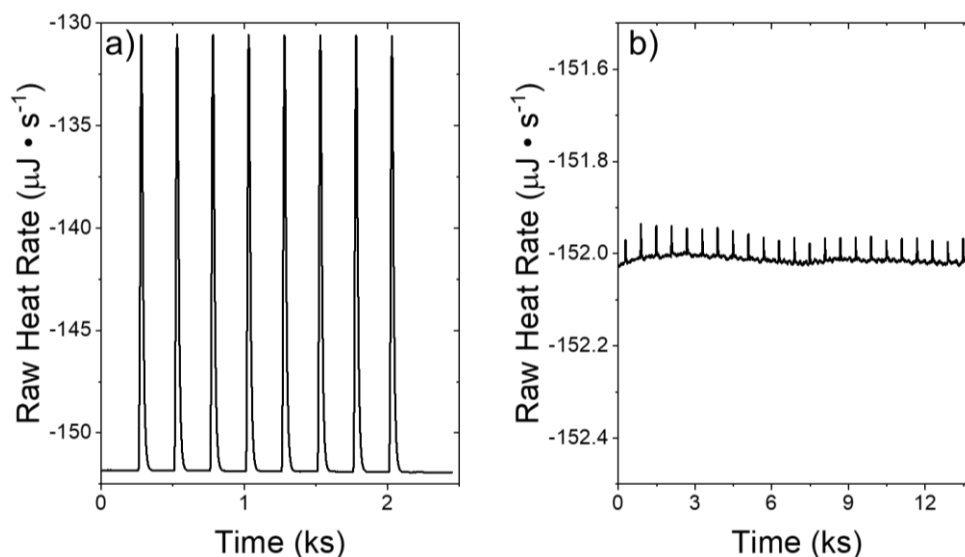


Figure A13. a) ITC thermogram from the electrical calibration of the NanoITC. b) ITC thermogram from the water-water adsorption to check the cleanliness of the ITC cell.

The plots in **Figure A13** were obtained during the cleaning and calibration procedures for isothermal titration calorimetry (ITC), as discussed in **Section 2.2.4**. **Figure A13a** shows the heat released from the sequential pulses during the electrical calibration. The instrument gave a calibration factor after the calibration completed, for which values greater than 0.98 were assumed to be satisfactory. **Figure A13b** shows the heat released during the water-water injection, during which each 1 μL injection led to a peak with an area between -3 and +3 μJ .

Figure A14 shows an acid-base titration of NaHCO_3 into HNO_3 , which was used as a standard to verify the results obtained from the NanoITC. The adsorption enthalpy calculated from **Figure A14b** was $-8.1 \pm 1.2 \text{ kJ mol}^{-1}$. This agrees well with the reported enthalpy of $-9.15 \text{ kJ mol}^{-1}$.^{1, 353-354} The ITC thermogram and heat release plots for all ITC experiments (other than that in **Figure 2.4**) are shown below. As discussed in **Section 2.3.5**, early injections often show lower

heat released than expected due to evaporation of liquid from the syringe needle. Although less common, some of the experiments below show outlier points at later injections, which may result from an inconsistent volume or epoxide concentration in those injections.

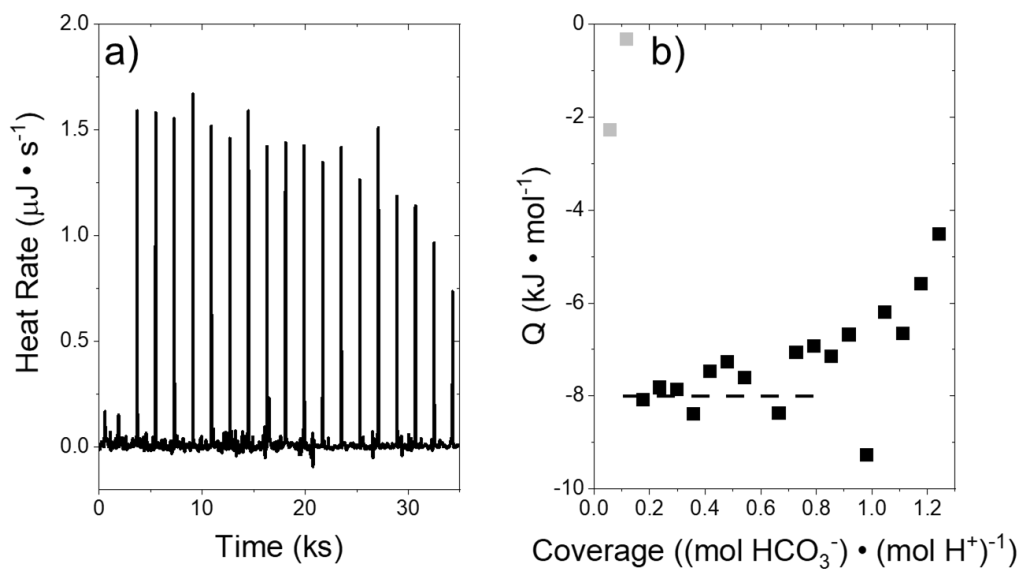


Figure A14. a) ITC thermogram from the acid-base titration of HNO_3 (0.0005 M in 0.1 M NaCl) with NaHCO_3 (0.0052 M in 0.1 M NaCl), b) the corresponding heats released as a function of bicarbonate ion coverage.

A11.2 Thermograms and Heats Per 1,2-Epoxy Injection

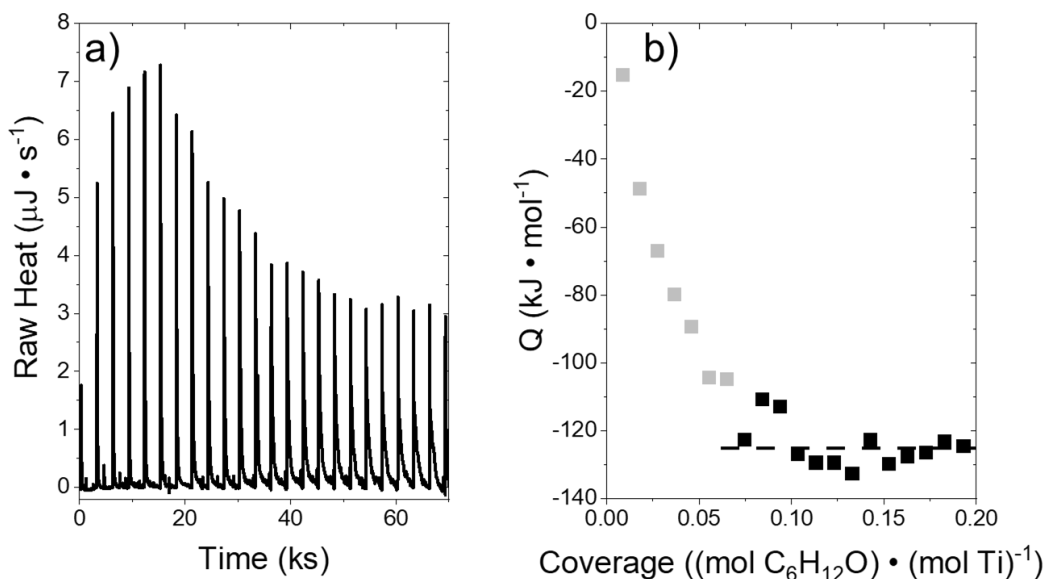


Figure A15. a) ITC thermogram from the titration of Ti-BEA-OH with 1,2-epoxyhexane (5 mM $\text{C}_6\text{H}_{12}\text{O}$ in CH_3CN with 200 mM H_2O , 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

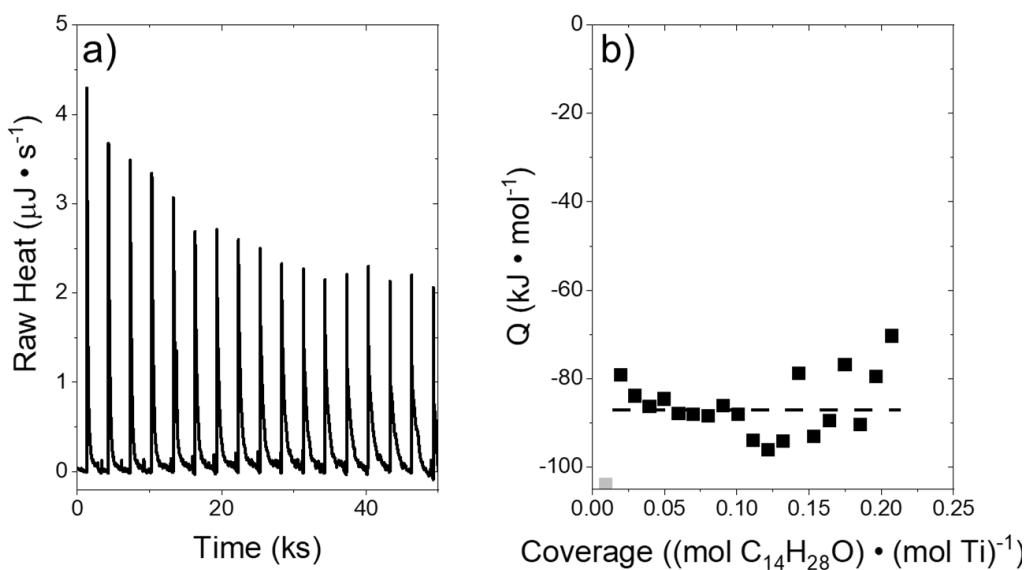


Figure A16. a) ITC thermogram from the titration of Ti-BEA-OH with 1,2-epoxytetradecane (3 mM $\text{C}_{14}\text{H}_{28}\text{O}$ in CH_3CN with 200 mM H_2O , 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxytetradecane coverage.

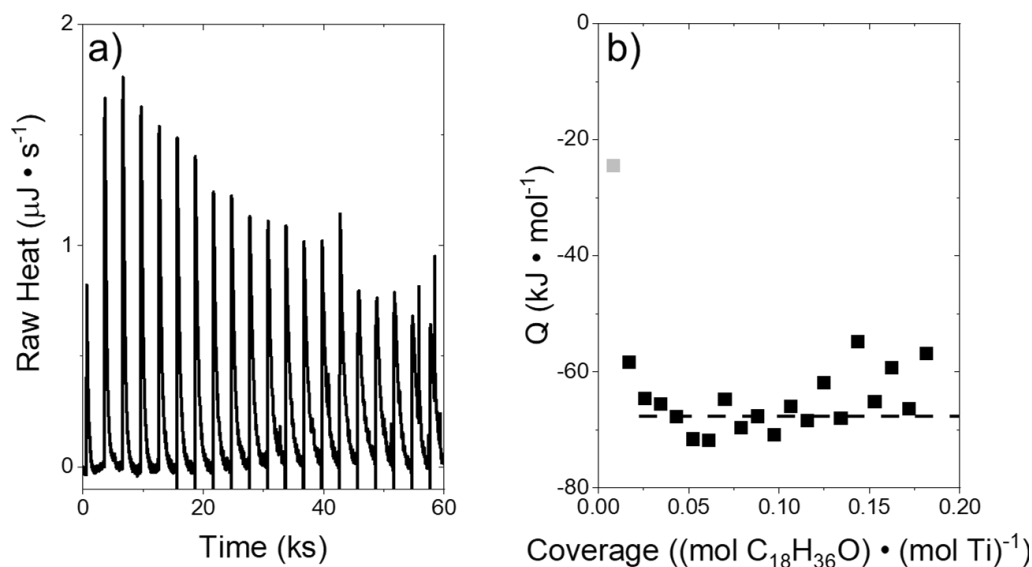


Figure A17. a) ITC thermogram from the titration of Ti-BEA-OH with 1,2-epoxyoctadecane (2 mM $\text{C}_{18}\text{H}_{36}\text{O}$ in CH_3CN with 200 mM H_2O , 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyoctadecane coverage.

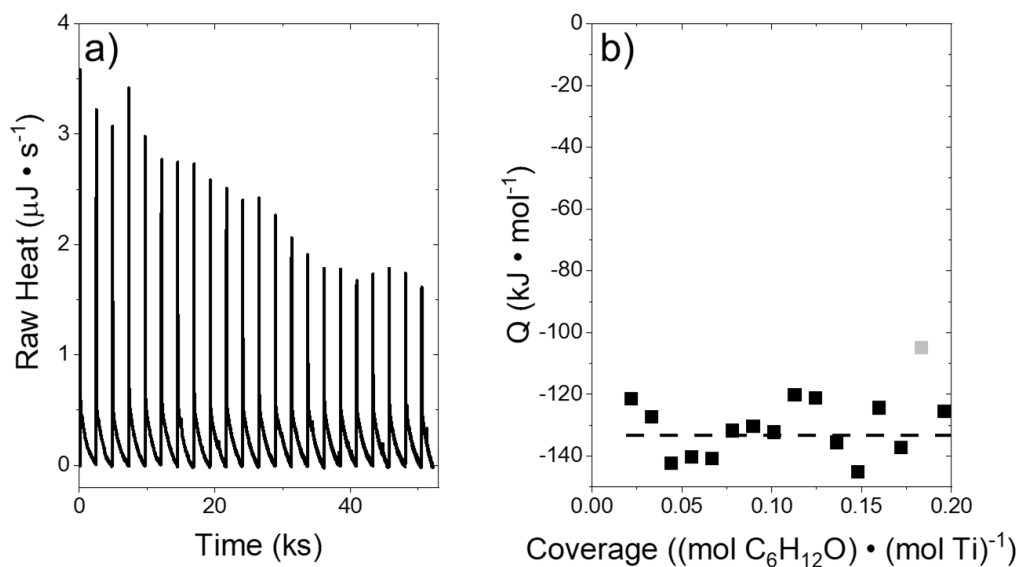


Figure A18. a) ITC thermogram from the titration of Ti-BEA-F with 1,2-epoxyhexane (2 mM $\text{C}_6\text{H}_{12}\text{O}$ in CH_3CN with 200 mM H_2O , 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

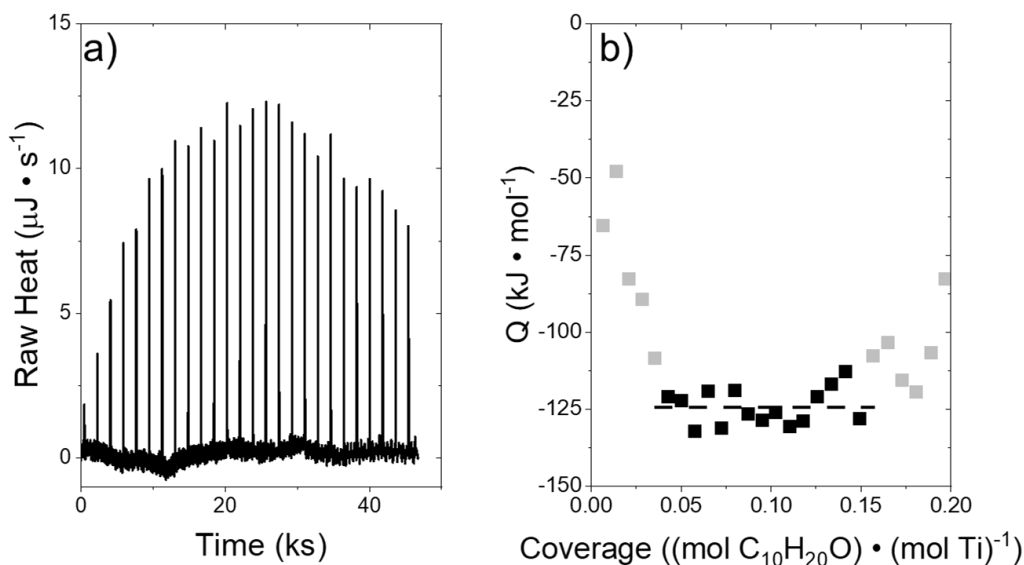


Figure A19. a) ITC thermogram from the titration of Ti-BEA-F with 1,2-epoxydecane (3 mM $\text{C}_{10}\text{H}_{20}\text{O}$ in CH_3CN with 200 mM H_2O , 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxydecane coverage.

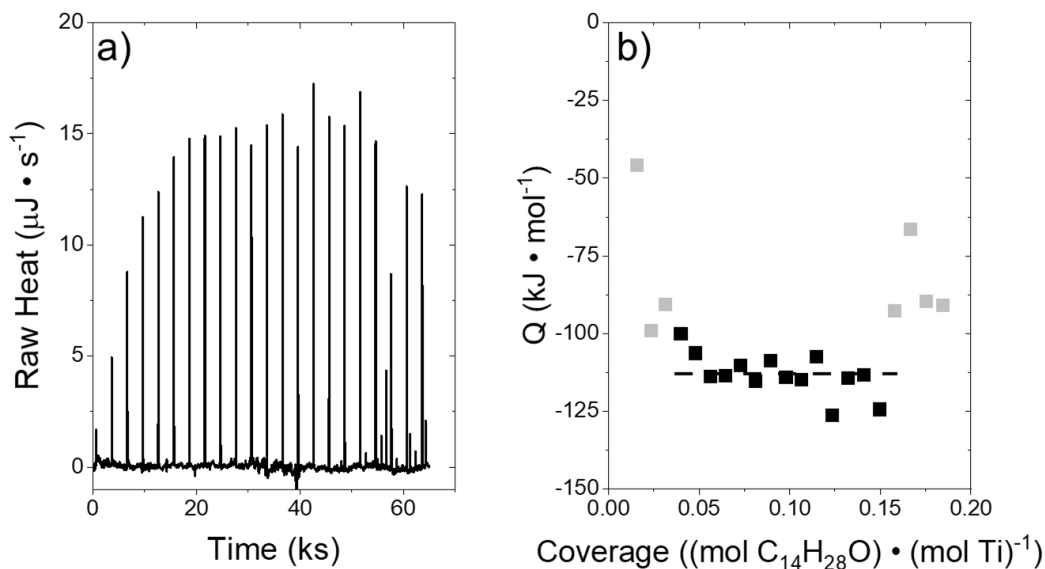


Figure A20. a) ITC thermogram from the titration of Ti-BEA-F with 1,2-epoxytetradecane (3 mM $\text{C}_{14}\text{H}_{28}\text{O}$ in CH_3CN with 200 mM H_2O , 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxytetradecane coverage.

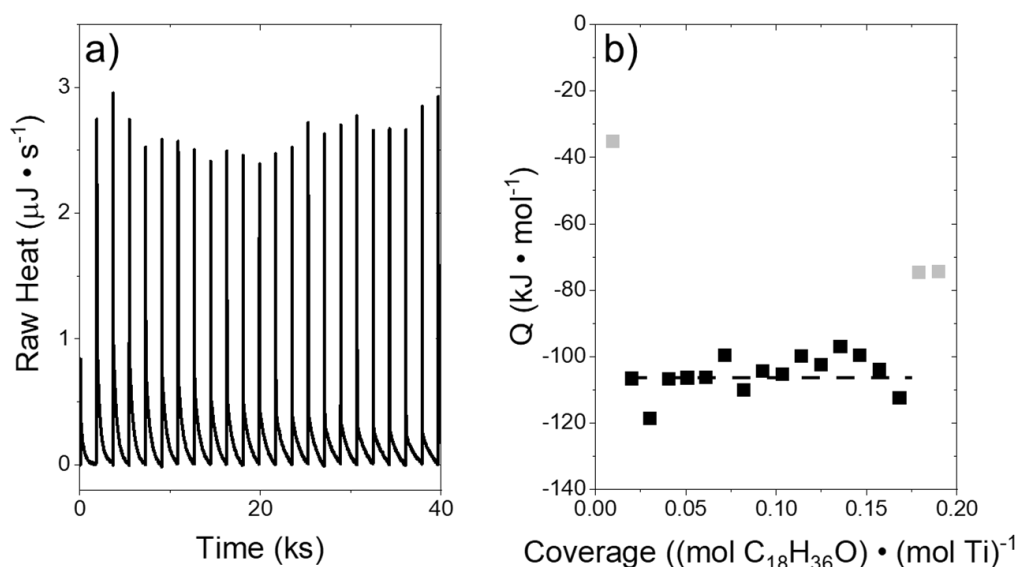


Figure A21. a) ITC thermogram from the titration of Ti-BEA-F with 1,2-epoxyoctadecane (3 mM $\text{C}_{18}\text{H}_{36}\text{O}$ in CH_3CN with 200 mM H_2O , 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyoctadecane coverage.

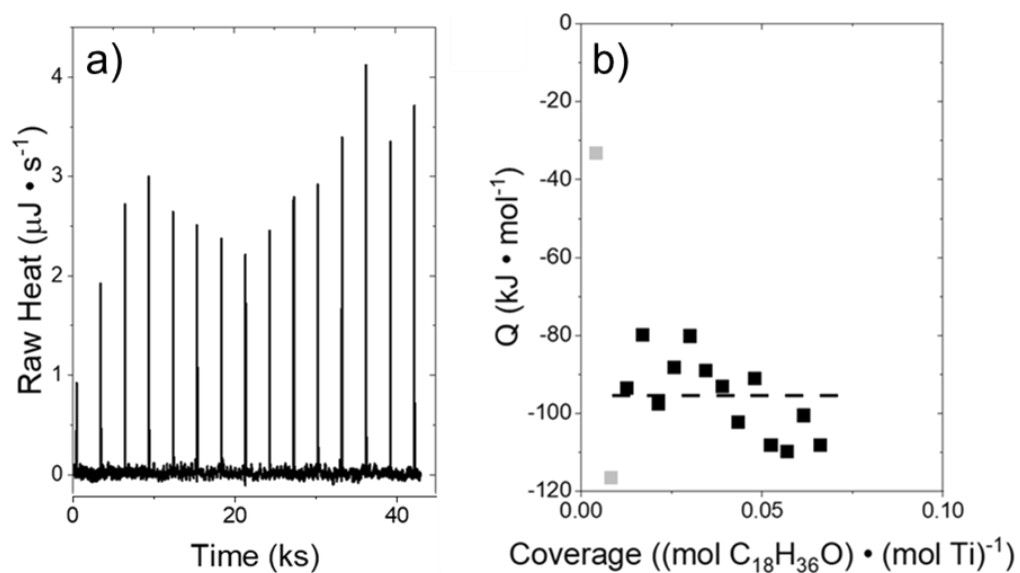


Figure A22. a) ITC thermogram from the titration of Ti-BEA-OH with 1,2-epoxyoctadecane (1 mM $\text{C}_{18}\text{H}_{36}\text{O}$ in CH_3CN with 39 mM H_2O , 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyoctadecane coverage.

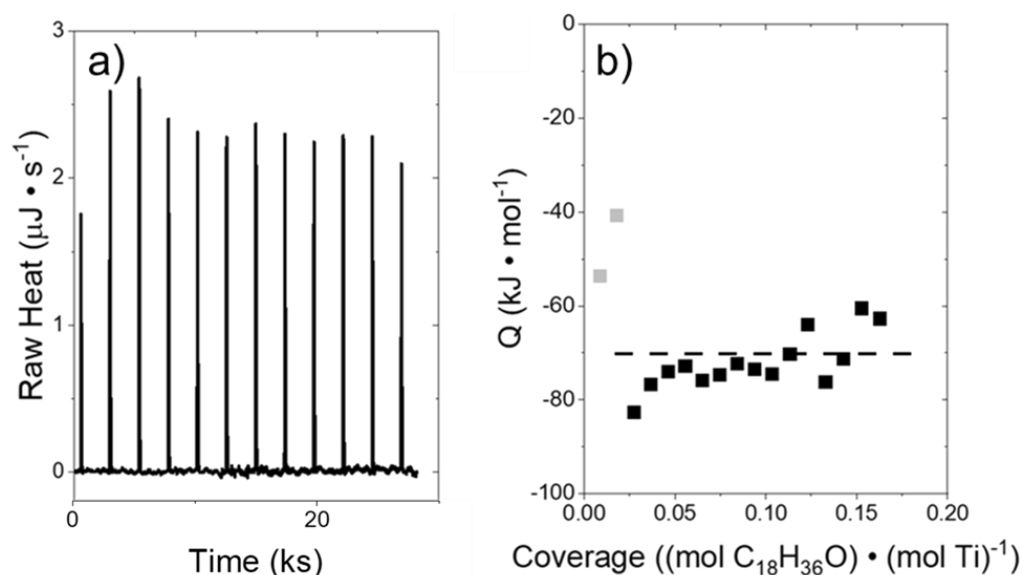


Figure A23. a) ITC thermogram from the titration of Ti-BEA-F with 1,2-epoxyoctadecane (1 mM $\text{C}_{18}\text{H}_{36}\text{O}$ in CH_3CN with 39 mM H_2O , 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyoctadecane coverage.

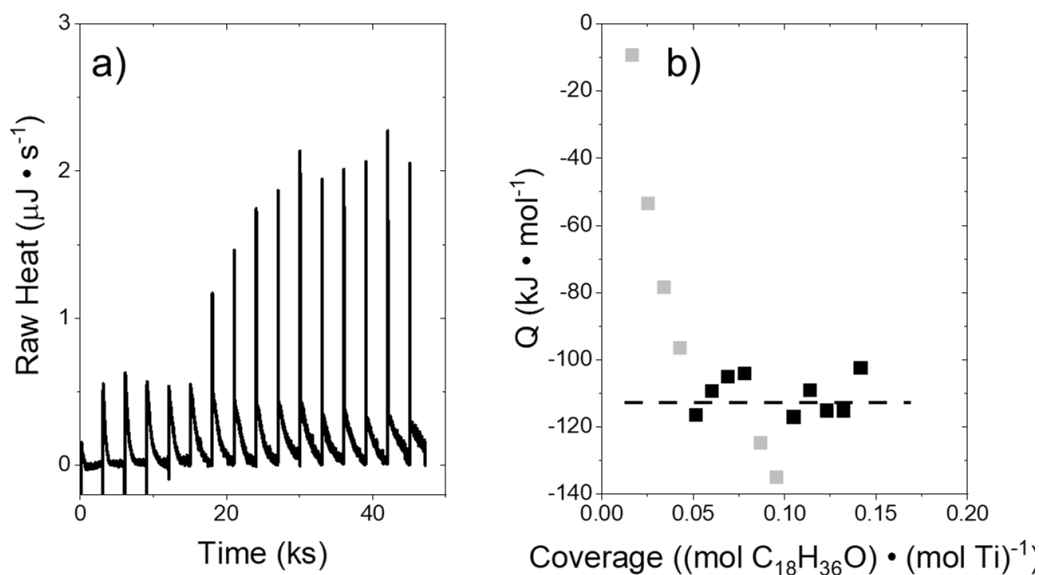


Figure A24. a) ITC thermogram from the titration of Ti-BEA-OH with 1,2-epoxyoctadecane (1 mM $\text{C}_{18}\text{H}_{36}\text{O}$ in CH_3CN with <0.3 mM H_2O , 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyoctadecane coverage.

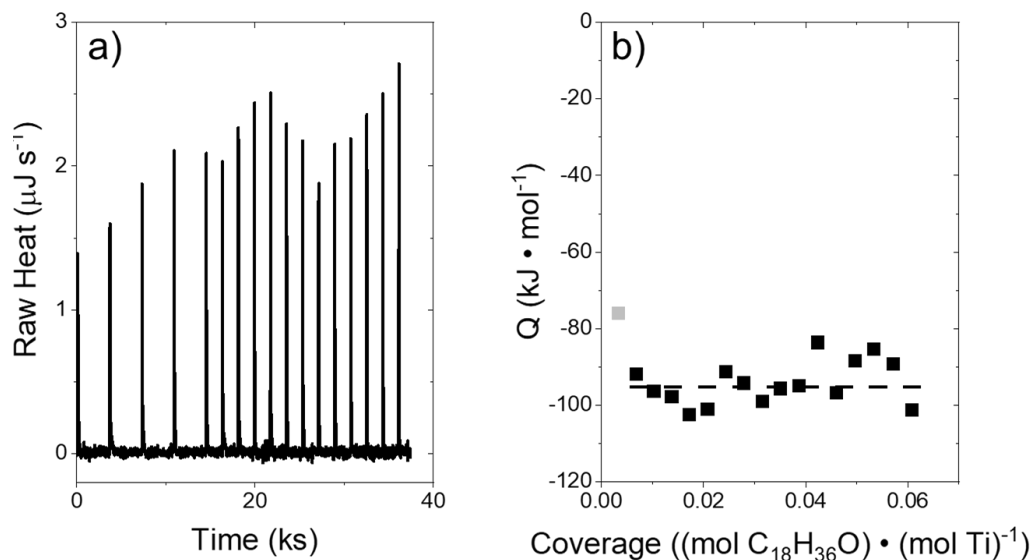


Figure A25. a) ITC thermogram from the titration of Ti-BEA-F with 1,2-epoxyoctadecane (3 mM $\text{C}_{18}\text{H}_{36}\text{O}$ in CH_3CN with <0.3 mM H_2O , 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyoctadecane coverage.

A12. Generation of Ti-BEA-OH Structures

Defects in zeolites can have a significant effect on their catalytic properties. For example, engineered Al defects enhance the hydrocarbon cracking efficiency of zeolite *BEA and increase the zeolite performance (e.g., rates, selectivities, catalyst stability) in acid-catalyzed reactions.³⁵⁵ $(\text{SiOH})_x$ nests alter rates of liquid-phase zeolite-catalyzed reactions, such as epoxidation and glucose isomerization.¹²⁴ Intrapore spatial correlations between defects, substrates, reaction intermediates, and solvent molecules modulate the catalytic activity and can be understood through molecular simulations.

The development of a computational model for a defected zeolite is challenged by the unknown spatial defect distribution in a synthesized zeolite sample that depends on the defect generation procedure (e.g., calcination, radical-assisted approach, reaction with silane-based molecules, dealumination, etc.).³⁵⁶ In the absence of any information on the defect distribution in

the synthesized Ti-BEA-OH, we assume it as random and later validate this assumption by comparing experimental and computed adsorption enthalpies of epoxides in Ti-BEA-OH zeolites.

Figure A26 summarizes our algorithm for random defect generation. In a dealuminated zeolite, the position of the $(\text{SiOH})_4$ nests correspond to the initial position of Al-atoms in the parent material. The position of those Al-atoms depends on various factors during the hydrothermal synthesis of the Al-containing parent zeolite. The algorithm mimics an experiment in which $(\text{SiOH})_4$ defects form by removing framework Al-atoms. First, we generated 1000 structures by random substitution of 11 of 255 Si-atoms for Al within the main image of a $(2 \times 2 \times 1)$ supercell to mimic the precursor for the experimental Ti-BEA-OH structure containing $2.75 (\text{SiOH})_4$ (unit cell)⁻¹. Since 52 out of 255 Si-atoms lie near cell boundaries and are bonded to O-atoms belonging to more than one periodic image, we did not consider these atoms for Al substitutions to avoid forming partial silanol groups crossing supercell boundaries that cannot be handled by the RASPA software. As many formed structures were not physically possible, we eliminated them by applying a series of filters. First, we removed the structures containing Al–Al and Ti–Al distances of less than 4 Å to avoid energetically unfavorable Ti–OH formation after dealumination. Among the 105 structures that passed the filter, we selected the 32 most diverse structures that did not contain more than three identical substitutions (25% of total defects). Identical substitutions were defined as structures containing identical coordinates for Al-atoms. In the next step, we selected the structures with the most random defect distribution using the qualitative similarity between Al–Al and Si–Si radial distribution functions (RDF) as a selection criterion. We eliminated the structures with clustered, largely separated, and/or nonmonotonically decaying peak heights, which we interpreted as having uneven defect distribution. We ended up with four final structures with Al–Al RDFs shown in **Figure A27**. Finally, the Ti-BEA-OH models were generated by removing Al-

atoms and adding H-atoms to the undercoordinated O-atoms formed. During equilibration, one of the silanol-H atoms (present near the periodic boundary) detached from the structure with the RDF shown in **Figure A27c**, likely due to an error in the code while reading connectivity during restart. Therefore, the unstable structure in **Figure A27c** was not used in further simulations. The three defect distributions corresponding to **Figures A27a**, **A27b**, and **A27d** are shown in **Figure A28**.

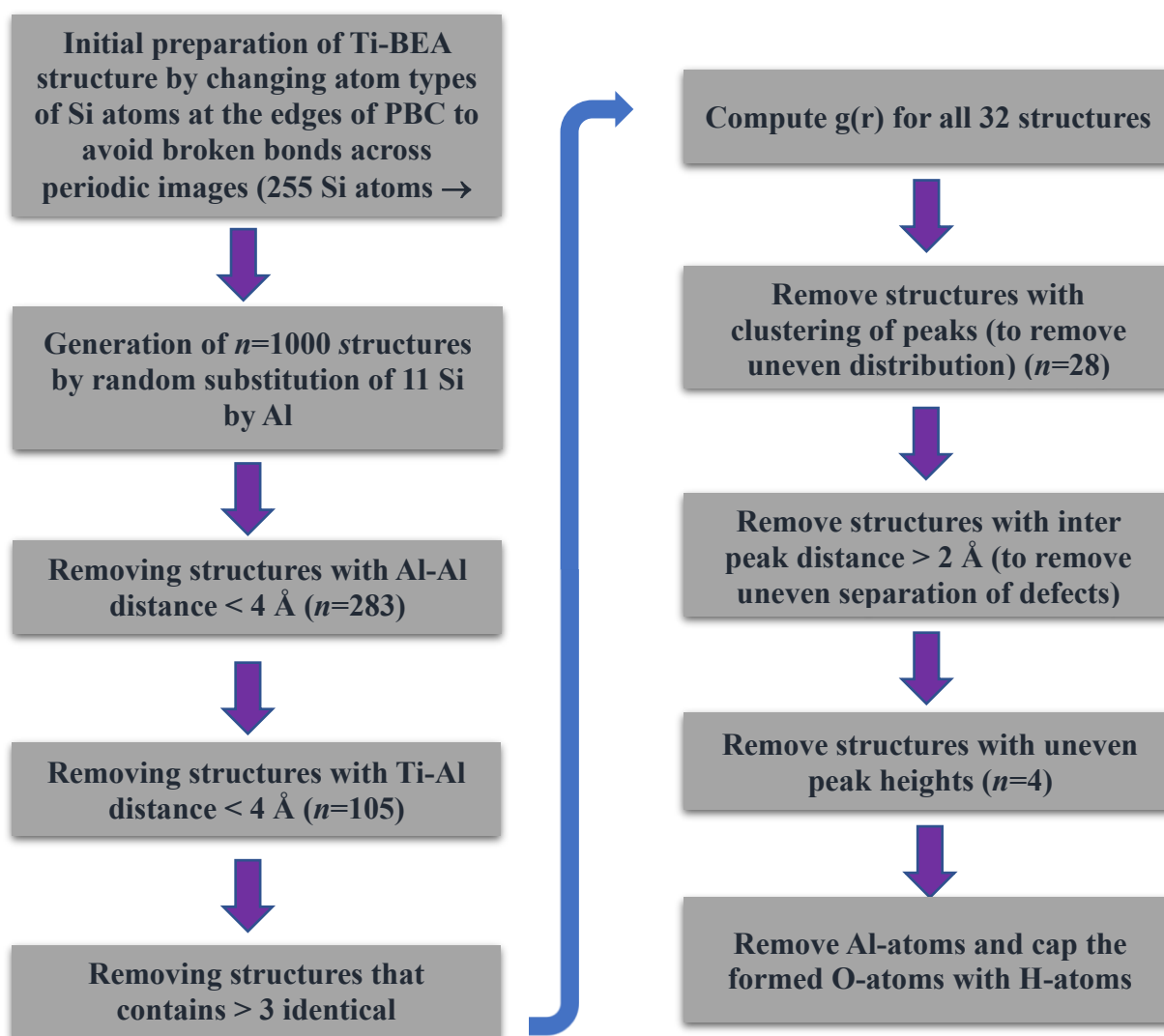


Figure A26. Algorithm used for the generation of random silanol defects in Ti-BEA.

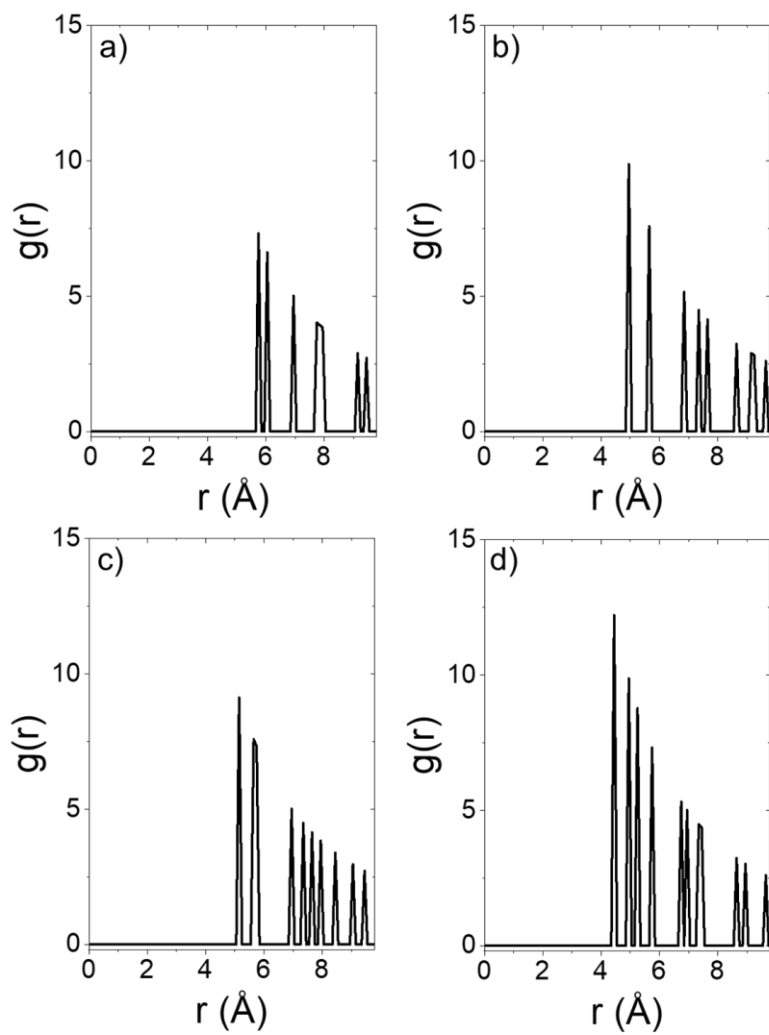


Figure A27. Al-Al radial distribution functions for the precursors of the four selected defect distributions.

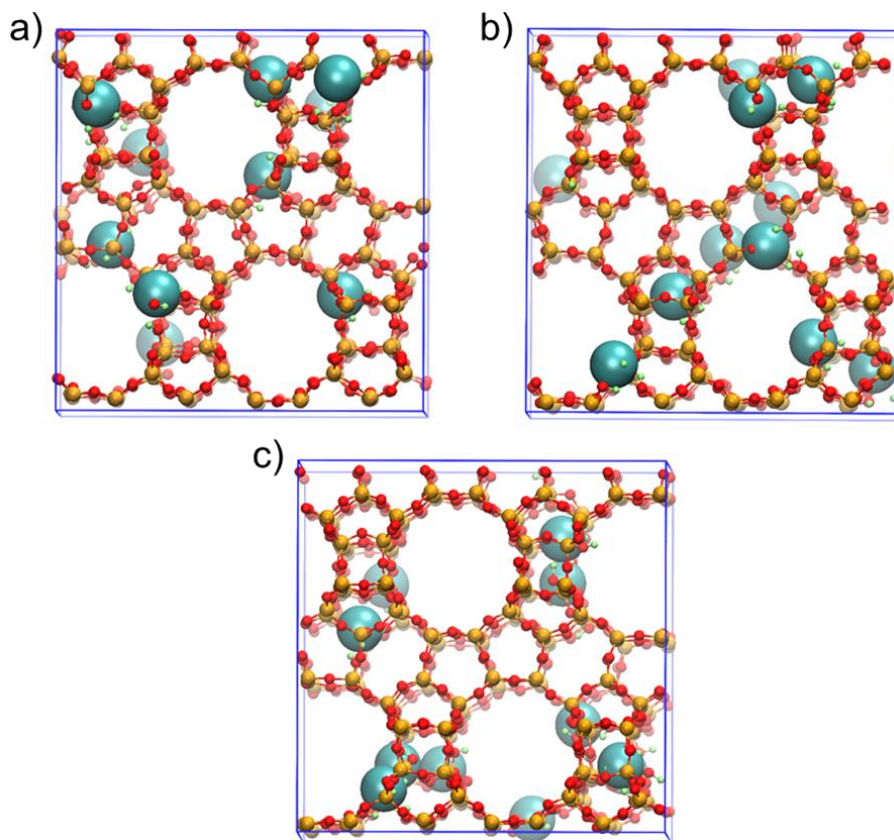


Figure A28. Defect distribution in three generated Ti-BEA-OH structures. Zeolite is shown using the ball and stick model, where Si-atoms are orange and O-atoms are red. Large, teal-colored spheres depict the positions of the defects. Periodic boundary conditions are shown in blue.

A13. Gibbs Ensemble Monte Carlo (GEMC) Simulations

Gibbs ensemble Monte Carlo (GEMC)³⁵⁷ is a versatile approach to study the thermodynamic equilibrium between two or more phases. GEMC was employed in this work to validate less costly methods to simulate bulk phase fugacities and phase equilibria that are described in **Section A14**. We carried out GEMC simulations of adsorption of liquid solvent mixtures in the zeolites using the GPU Optimized Monte Carlo (GOMC) software package³⁵⁸. Unlike other packages (such as RASPA), GOMC is OpenMP-parallelized and is thus suitable for large-scale GEMC simulations. The rigid Ti-BEA-OH or Ti-BEA-F structures were used as “box1”, and the bulk solution containing 900 CH₃CN and 10 – 100 H₂O molecules was defined as

the “reservoir box” (“box2”). Only the solvent molecules were allowed to swap between the boxes. CHARMM force field parameters used were described in **Section 2.2.7**. The reservoir box was allowed to change its volume during the simulation. A cutoff of 10 Å was employed for Lennard-Jones and Coulombic interactions. The molecules were allowed to move with the translational probability 0.6, rotational probability 0.19, swap probability 0.01, and volume change probability 0.1. The acceptance rates for these moves were 49% (translational), 41% (rotational), 32% (swap), 66% (volume change). GEMC simulations were carried out for 5×10^5 cycles for equilibration and 10^6 cycles for the production run. The uptake values were averaged over 1000 cycles, and errors were computed by splitting the trajectories into five samples. **Table A7** shows the uptakes of H₂O and CH₃CN in Ti-BEA-OH and Ti-BEA-F.

The computed GEMC H₂O uptakes agree well with the experimental uptakes in Ti-BEA-OH and Ti-BEA-F from the 200 mM H₂O solution in CH₃CN ($x_{H_2O} = 0.01$) (1.45 and 0.05, respectively). However, 10^6 cycles of the GEMC simulations required large computational time (452 hours of wall time on average for calculations running on 68 cores/272 threads on a single node of Knights Landing type on Stampede2), even with OpenMP parallelization. To reduce the computational cost, we computed fugacity coefficients for both CH₃CN and H₂O, using three

Ti-BEA-OH				Ti-BEA-F	
x_{H_2O} (initial)	x_{H_2O} (final)	n_{H_2O}	n_{CH_3CN}	n_{H_2O}	n_{CH_3CN}
0.01	0.008	1.03 ± 0.03	11.79 ± 0.15	0.06 ± 0.003	10.43 ± 0.28
0.04	0.039	2.89 ± 0.07	11.23 ± 0.12	0.07 ± 0.008	9.88 ± 0.51
0.06	0.058	3.55 ± 0.10	10.57 ± 0.06	0.09 ± 0.002	9.21 ± 0.30
0.10	0.094	5.88 ± 0.14	8.23 ± 0.08	0.12 ± 0.008	8.22 ± 0.07

Table A7. Uptake values of H₂O and CH₃CN from GEMC simulations as a function of liquid-phase mole fraction of H₂O (x_{H_2O}) (313 K, 1 atm). Initial H₂O concentration corresponds to the composition of the liquid-phase compartment before the simulation. Final H₂O concentration is the average value after equilibration.

methods described in **Section A14**, for use in the less costly GCMC (Grand Canonical Monte Carlo) and GCMD (Grand Canonical Molecular Dynamics) adsorption simulations. The computed fugacity coefficients were validated by comparing GCMC/GCMD and GEMC solvent uptakes.

A14. Calculation of CH₃CN and H₂O Fugacity Coefficients

GCMC/GCMD adsorption simulations of zeolites require the knowledge of fugacities and fugacity coefficients (ϕ_i) for every species in the bulk solution. We evaluated ϕ_i using three approaches: (1) using gas and liquid-phase free energies calculated from the NIST thermodynamic data³⁵⁹ and activity coefficients (γ_i) computed in CHEMCAD,³⁶⁰ (2) using the modified Raoult's law, experimental saturated vapor pressures (P_i^{sat}), and the same activity coefficients as in (1); (3) by carrying out the Monte Carlo (MC) simulation of the bulk solution using the CFCNPT ensemble and extracting ϕ_i from the excess chemical potential. The accuracy of the methods was evaluated by comparing solvent adsorption uptakes with GEMC simulations chosen as a reference. We found that method (3) produced uptakes that most closely resemble GEMC uptakes. Consequently, it was used to generate all GCMD results reported in this work.

Method 1:

Chemical potentials of species i at temperature T in the ideal gas state (μ_i^{ig}) and in solution (μ_i) are given by **Equations A27** and **A28**,³⁶¹ respectively:

$$\mu_i^{ig} = \Gamma_i(T) + RT \ln x_i P \quad (\text{A27})$$

$$\mu_i = \Gamma_i(T) + RT \ln \hat{f}_i \quad (\text{A28})$$

Here, $\Gamma_i(T)$ represents the chemical potential of pure species i at 1 bar and the ideal gas state, x_i is the mole fraction of species i , P is the external pressure, and $\hat{f}_i$ is the fugacity of species i in the mixture.

Subtracting **Equation A27** from **A28** yields:

$$\mu_i - \mu_i^{ig} = RT \ln \frac{\hat{f}_i}{x_i P} = RT \ln \hat{\phi}_i, \quad (\text{A29})$$

where $\hat{\phi}_i$ is the fugacity coefficient of species i in the mixture.

Subtracting and adding μ_i^{id} and rearranging **Equation A29** gives:

$$RT \ln \hat{\phi}_i = \mu_i - \mu_i^{ig} = \mu_i - \mu_i^{id} + (\mu_i^{id} - \mu_i^{ig}) \quad (\text{A30})$$

where μ_i^{id} is the chemical potential of species i in the liquid-phase ideal solution.

The quantities μ_i^{id} and μ_i^{ig} are related to molar fractions as:

$$\mu_i^{id} = G_i(T, P) + RT \ln x_i \quad (\text{A31})$$

$$\mu_i^{ig} = G_i^{ig}(T, P) + RT \ln x_i \quad (\text{A32})$$

Here $G_i(T, P)$ and $G_i^{ig}(T, P)$ are the free energy of pure species i at standard conditions in pure liquid and the ideal gas state, respectively.

Therefore, subtracting **Equation A32** from **A31** gives:

$$(\mu_i^{id} - \mu_i^{ig}) = G_i(T, P) - G_i^{ig}(T, P) \quad (\text{A33})$$

μ_i and μ_i^{id} are related to the activity coefficient γ_i by **Equation A34**:

$$\mu_i - \mu_i^{id} = RT \ln \gamma_i \quad (\text{A34})$$

Substituting **A33** and **A34** in **Equation A30** yields:

$$RT \ln \hat{\phi}_i = RT \ln \gamma_i + G_i(T, P) - G_i^{ig}(T, P) \quad (\text{A35})$$

Rearranging **Equation A35** gives:

$$\hat{\phi}_i = \gamma_i e^{\frac{G_i - G_i^{ig}}{RT}} \quad (\text{A36})$$

Equation A36 gives the relation between the fugacity coefficient of species i and its activity coefficient. The activity coefficients of H₂O and CH₃CN were computed by taking the average

value of the activity coefficients from five methods on CHEMCAD (VTPR, UNIFAC, Modified UNIFAC, UNIQUAC, and NRTL). The five methods used are common to calculate liquid-phase activity coefficients and were chosen because they gave close agreement for H₂O and CH₃CN activity coefficients. The average activity coefficients are shown in **Figure A29**. The largest discrepancy between methods occurred for H₂O at the most dilute H₂O fraction in **Figure A29** ($x_{H_2O} = 0.01$), with a range of activity coefficients of 7.0 to 10.1.

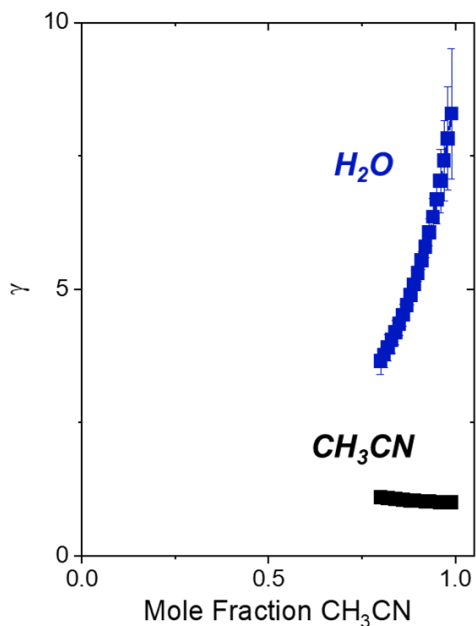


Figure A29. Activity coefficients for CH₃CN and H₂O as a function of mole fraction of CH₃CN in liquid-phase mixtures, averaged across five methods from ChemCAD (VTPR, UNIFAC, Modified UNIFAC, UNIQUAC, and NRTL).

G_i^{ig} and G_i values of pure species at 313 K were calculated using the change in enthalpy and entropy of each solvent species between 298 and 313 K evaluated as:

$$\Delta H_i = C_{P,i}(T_2 - T_1) \quad (A37)$$

$$\Delta S_i = C_{P,i} \ln \frac{T_2}{T_1} \quad (A38)$$

Finally, the free energy of every species in the pure state was calculated as:

$$G_i = (H_i(298) + \Delta H_i) - T(S_i(298) + \Delta S_i) \quad (A39)$$

Where $H_i(298)$ and $S_i(298)$ are the standard enthalpy and entropy of formation of each species at 298 K and 1 atm taken from the NIST database, ΔH_i and ΔS_i are changes in enthalpy and entropy between two different temperatures (298 K and 313 K), and C_p is the specific heat capacity at a constant pressure obtained from the NIST database. C_p for CH₃CN and H₂O are 91.69 and 52.21 J mol⁻¹ K⁻¹, respectively, in the gas-phase. For the liquid-phase CH₃CN, C_p is 91.69 J mol⁻¹ K⁻¹. For the liquid-phase H₂O, enthalpy and entropy differences were calculated using the Schomate equation provided in the NIST database, as it provides a more accurate description of temperature-dependent enthalpy and entropy of water in the liquid-phase. Activity coefficients were computed using CHEMCAD.

Table A8 reports the calculated free energies of H₂O and CH₃CN in gas- and liquid-phases, CHEMCAD-predicted activity coefficients, and the predicted fugacity coefficients of the components in the mixture. The table also includes solvent uptake values (per unit cell) in Ti-BEA-F from the 200 mM H₂O in CH₃CN solution calculated using the GCMC method.

The uptake values of H₂O and CH₃CN in Ti-BEA-F clearly underestimate the experimental (0.05 for H₂O) and GEMC uptakes (0.06 for H₂O and 10.43 for CH₃CN). We attribute the errors to the high sensitivity of the predicted fugacity coefficients to errors in the reported experimental enthalpies and entropies due to the exponential relationship in **Equation A36**. We conclude that method (1) is unsuitable for calculations of fugacity coefficients.

Molecule	G_i^{ig} (J mol ⁻¹)	G_i (J mol ⁻¹)	γ_i	$\hat{\phi}_i$	Uptake in Ti-BEA-F
H ₂ O	-300977.722	-307761.402	8.86	0.654	0.018 ± 0.005
CH ₃ CN	-2037.098	-6302.840	1.00	0.194	6.05 ± 0.41

Table A8. Calculated free energies, activity, and fugacity coefficients of H₂O and CH₃CN in the 200 mM of H₂O in CH₃CN solution using method (1).

x_{H_2O}	γ_{H_2O}	γ_{CH_3CN}	y_{H_2O}	y_{CH_3CN}	f_{H_2O}	f_{CH_3CN}	P^{tot}
0.2	3.75	1.08	0.22	0.78	0.06	0.19	0.25
0.15	4.37	1.04	0.18	0.82	0.05	0.21	0.25
0.1	5.14	1.02	0.15	0.85	0.04	0.21	0.25
0.05	6.09	1.00	0.09	0.91	0.02	0.22	0.24
0.01	7.04	1.00	0.02	0.98	0.005	0.23	0.23

Table A9. Calculated y_i , f_i and P^{tot} for H₂O and CH₃CN at different compositions (313 K, $P_{H_2O}^{sat} = 0.074$ atm, $P_{CH_3CN}^{sat} = 0.23$ atm). Pressure/fugacity values are reported in atm.

Method 2:

The modified Raoult's law states that:

$$f_i = y_i P^{tot} = \gamma_i x_i P_i^{sat} \quad (A40)$$

Where f_i is the fugacity of species i , y_i is the gas-phase mole fraction of species i in equilibrium with the liquid, $P^{tot} = \sum_i \gamma_i x_i P_i^{sat}$ (H₂O saturation pressures from reference³⁶²) is the total vapor pressure, γ_i is the liquid-phase activity coefficient of species i , x_i is the liquid-phase mole fraction of species i , and P_i^{sat} is the saturation vapor pressure of pure species i . The activity coefficients were computed using the same approach as in method (1). The modified Raoult's law assumes that the gas obeys the ideal gas law,³⁶¹ which is a reasonable assumption given that P^{tot} is low (0.23-0.25 atm) at experimental conditions (313 K). We computed y_i from **Equation A40** and used it with P^{tot} in the GCMD/GCMC input. We used GCMC to simulate adsorption in Ti-BEA-F and GCMD for Ti-BEA-OH, as Ti-BEA-OH, unlike Ti-BEA-F, contains flexible silanol OH groups that required proper description of their dynamics in the model. **Table A9** reports the calculated values of y_i , P^{tot} and f_i at various solvent compositions. The composition used in the adsorption experiments with ITC is highlighted in bold.

The computed uptake values in pristine Ti-BEA-F are $n_{H_2O} = 0.008 \pm 0.01$ and $n_{CH_3CN} = 8.22 \pm 0.12$ per unit cell for $x_{H_2O} = 0.01$ solution and $n_{CH_3CN} = 8.56 \pm 0.11$ for the pure CH_3CN solvent. The H_2O uptake is significantly underestimated by this method in comparison with the experimental value (0.05). The uptake values also deviate significantly from GEMC values for H_2O (0.06) and CH_3CN (10.43). Again, we conclude that method (2) is unsuitable for the study.

Method 3:

In method (3), we computed the fugacity coefficients directly in a Monte Carlo (MC) simulation of a bulk solvent mixture using the same modified CHARMM force field as described in **Section 2.2.7**. 900 CH_3CN and 10 H_2O molecules were packed inside a box with an edge length of 43.3 Å, and the MC simulation was carried out at 313 K and 1 atm for 10^6 cycles. The first 10^5 cycles were used in the equilibration run. We employed the CFCMC-NPT³⁶³ ensemble implemented in the BRICK-CFCMC code,³⁶³ in which an extra “fractional” molecule (i.e., solvent molecule whose interactions with the environment are scaled by a fractional value) was added to the box using an additional degree of freedom λ . The interactions between the new molecule and other molecules were scaled by λ . The λ value varied from 0 (no interaction with the system) to 1 (full interaction). In this simulation, a cutoff of 14 Å was used for Lennard-Jones and electrostatic interactions. The Ewald method was employed for electrostatic interactions.¹⁷³ The random trial moves were chosen with the following probabilities: 40% translational, 19% rotational, 1% volume change, 20% λ moves, 10% identity change, and 10% re-insertion. The acceptance rates for the moves were 50% translational, 48% rotational, 72% volume change, 66% λ moves, 42% identity change, and 35% re-insertion. The fugacity coefficient was computed by the software as:

$$\phi_i = \frac{e^{\frac{\mu_i^{ex}}{RT}}}{Z_m} \quad (A41)$$

Framework	Uptake of H ₂ O (unit cell) ⁻¹	Uptake of CH ₃ CN (unit cell) ⁻¹
Ti-BEA-F	0.035	9.52
Ti-BEA-OH	1.06	12.25

Table A10. Uptake of H₂O and CH₃CN from $x_{H_2O} = 0.01$ bulk solution into Ti-BEA-F and Ti-BEA-OH (313 K, 1 atm).

Where $\mu_i^{ex} = -RT \ln \frac{p(\lambda_i=1)}{p(\lambda_i=0)}$ is the excess chemical potential, $p(\lambda_i)$ is the unbiased Boltzmann probability distribution of λ of the fractional molecule, and $Z_m = \frac{NRT}{P\langle V \rangle}$ is the compressibility factor of the solution. BRICK-CFCMC software³⁶⁴ was used to compute the excess chemical potential and the fugacity coefficient. The calculated fugacity coefficients for CH₃CN and H₂O are 0.264 and 1.37, respectively. **Table A10** provides the uptake values of solvents in Ti-BEA-OH and Ti-BEA-F from the bulk liquid-phase using GCMD simulations and the obtained fugacity coefficients.

The uptake values per unit cell using “method (3)” fugacity coefficients match experimental data ($n_{H_2O} = 0.05$) as well as GEMC uptake values for Ti-BEA-F ($n_{H_2O} = 0.06$; $n_{CH_3CN} = 10.43$) and Ti-BEA-OH ($n_{H_2O} = 1.03$; $n_{CH_3CN} = 11.79$) very well. Due to its superior accuracy, method (3) was employed to compute the fugacity coefficients for all species for all systems explored with GCMD/GCMC simulations. On average, each GCMD/GCMC simulation (107 cycles) required 220 hours of wall-time, running on a single processor on the Knights Landing type of a node on Stampede2. Overall, the new computational protocol based on GCMC/GEMC and the separately computed fugacity coefficients is less expensive than GEMC by nearly three orders of magnitude. The comparison of computed and experimental uptake values for all systems is provided in subsequent sections and in **Chapter 2**.

A15. Computed Solvent Uptakes Before and After Epoxide Adsorption

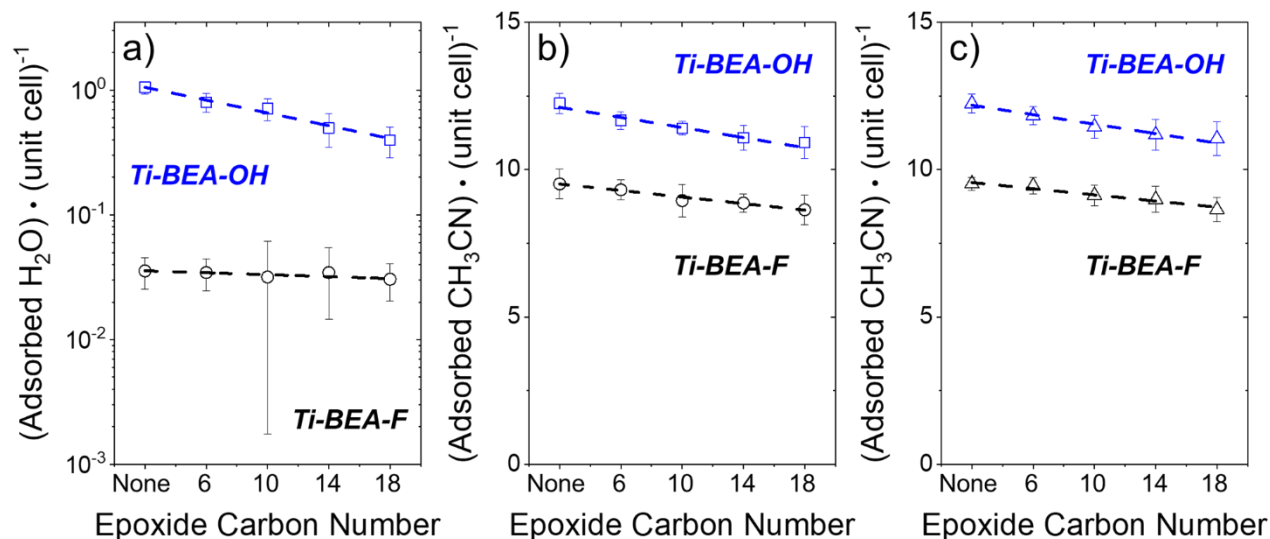
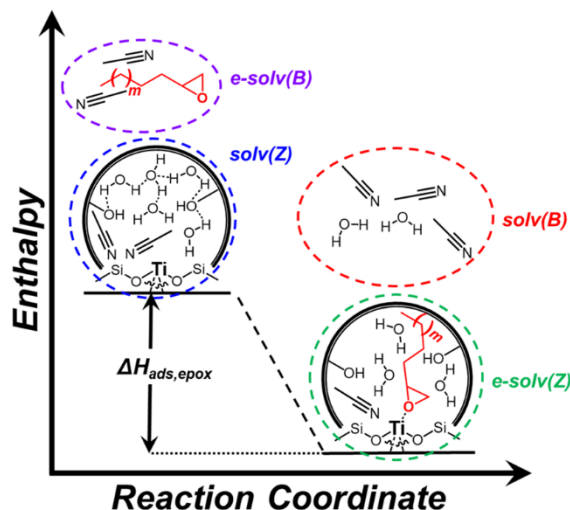


Figure A30. Uptake of a) H₂O in CH₃CN + 200 mM H₂O, b) CH₃CN in CH₃CN + 200 mM H₂O, and c) CH₃CN in pure CH₃CN into Ti-BEA-OH (blue) and Ti-BEA-F (black) without and with each epoxide present, calculated with GCMD simulations.

Figure A30 shows computed H₂O and CH₃CN absorption uptakes per unit cell as a function of epoxide carbon number. The computed values match well with the experimentally measured H₂O uptake data (**Section 2.3.3**). The uptake of CH₃CN and H₂O decreases as longer chain epoxides are introduced into the pores of Ti-BEA. Notably, the slope of the fitting line has a greater magnitude for the H₂O plot in Ti-BEA-OH. This signifies that epoxide adsorption requires disruption of greater quantities of H₂O in Ti-BEA-OH than Ti-BEA-F, which leads to greater enthalpic penalties for epoxide adsorption and less negative $\Delta H_{ads,epox}$ (**Figure 2.10**).

A16. Details of Adsorption Enthalpy ($\Delta H_{ads,epox}$) Calculations

The enthalpy of epoxide adsorption in Ti-BEA-F and Ti-BEA-OH was computed using the thermodynamic process depicted in **Scheme A2**.



Scheme A2. Epoxide adsorption in Ti-BEA-OH zeolite pores with a concomitant displacement of solvent into the bulk. Subscript “B” is used to differentiate solvent in the bulk from solvent inside the pores.

Here, ZS represents the state of the zeolite filled with solvent molecules in equilibrium with the bulk phase; the CS_B and SS_B states represent epoxide and solvent molecules, respectively, in the bulk solvent; and the ZCS state corresponds to the zeolite containing both adsorbed solvent and epoxide, also in equilibrium with the bulk solvent.

$\Delta H_{ads,epox}$ was computed using **Equation A42**:

$$\Delta H_{ads,epox} = H_e(solv[Z]) + \Delta n_{H_2O} \bar{H}_{H_2O}(solv[B]) + \Delta n_{CH_3CN} \bar{H}_{CH_3CN}(solv[B]) - H(solv[Z]) - \bar{H}_e(solv[B]) \quad (A42)$$

where $H_e(solv[Z])$ represents the molar enthalpy of the zeolite-adsorbed epoxide-solvent system, $H(solv[Z])$ equals the molar enthalpy of the zeolite-solvent system, $\bar{H}_{H_2O}(solv[B])$, $\bar{H}_{CH_3CN}(solv[B])$, and $\bar{H}_e(solv[B])$ are the partial molar enthalpies of H₂O, CH₃CN, and the

epoxide in the bulk solvent, and Δn_{H_2O} and Δn_{CH_3CN} equal the computed average (fractional) numbers of solvent molecules desorbed into the bulk upon epoxide adsorption.

$H_{e-solv(Z)}$ and $H_{solv(Z)}$ were calculated assuming $H \approx U$ and neglecting the PV term due to the small molar volume of adsorbates in the zeolite that approach liquids in density. The average total (kinetic + potential) energy (U) was computed directly during the production run of GCMD simulations using the RASPA software.

The partial molar quantities $\bar{H}_{H_2O}(solv[B])$, $\bar{H}_{CH_3CN}(solv[B])$, and $\bar{H}_e(solv[B])$ were computed according to $\bar{H}_i = \bar{H}_i^{IG} + \bar{H}_i^{ex}$, where $\bar{H}_i^{ex}$ is the excess enthalpy of species i (herein, we use the convention typical for molecular simulations³⁶⁵) and $\bar{H}_i^{IG}$ is the corresponding ideal-gas enthalpy. $\bar{H}_i^{ex}$ was computed using the **Equation A43** derived by Rahbari et al.³⁶⁶ in the CFCNPT ensemble as implemented in the BRICK software³⁶³:

$$\bar{H}_i^{ex} = -\frac{1}{\beta} + \langle H(\lambda_i = 1) \rangle - \frac{\langle H/V(\lambda_i=0) \rangle}{\langle 1/V(\lambda_i=0) \rangle} \quad (A43)$$

Here $\bar{H}_i^{ex}$ is the partial molar excess enthalpy of species i , $\beta = 1/k_B T$, $\langle H(\lambda_i = 1) \rangle$ is the ensemble average enthalpy at which λ_i approaches 1, $\langle H/V(\lambda_i = 0) \rangle$ is the ensemble average of the ratio between total enthalpy and total volume of the system at which λ_i approaches 0, and $\langle 1/V(\lambda_i = 0) \rangle$ is the ensemble average of the inverse of the total volume of the system at which λ_i approaches 0. Here λ_i is the scaling factor for the component i . The CFCNPT simulations were carried out individually for each species present in a solvent box containing 900 molecules of CH_3CN and 10 molecules of H_2O at the conditions and simulation parameters described in **Section A14** (Method 3). H_2O and CH_3CN were treated as rigid, whereas the solvated epoxides were treated as partially flexible. In particular, the epoxide group (CH_2-O-CH_2) was rigid and the alkyl chain was flexible. The intramolecular potentials associated with bending and dihedral motions were described using the Trappe force field, compatible with the BRICK software, while the

Molecule	Excess partial molar enthalpy (kJ mol ⁻¹)
H ₂ O	-34.85 ± 2.76
CH ₃ CN	-32.59 ± 0.50
C ₆ H ₁₂ O	-32.09 ± 1.88
C ₁₀ H ₂₀ O	-47.66 ± 2.17
C ₁₄ H ₂₈ O	-58.74 ± 2.64
C ₁₈ H ₃₆ O	-71.84 ± 2.85

Table A11. Excess partial molar enthalpies (solvation enthalpies) obtained from CFCMC-NPT simulations (313 K, 1 atm, CH₃CN, 200 mM H₂O).

intermolecular interactions were treated using the CHARMM charges and van der Waals parameters as employed throughout this work.³⁶⁷ Since the intramolecular energy only enters in $\bar{H}_i^{IG}$, it is computed separately in single-molecule simulations using the modified CHARMM force field (*vide infra*). As the $\bar{H}_i^{ex}$ property is intermolecular in nature, it should only be weakly affected by choice of the force field for the intramolecular interactions (Trappe vs. modified CHARMM).

Table A11 provides the calculated excess molar enthalpies of H₂O, CH₃CN, and epoxides.

The enthalpy of each species in the ideal gas state ($\bar{H}_i^{IG}$) is calculated from the average total energy (U_i^{IG}) computed in a single-molecule molecular dynamic simulation, using **Equation A44**.

$$\bar{H}_i^{IG} = U_i^{IG} + P\langle V \rangle \quad (\text{A44})$$

where $P\langle V \rangle$ is the product of external pressure (1 atm) in the simulation box and the average volume of the box calculated during the production run of the GCMD simulation.

A17. Details of Energy Decomposition of $\Delta H_{ads,epox}$

We decomposed $\Delta H_{ads,epox}$ into physically meaningful contributions to give $\Delta H_{ads,epox(ED)}$ based on the thermodynamic cycle shown in **Scheme 2.3**. $\Delta H_{ads,epox(ED)}$ can be decomposed into various terms as shown in **Equation A45**:

$$\Delta H_{ads,epox(ED)} = -\Delta H_{e,solvation} + \Delta H_{\Delta solv} + \Delta H_{e-zeo} + \Delta H_{e-solv} \quad (A45)$$

$\Delta H_{e,solvation}$ refers to the excess partial molar enthalpy of an epoxide in the bulk phase, computed according to the procedure described in **Section A16** and reported in **Table A11**. $\Delta H_{\Delta solv}$ quantifies the difference between solvent enthalpy in the bulk (B) and in zeolite pores (Z). It is calculated as:

$$\Delta H_{\Delta solv} = \Delta n_{H_2O} [\bar{H}_{H_2O}(solv[B]) - \bar{H}_{H_2O}(solv[Z])] + \Delta n_{CH_3CN} [\bar{H}_{CH_3CN}(solv[B]) - \bar{H}_{CH_3CN}(solv[Z])] \quad (A46)$$

The protocol for computing $\bar{H}_{H_2O}(solv[B])$ and $\bar{H}_{CH_3CN}(solv[B])$, referred to as the partial molar enthalpies of H₂O and CH₃CN in the bulk phase, is described in **Section A16**. $\bar{H}_{H_2O}(solv[Z])$ and $\bar{H}_{CH_3CN}(solv[Z])$ refer to the partial molar enthalpy of H₂O and CH₃CN in the adsorbed phase and are computed according to the following procedure. $\bar{H}_i(solv[Z])$ can be expressed as a sum of the enthalpy in the ideal gas state ($\bar{H}_i^{IG}$) and the excess enthalpy in the adsorbed phase ($\bar{H}_i^{ex}(Z)$). Do et al.³⁶⁸ showed that the isosteric heat of adsorption of species i (q_i^{st}) can be related to $\bar{H}_i^{ex}(Z)$, as shown in **Equation A47**, with respect to the ideal gas reference state.

$$-q_i^{st} = \bar{H}_i^{ex}(Z) \quad (A47)$$

q_i^{st} for adsorption of a guest molecule i in a host framework (Z) is defined using **Equation A48**¹⁷³:

$$-q_i^{st} = \frac{\langle U \times N_i \rangle_{\mu_i} - \langle U \rangle_{\mu_i} \langle N_i \rangle_{\mu_i}}{\langle N_i^2 \rangle_{\mu_i} - \langle N_i \rangle_{\mu_i}^2} - \langle U_g \rangle_i - RT \quad (A48)$$

where U and N are the total energy of the system and the instantaneous number of adsorbed molecules i , respectively, at a constant chemical potential μ_i . $\langle U_g \rangle_i$ is the average energy of an isolated single molecule of species i . The isosteric heat q_i^{st} without $\langle U_g \rangle_i$ term was computed directly by the RASPA software.¹⁷³ Later, $\langle U_g \rangle_i$ was subtracted from those values to obtain the final q_i^{st} . The ideal gas state enthalpies ($\bar{H}_i^{IG}$) for each species were calculated as described in **Section A16**. ΔH_{e-zeo} and ΔH_{e-solv} were calculated as $\Delta H_{e-zeo} = \Delta U_{e-zeo}$ and $\Delta H_{e-solv} = \Delta U_{e-solv}$, where ΔU_{e-zeo} and ΔU_{e-solv} are the interaction energies of the epoxides with zeolite and solvent, respectively. The interaction energies were calculated by the RASPA code at every simulation step. It should be noted that the PV is neglected here due to a very small molar volume of liquids and solids. **Tables A12 to A15** provide all the values represented in **Equation 2.7**.

Epoxide	$\Delta H_{e,solvation}$	$\Delta H_{\Delta solv}$	ΔH_{e-zeo}	ΔH_{e-solv}	$\Delta H_{ads,epox} (ED)$	$\Delta H_{ads,epox}$
C ₆ H ₁₂ O	-32.06 ± 1.9	8.04 ± 1.1	-150.80 ± 2.9	-21.41 ± 3.4	-132.11 ± 4.9	-138.41 ± 3.2
C ₁₀ H ₂₀ O	-47.61 ± 2.2	12.68 ± 2.9	-161.81 ± 2.4	-19.83 ± 4.0	-121.34 ± 5.9	-129.64 ± 6.3
C ₁₄ H ₂₈ O	-58.69 ± 2.6	25.78 ± 3.2	-177.49 ± 1.9	-18.13 ± 3.1	-111.16 ± 5.5	-121.21 ± 3.6
C ₁₈ H ₃₆ O	-71.77 ± 2.8	34.93 ± 3.9	-186.11 ± 3.2	-17.71 ± 3.8	-97.11 ± 6.9	-115.46 ± 2.6

Table A12. Decomposition of $\Delta H_{ads,epox}$ in Ti-BEA-F (CH₃CN, 200 mM H₂O, 313 K).

Epoxide	$\Delta H_{e,solvation}$	$\Delta H_{\Delta solv}$	ΔH_{e-zeo}	ΔH_{e-solv}	$\Delta H_{ads,epox} (ED)$	$\Delta H_{ads,epox}$
C ₆ H ₁₂ O	-32.06 ± 1.9	34.97 ± 4.0	-153.88 ± 4.8	-30.41 ± 3.1	-117.26 ± 7.2	-129.44 ± 6.8
C ₁₀ H ₂₀ O	-47.61 ± 2.2	49.35 ± 3.8	-171.54 ± 3.5	-26.83 ± 4.2	-101.41 ± 7.0	-104.53 ± 5.1
C ₁₄ H ₂₈ O	-58.69 ± 2.6	72.1 ± 5.4	-190.11 ± 5.2	-23.13 ± 3.7	-82.44 ± 8.8	-88.96 ± 4.7
C ₁₈ H ₃₆ O	-71.77 ± 2.8	83.11 ± 4.9	-210.66 ± 4.6	-15.32 ± 4.3	-71.10 ± 8.5	-71.49 ± 5.1

Table A13. Decomposition of $\Delta H_{ads,epox}$ in Ti-BEA-OH (CH₃CN, 200 mM H₂O, 313 K).

Epoxide	$\Delta H_{e,solvation}$	$\Delta H_{\Delta solv}$	ΔH_{e-zeo}	ΔH_{e-solv}	$\Delta H_{ads,epox} (ED)$	$\Delta H_{ads,epox}$
C ₆ H ₁₂ O	-32.06 ± 1.9	15.94 ± 2.9	-153.88 ± 4.8	-22.62 ± 4.1	-128.49 ± 7.2	-135.45 ± 3.4
C ₁₀ H ₂₀ O	-47.61 ± 2.2	31.10 ± 3.7	-171.54 ± 3.5	-17.34 ± 3.9	-110.17 ± 6.8	-116.22 ± 5.5
C ₁₄ H ₂₈ O	-58.69 ± 2.6	41.67 ± 4.3	-190.11 ± 5.2	-12.53 ± 4.7	-102.28 ± 8.6	-100.60 ± 2.9
C ₁₈ H ₃₆ O	-71.77 ± 2.8	46.85 ± 4.9	-210.66 ± 4.6	-6.99 ± 3.3	-99.03 ± 8.0	-89.24 ± 4.6

Table A14. Decomposition of $\Delta H_{ads,epox}$ in Ti-BEA-OH (neat CH₃CN, 313 K).

Epoxide	$\Delta H_{e,solvation}$	$\Delta H_{\Delta solv}$	ΔH_{e-zeo}	ΔH_{e-solv}	$\Delta H_{ads,epox} (ED)$	$\Delta H_{ads,epox}$
C ₆ H ₁₂ O	-32.06 ± 1.9	2.79 ± 0.6	-150.80 ± 2.9	-19.81 ± 4.5	-135.76 ± 5.7	-144.84 ± 4.6
C ₁₀ H ₂₀ O	-47.61 ± 2.2	15.28 ± 2.7	-161.81 ± 2.4	-18.91 ± 4.8	-117.82 ± 6.4	-140.23 ± 5.8
C ₁₄ H ₂₈ O	-58.69 ± 2.6	20.65 ± 3.2	-177.49 ± 1.9	-18.11 ± 3.0	-116.27 ± 5.5	-133.97 ± 4.3
C ₁₈ H ₃₆ O	-71.77 ± 2.8	34.18 ± 3.6	-186.11 ± 3.2	-17.41 ± 4.6	-97.57 ± 7.2	-125.30 ± 3.7

Table A15. Decomposition of $\Delta H_{ads,epox}$ in Ti-BEA-F (neat CH₃CN, 313 K).

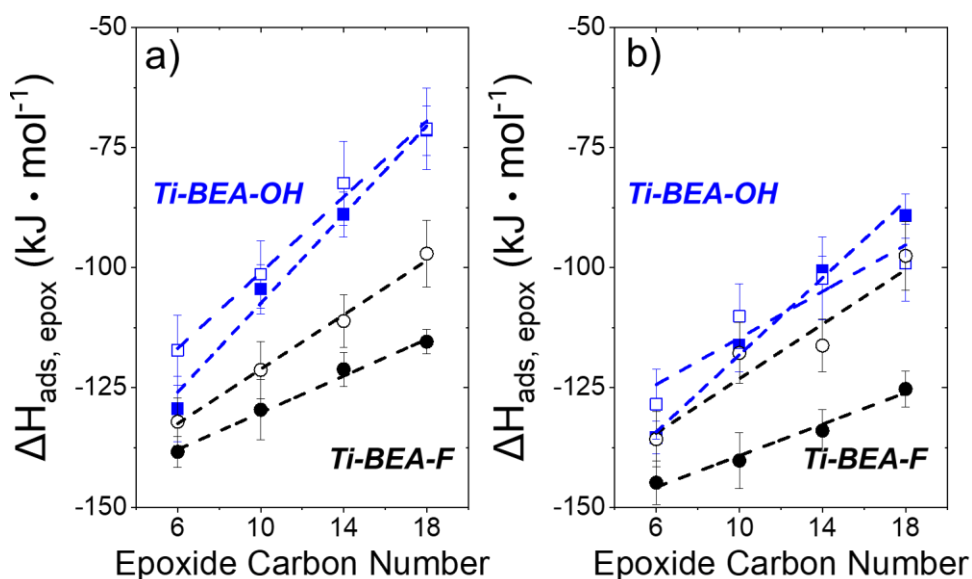


Figure A31. Computational $\Delta H_{ads,epox}$ (■,●) and $\Delta H_{ads,epox} (ED)$ (□,○) values as a function of epoxide carbon number in a) CH₃CN + 200 mM H₂O and b) pure CH₃CN over Ti-BEA-OH (blue) and Ti-BEA-F (black).

Figure A31 shows that $\Delta H_{ads,epox}$ from **Equation A43** differs slightly from $\Delta H_{ads,epox(ED)}$ from **Equation A46**. This results because $\Delta H_{ads,epox(ED)}$ values were computed with NVT dynamics that use integer numbers of solvent molecules, while $\Delta H_{ads,epox}$ values were calculated with GCMD simulations that can involve fractional numbers of solvent molecules. The fractional differences in solvent molecules between the two calculation methods contribute to the deviation between the two quantities.

A18. Computed $\Delta H_{ads,epox}$ in Neat CH_3CN

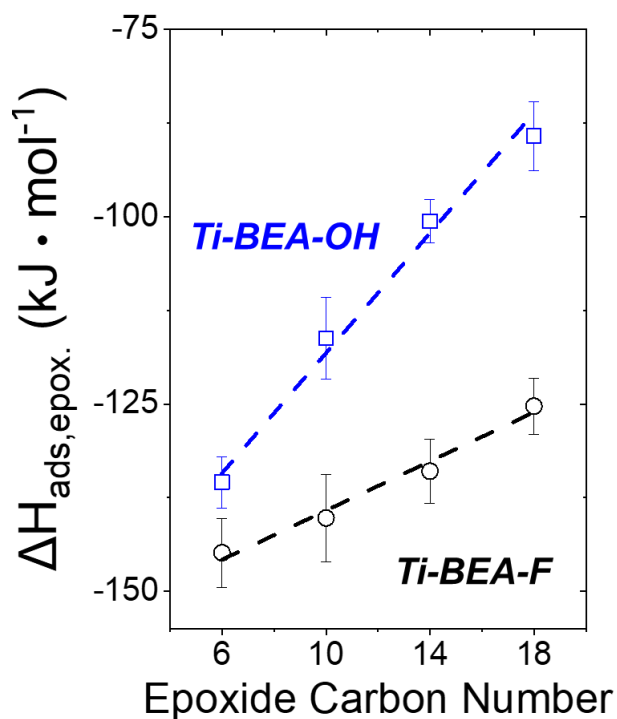


Figure A32. Enthalpies of adsorption for 1,2-epoxides obtained computationally as a function of epoxide carbon number in Ti-BEA-OH (blue) and Ti-BEA-F (black) (neat CH_3CN , 313 K).

Figure A32 shows that $\Delta H_{ads,epox}$ increases as epoxide carbon number increases, even without H_2O present. This data shows that disrupting greater quantities of CH_3CN leads to greater enthalpic penalties and lower $\Delta H_{ads,epox}$. Ti-BEA-OH gives more positive $\Delta H_{ads,epox}$ values for

each epoxide and a stronger dependence of $\Delta H_{ads,epox}$ on epoxide carbon number, indicating that the disruption of CH_3CN bound to $(\text{SiOH})_4$ groups requires a greater enthalpic penalty than unbound CH_3CN in the pore. The magnitude of $\Delta H_{ads,epox}$ differences across the range of epoxides is smaller than with the binary solvent system containing H_2O , meaning that the disruption of H_2O molecules affects epoxide stability more strongly than CH_3CN molecules.

A19. Enthalpies from Epoxide Interactions with the Solvent and Zeolite

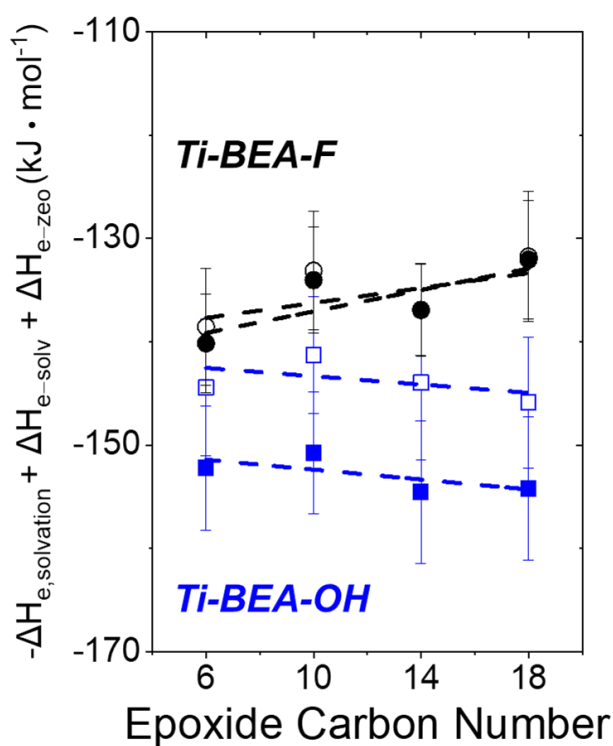


Figure A33. Summation of enthalpies for interactions between 1,2-epoxides and the solvent and zeolite, obtained computationally as a function of epoxide carbon number in CH_3CN + 200 mM H_2O (■,●) and pure CH_3CN (□,○) at 313 K over Ti-BEA-OH (blue) and Ti-BEA-F (black).

Figure A33 shows the sum of the de-solvation enthalpy of the epoxide from bulk solvent ($\Delta H_{e,solvation}$) and interaction enthalpies between the adsorbed epoxide and solvent molecules (ΔH_{e-solv}) and zeolite pore walls (ΔH_{e-zeo}). This summation enthalpy varies weakly with carbon

number for both zeolites and solvent systems (binary and pure CH₃CN), indicating that the enthalpy change from solvent displacement during epoxide adsorption ($\Delta H_{\Delta solv}$) primarily leads to differences in epoxide adsorption enthalpies (see **Equation 2.7**).

A20. Error Propagation

The average errors reported in this article for the computational measurements are calculated using the following formulae:

$$\text{If, } x = a + b - c, \text{ then } \sigma_x = \sqrt{\sigma_a^2 + \sigma_b^2 + \sigma_c^2} \quad (\text{A49})$$

$$\text{If, } x = \frac{ab}{c}, \text{ then } \sigma_x = x \sqrt{\left(\frac{\sigma_a}{a}\right)^2 + \left(\frac{\sigma_b}{b}\right)^2 + \left(\frac{\sigma_c}{c}\right)^2} \quad (\text{A50})$$

Where a , b and c are observed values and σ_a , σ_b and σ_c are the uncertainties in a , b and c values. As an example, the error bar limits for C₆H₁₂O in **Table A10** corresponding to $\Delta H_{e,solvation}$, $\Delta H_{\Delta solv}$, ΔH_{e-zeo} and ΔH_{e-solv} are 1.9, 1.1, 2.9 and 3.4 kJ mol⁻¹, respectively. Therefore, the error bar limit for $\Delta H_{ads,epox (ED)}$ is calculated to be $\sqrt{1.9^2 + 1.1^2 + 2.9^2 + 3.4^2} = 4.98$ kJ mol⁻¹. The error bars shown signify a single standard deviation from the mean value.

A21. Density Calculations

A21.1 Void Fraction Calculation

The void fraction/porosity of Ti-BEA-F and Ti-BEA-OH in the presence and absence of epoxide was calculated using the Widom insertion method of a helium atom probe into the zeolite, as implemented in the RASPA software. The particle insertion was conducted for 5×10⁵ cycles at 313 K and 1 atm. The following table provides the void fractions computed for each system.

A21.2 Pore Volume Calculation

Void fraction is defined as the ratio of the volume occupied by the adsorbed gas to the total volume of the system. For calculating the density of solvent in the adsorbed phase, the pore volume V_p is necessary. This was calculated by multiplying the void fraction (ξ) and the total volume of the super cell (V) used for the simulation. The calculated pore volumes of Ti-BEA-F and Ti-BEA-OH were 0.263 and 0.262 $\text{cm}^{-3} \text{g}^{-1}$, respectively. Compared to experimentally measured pore volumes (0.173 $\text{cm}^{-3} \text{g}^{-1}$ for Ti-BEA-F and 0.172 $\text{cm}^{-3} \text{g}^{-1}$ for Ti-BEA-OH using Ar), the computed values are greater by a factor of ≈ 1.5 . We attribute this difference to a smaller size of a He atom used in simulations compared to Ar employed in experimental pore volume measurements, and to the fact that the computer model is an idealization of the complex experimentally tested material.

The density of solvent of species i inside the pore is calculated as:

$$\rho_i = \frac{\text{Number of molecules of species } i (n_i) \times \text{Molecular weight of species } i}{N_A \times \text{pore volume } (V_p) \text{ in cm}^3} \quad (\text{A51})$$

Here, N_A is the Avogadro constant.

A22. Analysis of Intraporous Epoxide Solvent Environment using CH₃CN Radial Distribution Functions and Coordination Numbers

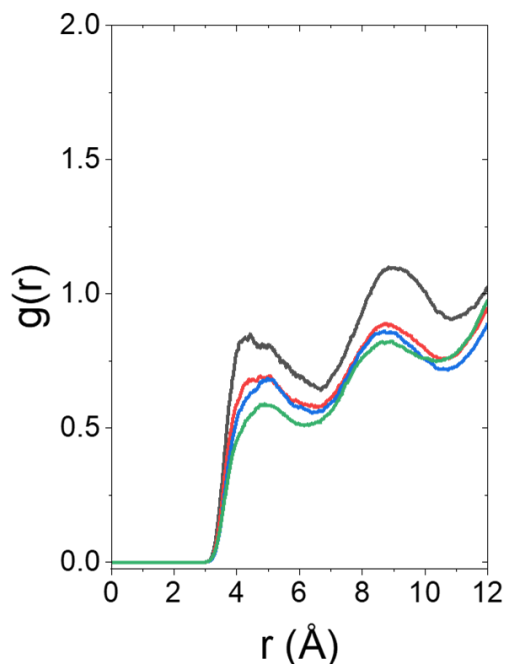


Figure A34. Radial distribution function $g(r)$ between CH₃CN center of mass and any of C and O atoms of C₆H₁₂O (black), C₁₀H₂₀O (red), C₁₄H₂₈O (blue), and C₁₈H₃₆O (green) in Ti-BEA-OH exposed to 200 mM in CH₃CN solution at 313 K.

Zeolite	System	Void fraction
Ti-BEA-F	Pristine	0.3950±0.0010
	C ₆	0.3791±0.0002
	C ₁₀	0.3734±0.0009
	C ₁₄	0.3669±0.0008
	C ₁₈	0.3579±0.0011
Ti-BEA-OH	Pristine	0.3938±0.0002
	C ₆	0.3781±0.0003
	C ₁₀	0.3715±0.0002
	C ₁₄	0.3652±0.0001
	C ₁₈	0.3555±0.0001

Table A16. Calculated void fraction (ξ) for Ti-BEA-F and Ti-BEA-OH in the presence and absence of epoxides

To understand the trend in ΔH_{e-solv} as a function of the carbon number of epoxides, we investigated the solvent structure around the adsorbed epoxide by computing radial distribution functions (RDFs). The RDF between the center of mass of one of the adsorbed CH₃CN molecules and any of C -or O-atoms of an adsorbed epoxide in the zeolite is shown in **Figure A34** (200 mM H₂O in CH₃CN solution) and **Figure A35** (pure CH₃CN solvent). RDF for H₂O is not reported here due to the low occurrence of H₂O molecules near epoxides in simulations. In Ti-BEA-F, RDFs in both solvent compositions are very similar, as H₂O absorption is very small, and the intraporous environment is almost identical. Therefore, the subsequent analysis only describes Ti-BEA-F in pure CH₃CN. In Ti-BEA-F (**Figure A35b**) and Ti-BEA-OH with 200 mM of H₂O (**Figure A34**), RDF peak intensities decrease with the carbon number of an epoxide. In comparison, in Ti-BEA- OH in pure CH₃CN (**Figure A35a**), the peaks remain similar among all epoxides. Evidently, there is no correlation between RDF peak heights and ΔH_{e-solv} .

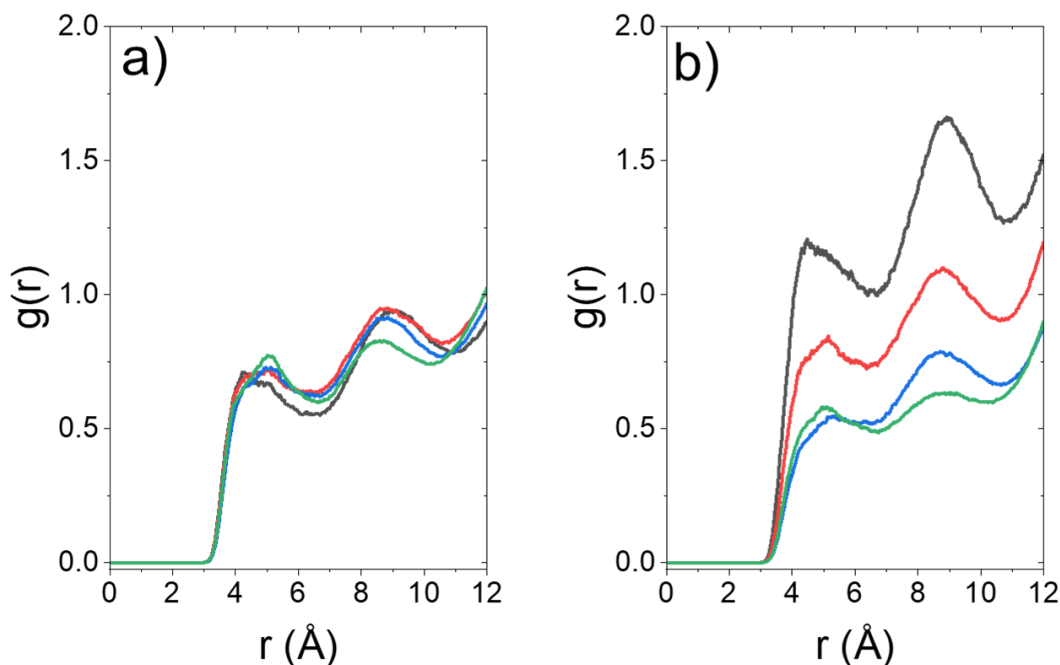


Figure A35. Radial distribution function $g(r)$ between CH₃CN center of mass and any of C and O atoms of C₆H₁₂O (black), C₁₀H₂₀O (red), C₁₄H₂₈O (blue), and C₁₈H₃₆O (green) in Ti-BEA-OH (a) and Ti-BEA-F (b) exposed to pure CH₃CN at 313 K.

It should be noted that the RDF curves reveal local density build-up relative to the average solvent density in the simulation cell and do not account for the differences in the adsorbed solvent densities (herein referred to as "global densities") between systems. However, solvent densities differ considerably between Ti-BEA-OH and Ti-BEA-F (0.48 g cm^{-3} and 0.412 g cm^{-3} , respectively), which may have consequences for epoxide-solvent interactions. To account for the effects of both "local" and "global" density variations on intraporous interaction energetics, the coordination numbers $n(r')$ between C/O atoms of an epoxide and CH_3CN center of mass were calculated using the relation $n(r') = 4\pi(N/V_p) \int_0^{r'} g(r)r^2 dr$, where N is the average CH_3CN uptake, V_p is the pore volume computed as a product of the volume of the unit cell and the computed void fraction, $g(r)$ is the RDF, and r' is the position of the first RDF minimum.

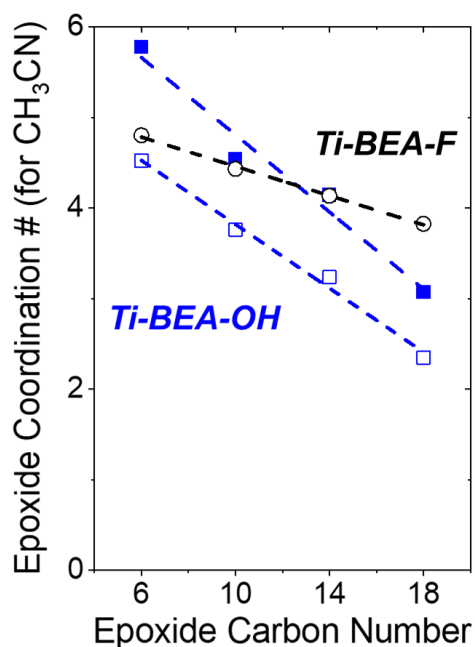


Figure A36. CH_3CN coordination numbers (CNs) of alkyl chains of adsorbed epoxides in Ti-BEA-OH exposed to 200 mM $\text{H}_2\text{O}+\text{CH}_3\text{CN}$ (■) and pure CH_3CN (□) solvents, or in Ti-BEA-F exposed to pure CH_3CN (○). CNs are obtained by integrating the first peak of the alkyl- CH_3CN radial distribution function in spherical coordinates up to the first minimum.

Figure A36 reveals that $n(r')$ decreases with the increasing carbon number for all the systems. Fewer CH₃CN neighbors of an epoxide translate to less attractive ΔH_{e-solv} , consistent with **Figure 2.13**. Notably, for Ti-BEA-F, both ΔH_{e-solv} and $n(r')$ decrease with smaller slopes compared to Ti-BEA-OH. This is explained by the fact that (1) the bulk density of CH₃CN is less sensitive to alkyl chain length variations in Ti-BEA-F compared to Ti-BEA-OH (see **Table A18**), and (2) the first RDF peak broadens at the higher carbon numbers, compensating for the significant RDF peak variations with the alkyl chain length in Ti-BEA-F (**Figure A35b**). Curiously, in Ti-BEA-OH with pure CH₃CN, $n(r')$ values are smaller than in Ti-BEA-F, despite higher observed CH₃CN uptakes in the presence of attracting (SiOH)₄ groups (**Figure A30**). Unlike in Ti-BEA-F with more prominent “global density” effects, the “local density” effects (solvent spatial correlations) become pivotal in defining the solvent environment of an epoxide in Ti-BEA-OH. Ti-BEA-OH contains (SiOH)₄ groups that act as attractors for solvent molecules, depleting the solvation shells around epoxides. This is revealed by comparing the first-peak RDF heights in Ti-BEA-OH that do not reach values higher than ~0.8 (**Figure A35a**) with the Ti-BEA-F peaks reaching values up to ~1.2 for C₆ (**Figure A34**). Longer alkyl chains lead to fewer accessible (SiOH)₄ groups in Ti-BEA-OH, reducing the CH₃CN uptake and causing the rapid drop in both $n(r')$ and ΔH_{e-solv} . A similar “local density” argument explains rapid $n(r')$ and ΔH_{e-solv} changes with the carbon number in Ti-BEA-OH exposed to H₂O-containing CH₃CN. Curiously, H₂O addition increases $n(r')$ as compared to pure CH₃CN by a nearly constant number of ~0.9 for all epoxides, which parallels the observed ΔH_{e-solv} constant shift between Ti-BEA-OH with and without H₂O present. This is attributed to the competitive binding of H₂O and CH₃CN to (SiOH)₄ groups. As H₂O interacts with (SiOH)₄ more strongly, it partially displaces CH₃CN that instead solvates the alkyl chain of an epoxide, increasing $n(r')$, making ΔH_{e-solv} more negative.

	Ti-BEA-OH (CH ₃ CN + 200 mM H ₂ O)		Ti-BEA-OH (pure CH ₃ CN)		Ti-BEA-OH (pure CH ₃ CN))	
Epoxide	vdW	ES	vdW	ES	vdW	ES
C ₆	-25.20	-5.21	-18.84	-3.78	-17.81	-3.60
C ₁₀	-22.33	-4.50	-14.45	-2.89	-16.69	-3.14
C ₁₄	-19.06	-4.07	-10.43	-2.10	-15.14	-2.99
C ₁₈	-12.60	-2.72	-5.82	-1.17	-14.63	-3.50

Table A17. Decomposition of ΔE_{e-solv} into van der Waals (vdW) and electrostatic (ES) interaction energies (kJ mol⁻¹).

Zeolite	Solvent	Epoxide	Intra-pore Density of CH ₃ CN [(N/V _p) × 10 ³ (Å ⁻³)]
Ti-BEA-OH	CH ₃ CN + 200 mM H ₂ O	C ₆	7.38
		C ₁₀	7.30
		C ₁₄	7.23
		C ₁₈	7.11
Ti-BEA-OH	CH ₃ CN	C ₆	7.45
		C ₁₀	7.38
		C ₁₄	7.29
		C ₁₈	7.18
Ti-BEA-F	CH ₃ CN	C ₆	5.96
		C ₁₀	5.92
		C ₁₄	5.88
		C ₁₈	5.85

Table A18. Intra-pore density of CH₃CN in Ti-BEA-OH in 200 mM H₂O in CH₃CN and pure CH₃CN and Ti-BEA-F in pure CH₃CN.

A23. Radial Distribution of CH₃CN and H₂O Near a Single (SiOH)₄ Site

Figure A37b and **A37c** show the RDF of CH₃CN and H₂O near a single (SiOH)₄ site, present adjacent to Ti as shown in **Figure A37a**. This structure corresponds to the defect configuration shown in **Figure A28b**.

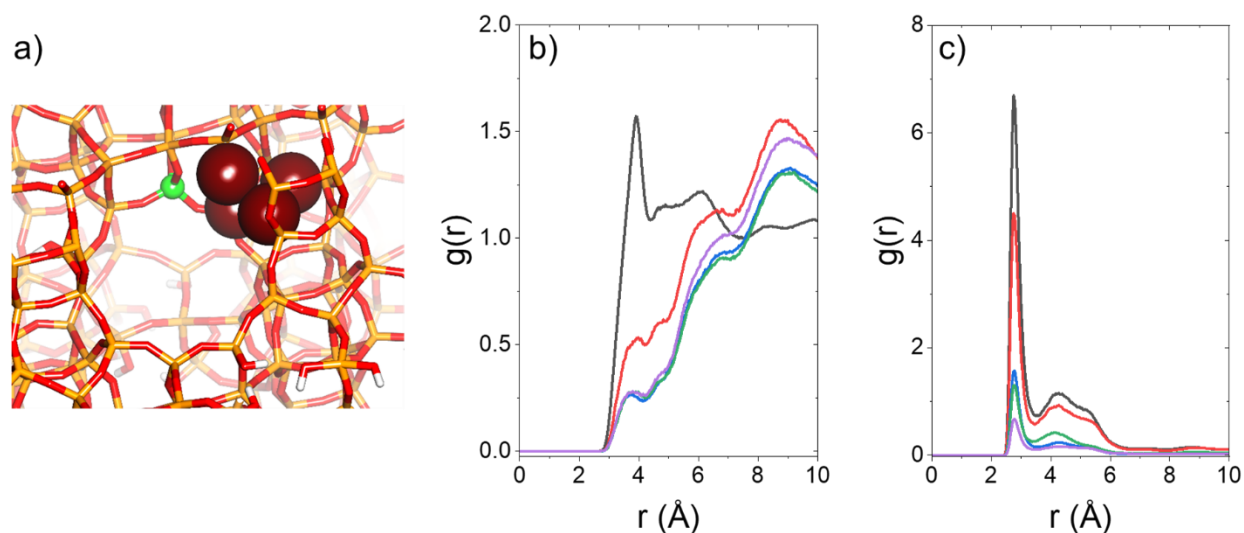


Figure A37. a) Representation of a single (SiOH)₄ site (wine red for O atoms; CPK spheres for O) near Ti (green), b) RDF of center of mass of CH₃CN near SGC of a single (SiOH)₄ site and c) RDF of center of mass of H₂O near the SGC of a single (SiOH)₄ site in the absence of epoxides (black) and with C₆H₁₂O (red), C₁₀H₂₀O (blue), C₁₄H₂₈O (green), and C₁₈H₃₆O (purple) adsorbed to Ti.

A24. Additional Details of the GCMD Simulations

Simulations were carried out in three stages. First, Ti-BEA-F and Ti-BEA-OH with or without pre-adsorbed epoxide were equilibrated at 313 K and 1 bar in the NVT ensemble. Second, solvent adsorption was simulated in the μ VT ensemble for an equilibration period of 5 ns (1×10^7 cycles) at the same conditions, followed by the production run for 7 ns (1.4×10^7 cycles). The trial moves were selected randomly with probabilities of 60% for translations, 29% for rotations, 10% for re-insertion, and 1% for swap changes in each cycle. The acceptance rates for translations, rotations, re-insertion moves, and swaps were 49%, 42%, 16%, and 26%, respectively. The error in solvent uptake values was calculated by dividing the production run trajectory into five segments for each random structure and by evaluating $\sigma/\sqrt{n}$, where σ and n represent the standard deviation and sample size, respectively. The overall error for uptake for all three Ti-BEA-OH structures was obtained by using the error propagation formula described in **Section A19**, and error bars for the enthalpy of adsorption were computed using the same method. GCMD solvent uptake results were validated against Gibbs Ensemble Monte Carlo (GEMC) simulations, as described in **Section A14**. Solvent uptake values were printed every 1000 cycles and averaged over 1.4×10^7 cycles. iRASPA³⁶⁹ and Visual Molecular Dynamics (VMD)¹⁷⁶⁻¹⁷⁷ software packages were used to visualize and render images.

APPENDIX B

SUPPLEMENTAL DATA AND ANALYSIS FOR CHAPTER 3

B1. Catalyst Characterization

B1.1 Diffuse Reflectance UV-Vis Spectra to Infer Ti Atom Dispersity

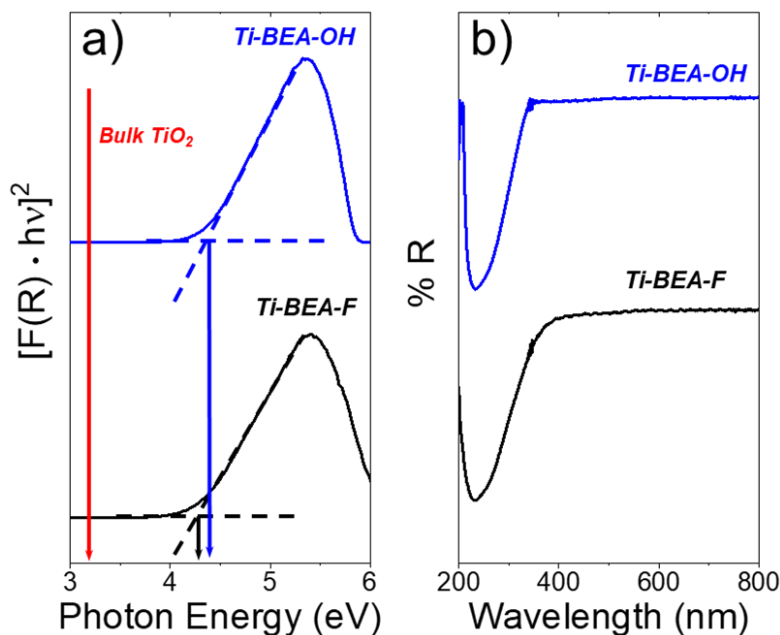


Figure B1. a) Tauc plots and b) DR-UV-Vis spectra obtained with a UV-Vis spectrophotometer at ambient conditions for Ti-BEA-OH (blue) and Ti-BEA-F (black). Spectra were normalized to the most intense feature around 5.5 eV and 225 nm and are vertically offset for clarity.

The band gaps for each Ti-BEA (see **Table 3.1**) were obtained by extrapolating the linear absorbance region of the Tauc plot in **Figure B1a** to the baseline. The intersection of the baseline and linear region represents the band gap photon energy. The band gaps for both Ti-BEA are much greater than the band gap for bulk titania (TiO₂, 3.2 eV),³³¹ suggesting that the titanium atoms are well dispersed within the *BEA framework.

The photon energy was obtained from the wavelength as follows:

$$\text{Photon Energy (eV)} = \frac{3 \cdot 10^8 \frac{\text{m}}{\text{s}}}{\text{Wavelength (nm)} \cdot \frac{1 \text{ m}}{10^9 \text{ nm}}} \cdot h \cdot \left(6.242 \cdot 10^{18} \frac{\text{eV}}{\text{J}} \right)$$

where h equals the Planck constant. The ordinate from **Figure B1a** was obtained from the ordinate of the raw spectra in **Figure B1b**. The Kubelka-Munk function was calculated from % R:

$$F(R) = \frac{\left(1 - \frac{\%R}{100}\right)^2}{2 * \left(\frac{\%R}{100}\right)}$$

$F(R)$ was then multiplied by the photon energy, and the resulting quantity was squared to yield the ordinate for **Figure B1a**.

B1.2 X-Ray Diffraction to Observe Crystallinity of Ti-BEA Catalysts

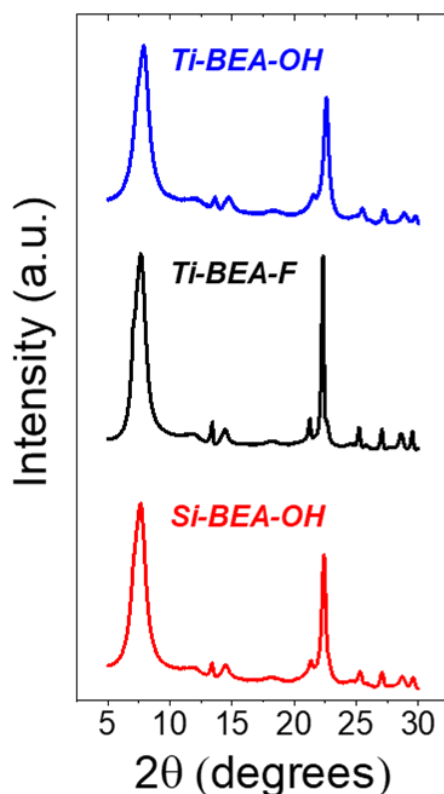


Figure B2. Powder X-ray diffractograms obtained with Cu K α radiation (0.15418 nm) under ambient conditions for Ti-BEA-OH (blue), Ti-BEA-F (black), and Si-BEA-OH (red). Spectra are vertically offset for clarity.

The crystallographic features for each Ti-BEA are representative of the *BEA framework. The sharper feature at ~22.5 degrees for Ti-BEA-F indicates a highly crystalline material, as expected for zeolites synthesized in fluoride media.³³⁰ The broader feature for Ti-BEA-OH

suggests a smaller crystallite size¹³⁸ and the presence of internal (SiOH)_x defects formed by dealumination of Al-BEA-OH (Si:Al = 20).

Notably, each Ti-BEA shows a weak feature at 25.5 degrees, whereas anatase TiO₂ shows a strong feature.²¹⁵ However, the XRD pattern for dealuminated *BEA (Si-BEA-OH, initial Si:Al = 20) also contains a weak feature in this region, suggesting that the feature is characteristic of the *BEA framework. The XRD patterns in **Figure B2** indicate that each Ti-BEA possesses the crystalline *BEA framework, with minimal to no TiO₂ present.

B1.3 *Ex situ* Raman Spectra of Ti-BEA Materials to Confirm Ti Coordination

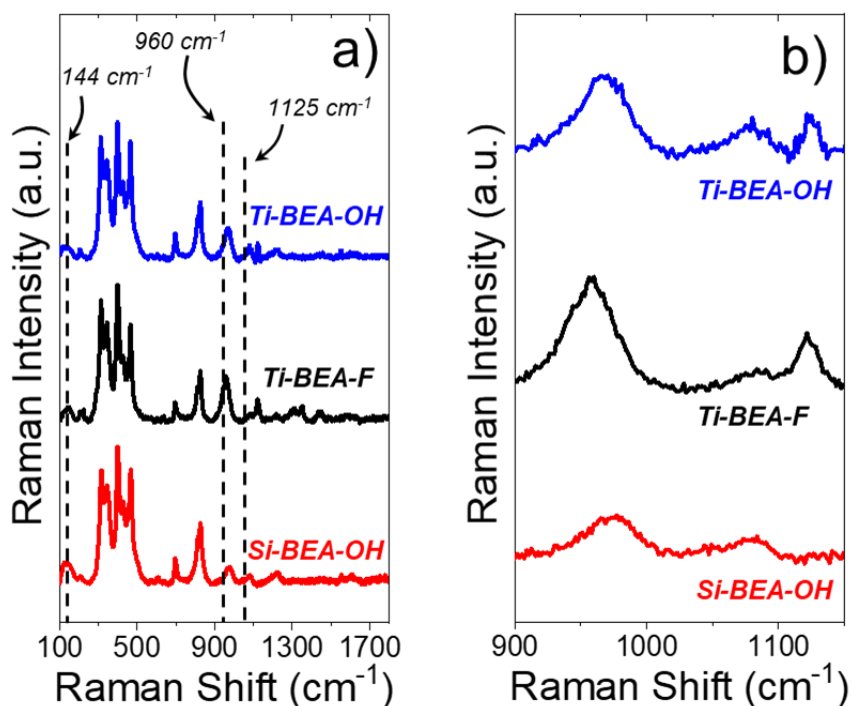


Figure B3. a) *Ex situ* Raman spectra of Ti-BEA-OH (blue), Ti-BEA-F (black), and Si-BEA-OH (red), and b) the *ex situ* spectra zoomed into the 900-1150 cm⁻¹ region. The spectra are an average of 10 scans with an exposure time of 20 s. Spectra are normalized by the maximum feature at ~400 cm⁻¹ and are vertically offset for clarity. The spectra were taken at ambient conditions with a Raman spectrometer (Renishaw, InVia) equipped with a 532 nm laser that delivered a power density of ~2 mW μm⁻².

Bulk anatase TiO₂ shows an intense E_g vibration peak at 144 cm⁻¹,^{254, 332} which is hardly observable in the Raman spectra of each Ti-BEA. The area of this feature is also slightly more intense in Si-BEA-OH, which suggests the feature results from a mode inherent to the *BEA framework instead of TiO₂. The intense peaks between 250 and 550 cm⁻¹ represent features of the *BEA framework: the peaks at 315 and 345 cm⁻¹ are assigned to six-membered rings, the peaks at 400 and 425 cm⁻¹ are assigned to five-membered rings, and the peak at 465 cm⁻¹ represents four-membered rings characteristic of the *BEA framework.³³³⁻³³⁴ The peak at ~695 cm⁻¹ has previously been reported on Raman spectra of crystalline *BEA zeolites, suggesting the feature may be characteristic of the *BEA framework.³³⁵⁻³³⁶ The peak at ~820 cm⁻¹ represents a symmetric skeletal mode of microporous silicates.³³⁷⁻³³⁸

The feature at ~960 cm⁻¹ has been commonly attributed to silanol defects^{150, 333, 339} and Ti atoms incorporated at tetrahedral positions in zeolite frameworks.^{150, 254, 339-343} The peak at ~1125 cm⁻¹ represents an additional feature of Ti atoms within the framework; previous studies assign the ~960 and ~1125 cm⁻¹ peaks to antisymmetric and symmetric Ti-O-Si vibrations, respectively.^{254, 342-344} **Figure B3b** shows that each Ti-BEA zeolite contains features at ~960 and 1125 cm⁻¹, consistent with the proposal that Ti atoms reside in the *BEA framework. Si-BEA-OH also contains a feature at ~960 cm⁻¹, likely resulting from contributions of silanol defects as reported in literature. Collectively, the Raman spectra suggest that Ti atoms predominately reside at tetrahedral framework positions within the *BEA zeolite framework.

B1.4 N₂, Ar, H₂O, and CH₃OH Adsorption Isotherms over Ti-BEA Materials

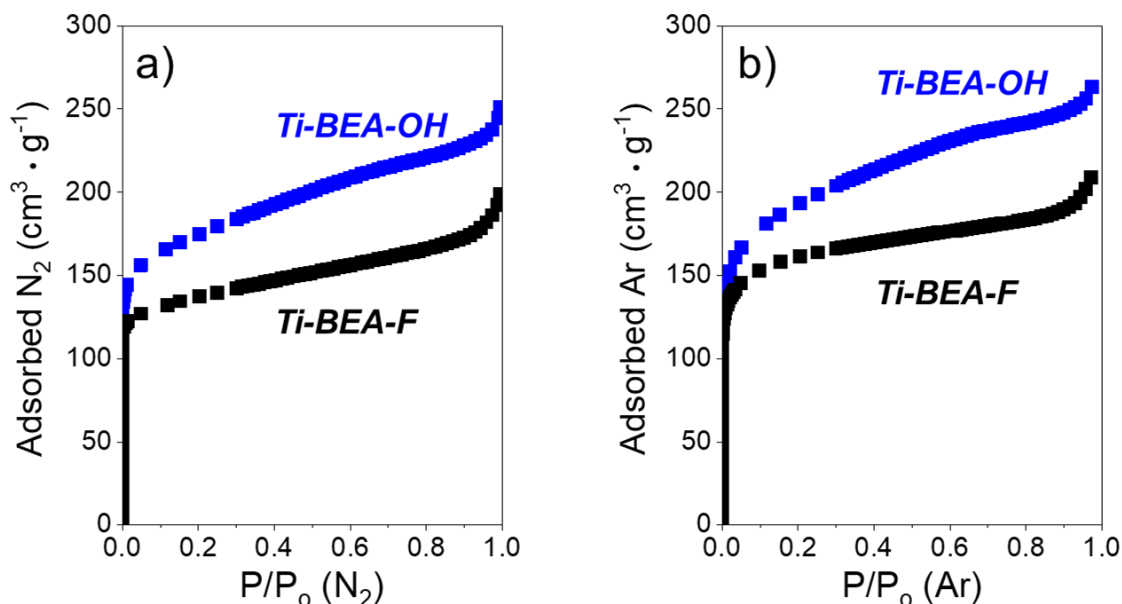


Figure B4. a) N₂ (77 K) and b) Ar (87 K) adsorption isotherms over Ti-BEA-OH (blue) and Ti-BEA-F (black). The samples were degassed under dynamic vacuum prior to adsorption ($< 7 \times 10^{-4}$ Pa, 673 K, 3 h).

The BET surface areas and micropore volumes reported in **Table 3.1** were calculated from the adsorption isotherms in **Figure B4**. The values in **Table 3.1** are consistent with previous reports of surface areas^{64, 85, 345} and micropore volumes^{64, 76, 132-133, 136} of *BEA zeolites, supporting that Ti-BEA-OH and Ti-BEA-F possess the *BEA framework.

The BET surface area of Ti-BEA-OH exceeds Ti-BEA-F by ~1.2 times for each method, while the micropore volume is ~1.1 times greater in Ti-BEA-OH for N₂ adsorption and nearly identical between the zeolites for Ar adsorption. While the external surface areas of Ti-BEA-OH are ~2 times greater than Ti-BEA-F, the total pore volumes (micropore + mesopore) differ by < 1.25 times between zeolites for each adsorption measurement (**Table B1**).

Catalyst	External Surface Area (N ₂) (m ² g ⁻¹)	External Surface Area (Ar) (m ² g ⁻¹)	BET Surface Area (N ₂) (m ² g ⁻¹)	Micropore Volume (N ₂) (m ³ g ⁻¹)	Total Pore Volume (N ₂) (cm ³ g ⁻¹)	Total Pore Volume (Ar) (cm ³ g ⁻¹)
Ti-BEA-OH	200	177	653	0.184	0.389	0.521
Ti-BEA-F	109	79	528	0.166	0.307	0.583

Table B1. External surface areas and mesopore volumes of Ti-BEA materials obtained from N₂ and Ar physisorption isotherms.

B1.5 Infrared Spectra of Ti-BEA Materials to Measure Silanol Density

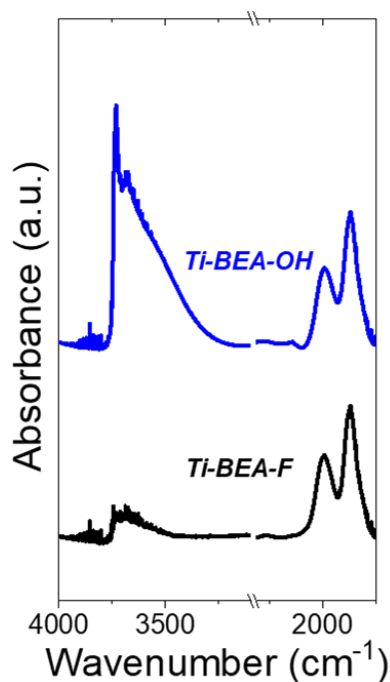


Figure B5. Infrared spectra of dehydrated samples of Ti-BEA-OH (blue) and Ti-BEA-F (black) used for this study. The samples were dehydrated under flowing He (101 kPa He, 50 cm³ min⁻¹) at 573 K prior to measurement. Spectra are vertically offset for clarity.

The significant difference in the $\nu(\text{O-H})$ area (3300-3750 cm⁻¹), with respect to the relatively unchanging $\nu(\text{Si-O-Si})$ area (1800-2100 cm⁻¹), shows that Ti-BEA-OH contains a much greater density of (SiOH)_x groups than Ti-BEA-F (i.e., more hydrophilic). Φ_{IR} values in **Table 3.1** were calculated by peak fitting on Origin 2021 (OriginLab Corporation). The peak areas for $\nu(\text{O-}$

H) and $\nu(\text{Si-O-Si})$ are shown in **Table B2** and were calculated with Gaussian fits, as illustrated in **Figures B6** and **B7**. During peak fitting, the peak centers were fixed at the values in **Table B2**.

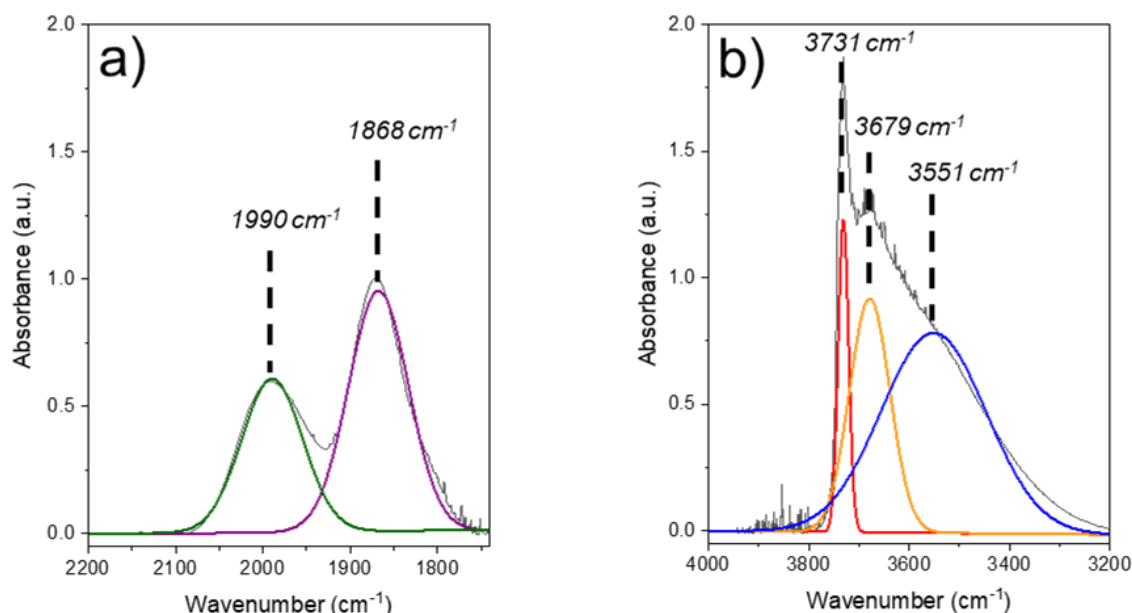


Figure B6. Fitted peaks for the a) Si-O-Si overtones at 1865 (purple) and 2000 cm^{-1} (green) and b) isolated (red) and networked (blue, orange) Si-OH regions for Ti-BEA-OH.

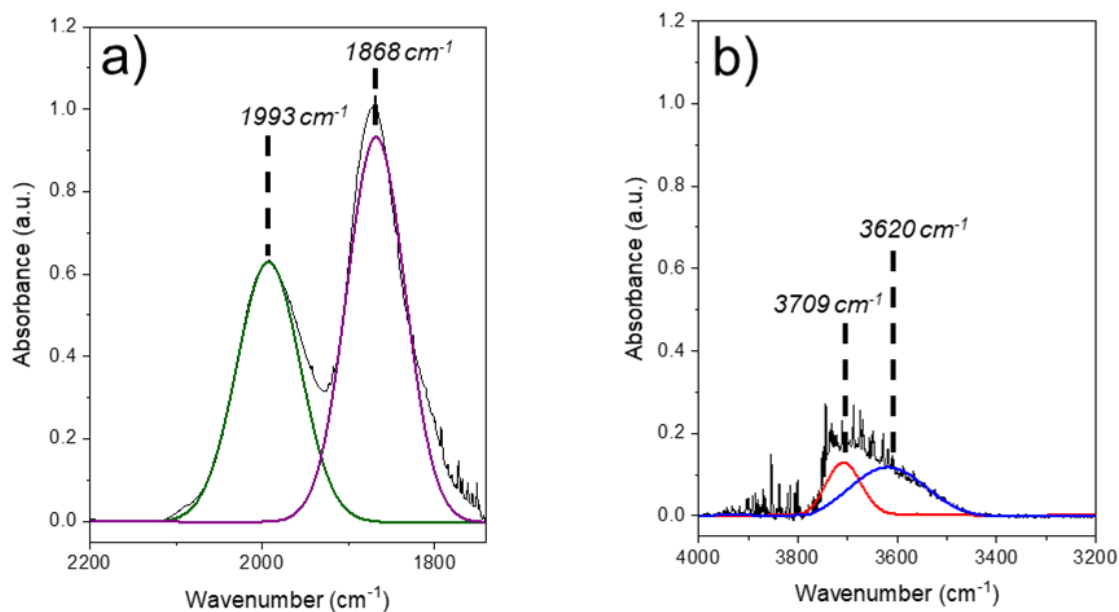


Figure B7. Fitted peaks for the a) Si-O-Si overtones at 1865 (purple) and 2000 cm^{-1} (green) and b) isolated (red) and networked (blue) Si-OH regions for Ti-BEA-F.

Ti-BEA-OH		Ti-BEA-F	
Peak Center (cm ⁻¹)	Integrated Area	Peak Center (cm ⁻¹)	Integrated Area
3731	32.1	3709	11.7
3679	93.4	3620	24.8
3551	207.5	1993	57.9
1990	52.8	1868	79.0
1868	81.2		

Table B2. Peak areas for fitted peaks from IR spectra of Ti-BEA samples.

As shown in **Equation 3.1**, the equation to calculate Φ_{IR} is:

$$\Phi_{IR} = \frac{A_{\nu(O-H)}}{A_{\nu(Si-O-Si)}} \quad (B1)$$

The blue and yellow peaks represent networked SiOH features which are summed to determine $A_{\nu(O-H)}$ for Ti-BEA-OH; only the blue peak was used in $A_{\nu(O-H)}$ for Ti-BEA-F. The green and purple peaks in the Si-O-Si region were summed together to get $A_{\nu(Si-O-Si)}$. The red peaks in $\nu(O-H)$ represent isolated SiOH features, so these peak areas were excluded from the Φ_{IR} calculations. Substituting the areas to **Equation B1** gives Φ_{IR} values of 2.25 and 0.27 for Ti-BEA-OH and Ti-BEA-F, respectively.

B1.6 Calculation of (SiOH)_x (unit cell)⁻¹ in Ti-BEA-OH

The density of (SiOH)_x per unit cell in Ti-BEA-OH was estimated based on the initial quantity of Al present in the commercial zeolite (Si:Al = 20). A BEA unit cell contains 64 heteroatoms (i.e., Si, Al, or Ti), so the initial quantity of Al per unit cell equals 3.047:

$$Al + Si = 64 \quad \longrightarrow \quad Al + 20Al = 64 \quad \longrightarrow \quad Al = 3.047$$

Assuming that all Al atoms are removed, the dealumination produces 3.047 (SiOH)_x (unit cell)⁻¹. The Ti weight loading was measured as 0.355% from EDXRF, which gives a Si/Ti ratio of

219. This can be used to calculate the number of Ti atoms per unit cell incorporated into the formed (SiOH)₄:

$$Ti + Si = 64 \longrightarrow Ti + 219Ti = 64 \longrightarrow Ti = 0.292$$

The final (SiOH)_x (unit cell)⁻¹ is equal to the quantity of removed Al subtracted by the added Ti:

$$(SiOH)_x = removed\ Al - added\ Ti = 2.75\ (SiOH)_x\ \text{per unit cell}$$

Ti-BEA-F was synthesized hydrothermally without Al present, so we cannot make the same calculation of (SiOH)_x (unit cell)⁻¹.

B2. ¹H NMR Spectroscopy to Calculate Intrapore Solvent Composition

The ratio of the peak areas for H₂O and the organic solvent was calculated for each sample. Then, the known initial mole fraction of H₂O ($x_{H_2O,bulk,initial}$) and organic solvent and peak area ratios before ($A_{H_2O:org,initial}$) and after ($A_{H_2O:org,final}$) contact with Ti-BEA were used to calculate the final bulk solvent fractions:

$$x_{H_2O,bulk,final} = x_{H_2O,bulk,initial} * \frac{A_{H_2O:org,final}}{A_{H_2O:org,initial}} \quad (B2)$$

$$x_{org,bulk,final} = 1 - x_{H_2O,bulk,final} \quad (B3)$$

The intrapore solvent fraction was then calculated, starting by estimating the fraction of solvent adsorbed from the bulk solvent ($V_{solvent,ads}$) and the fraction of the initial solvent volume remaining in the bulk solvent after adsorption ($x_{bulk,final}$):

$$V_{solvent,ads} = m_{zeolite} * V_{pore,*BEA} \quad (B4)$$

$$x_{bulk,final} = 1 - \left(\frac{V_{solvent,ads}}{V_{solvent,total}} \right) \quad (B5)$$

where $m_{zeolite}$ is the mass of Ti-BEA added to the solvent and $V_{pore,*BEA}$ is the pore volume of Ti-BEA-OH or Ti-BEA-F (Section B1.5). From there, the intrapore molar ratio ($\frac{n_{H_2O,pore}}{n_{org,pore}}$) and H₂O fraction ($x_{H_2O,pore}$) can be calculated:

$$\frac{n_{H_2O,pore}}{n_{org,pore}} = \frac{x_{H_2O,bulk,initial} - (x_{bulk,final} * x_{H_2O,bulk,final})}{x_{org,bulk,initial} - (x_{org,final} * x_{org,bulk,final})} \quad (B6)$$

$$x_{H_2O,pore} = \frac{\frac{n_{H_2O,pore}}{n_{org,pore}}}{1 - \frac{n_{H_2O,pore}}{n_{org,pore}}} \quad (B7)$$

B3. H₂O₂ Selectivity Dependences on H₂O Fraction

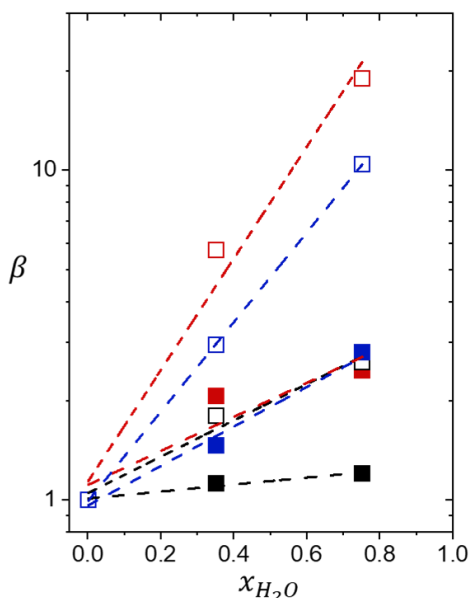


Figure B8. Relative H₂O₂ selectivities (β) for epoxidation (1 mM C₆H₁₂, 10 mM H₂O₂ (with 39 mM H₂O), 313 K) as a function of H₂O mole fraction (x_{H_2O}) in mixtures of CH₃CN (■, □), CH₃OH (■, □), and C₄H₆O₂ (■, □) with H₂O over Ti-BEA-OH (solid points) and Ti-BEA-F (hollow points).

The relative H₂O₂ selectivity (β) plotted in **Figure B8** is defined as:

$$\beta = \frac{S_{H_2O_2,x}}{S_{H_2O_2,0.002}} \quad (S8)$$

which equals the ratio of H₂O₂ selectivities for epoxidation over H₂O₂ decomposition at $x_{H_2O} = x$ ($S_{H_2O_2,x}$) and $x_{H_2O} = 0.002$ ($S_{H_2O_2,0.002}$). This selectivity ratio quantifies the magnitude of H₂O₂

selectivity increases for C_6H_{12} epoxidation upon adding more H_2O to the organic solvent. In general, Ti-BEA-F shows greater increases in the relative H_2O_2 selectivity than Ti-BEA-OH at a higher x_{H_2O} . Among organic solvents, CH_3CN shows the smallest increases in relative selectivity, while CH_3OH and $C_4H_6O_2$ show similar magnitudes of relative selectivity increases. The data in **Figure B8** and **Figure 3.1c** show that adding more H_2O allows CH_3OH and $C_4H_6O_2$ mixtures to yield more similar selectivities to the best-performing organic solvent, CH_3CN .

B4. Rate Dependences on $[C_6H_{12}]$, $[H_2O_2]$, and x_{H_2O} for CH_3CN and $C_4H_6O_2$ Mixtures

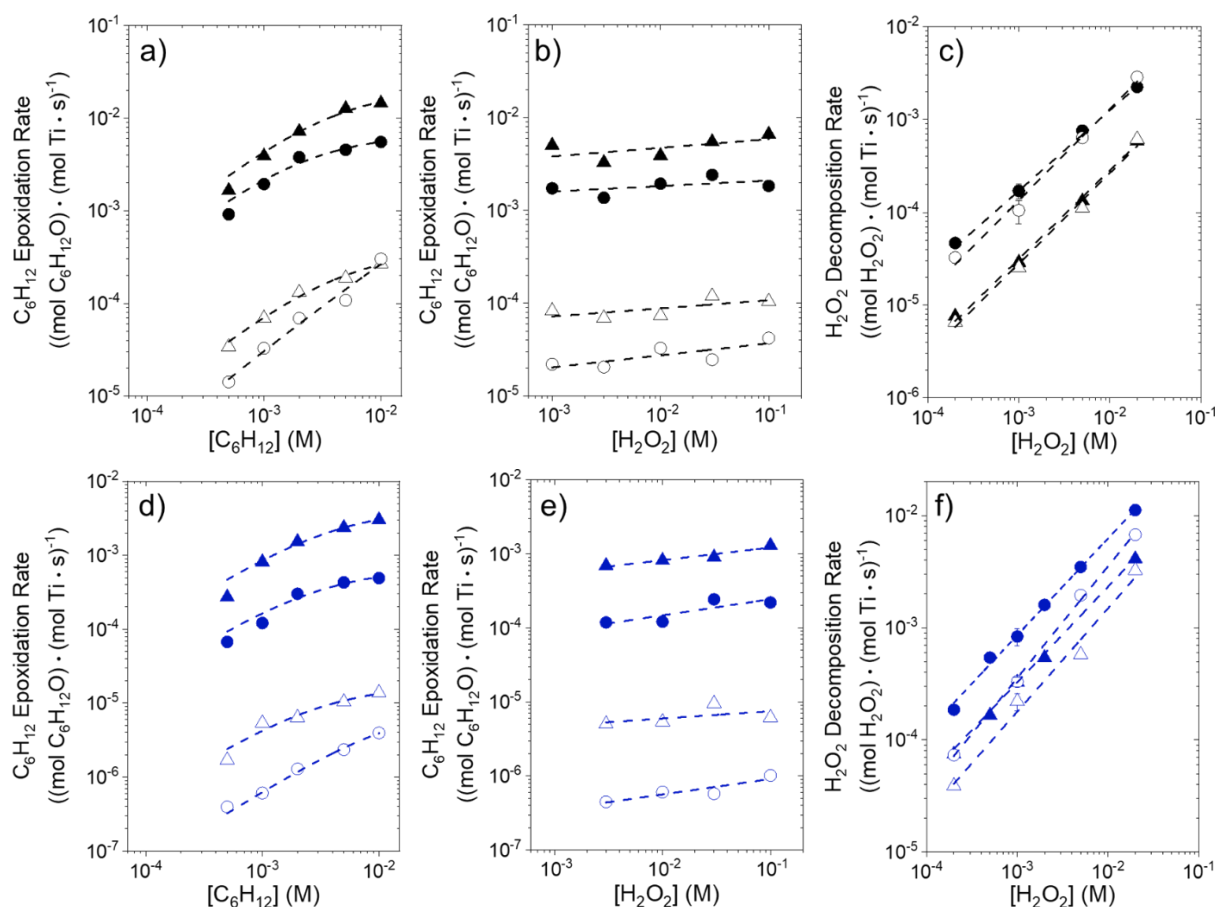


Figure B9. Turnover rates for C_6H_{12} epoxidation as a function of a,d) C_6H_{12} concentration (10 mM H_2O_2 , 313 K) and b,e) H_2O_2 concentration (1 mM C_6H_{12} , 313 K) and turnover rates for c,f) H_2O_2 decomposition (313 K) as a function of H_2O_2 concentration for a,b,c) CH_3CN mixtures containing $x_{H_2O} = 0.002$ (39 mM) ($\bullet$, $\circ$) or $x_{H_2O} = 0.75$ (~ 27.8 M) ($\blacktriangle$, $\triangle$) and d,e,f) $C_4H_6O_2$ mixtures containing $x_{H_2O} = 0.002$ ($\bullet$, $\circ$) or $x_{H_2O} = 0.75$ (~ 23.0 M) ($\blacktriangle$, $\triangle$) over Ti-BEA-OH (solid points) and Ti-BEA-F (hollow points).

Figure B9 reveals that C_6H_{12} epoxidation turnover rates in CH_3CN and $C_4H_6O_2$ mixtures with H_2O show a linear dependence on $[C_6H_{12}]$ (**Figures B9a** and **B9d**) and nearly zero-order dependence on $[H_2O_2]$ (**Figures B9b** and **B9e**) at low ratios of $[C_6H_{12}]$ to $[H_2O_2]$. H_2O_2 decomposition rates show a linear dependence on $[H_2O_2]$ at all H_2O_2 concentrations examined (**Figures B9c** and **B9f**). The rate dependences match those shown for CH_3OH mixtures in **Figure 3.2**. These data indicate that the reaction mechanisms for C_6H_{12} epoxidation and H_2O_2 decomposition do not change with the organic solvent, x_{H_2O} , or $(SiOH)_x$ density of the zeolite.

B5. *In situ* UV-Vis Spectroscopy to Examine H_2O_2 Activation over Ti-BEA Materials

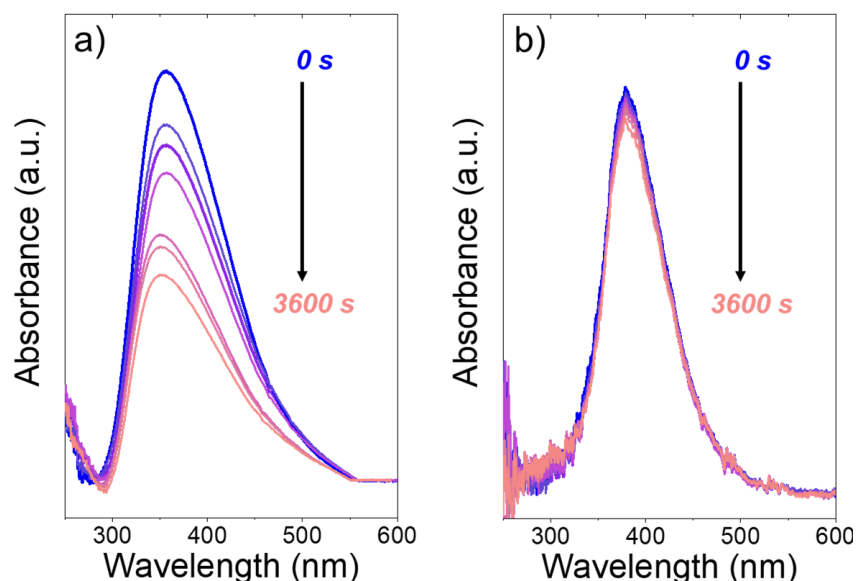


Figure B10. *In situ* UV-Vis spectra of Ti-BEA-F as a function of time within continuously flowing neat a) H_2O and b) $C_4H_6O_2$ (313 K, $1\text{ cm}^3\text{ min}^{-1}$) after H_2O_2 activation (100 mM H_2O_2 (with 390 mM H_2O), 313 K, $1\text{ cm}^3\text{ min}^{-1}$). The reported spectra were taken every 600 s after H_2O_2 activation.

The absorbance features from 300 – 550 nm in **Figure B10** in Ti-BEA-F match those observed in Ti-BEA-OH (**Figure 3.3**) and indicate that each Ti-BEA activates H_2O_2 to form a pool of Ti-OOH and $Ti-(\eta^2)\text{-O}_2$ in H_2O and $C_4H_6O_2$.^{30-31, 76} These absorbance features occur in the same region as previously reported over Ti-BEA in CH_3CN ³⁰⁻³¹ and CH_3OH .⁷⁶ The attenuation of the

peak areas for Ti-OOH and Ti-(η^2)-O₂ with time in H₂O and negligible changes in C₄H₆O₂ agree with those in Ti-BEA-OH. The peak areas attenuate by ~45% in H₂O ~5% in C₄H₆O₂ over 1 h. The slight decrease in features over C₄H₆O₂ with time may result from residual H₂O remaining in the pores from the aqueous H₂O₂ solution (390 mM H₂O) or reaction between C₄H₆O₂ molecules and the H₂O₂-derived intermediates. These trends suggest that the reversibility of H₂O₂ activation does not depend on the (SiOH)_x density of Ti-BEA.

Figure B11 displays the evolution of the peak areas for H₂O₂-derived intermediates with time after cutting off H₂O₂ flow over Ti-BEA-OH in H₂O (**Figure B11a**), equimolar H₂O and C₄H₆O₂ (**Figure B11b**), and over Ti-BEA-F in H₂O (**Figure B11c**). The data plots were fit to exponential decay functions to yield rate constants for desorption of Ti-OOH and Ti-(η^2)-O₂ (k_{-3}), shown in **Table B3**. Neat H₂O and equimolar H₂O and C₄H₆O₂ provide k_{-3} values that exceed neat C₄H₆O₂ by more than an order of magnitude, reinforcing that protic solvents facilitate reversible activation of H₂O₂ over Ti-BEA materials.

Solvent	Ti-BEA-OH k_{-3} (ks ⁻¹)	Ti-BEA-F k_{-3} (ks ⁻¹)
H ₂ O	0.43 ± 0.06	0.47 ± 0.08
H ₂ O/C ₄ H ₆ O ₂	0.56 ± 0.07	--
C ₄ H ₆ O ₂	0.03 ± 0.03	0.02 ± 0.06

Table B3. Rate constants for the re-formation of H₂O₂ from H₂O₂-derived intermediates (k_{-3}) over Ti-BEA. k_{-3} values and uncertainties are calculated from the exponential fits in **Figure B11**.

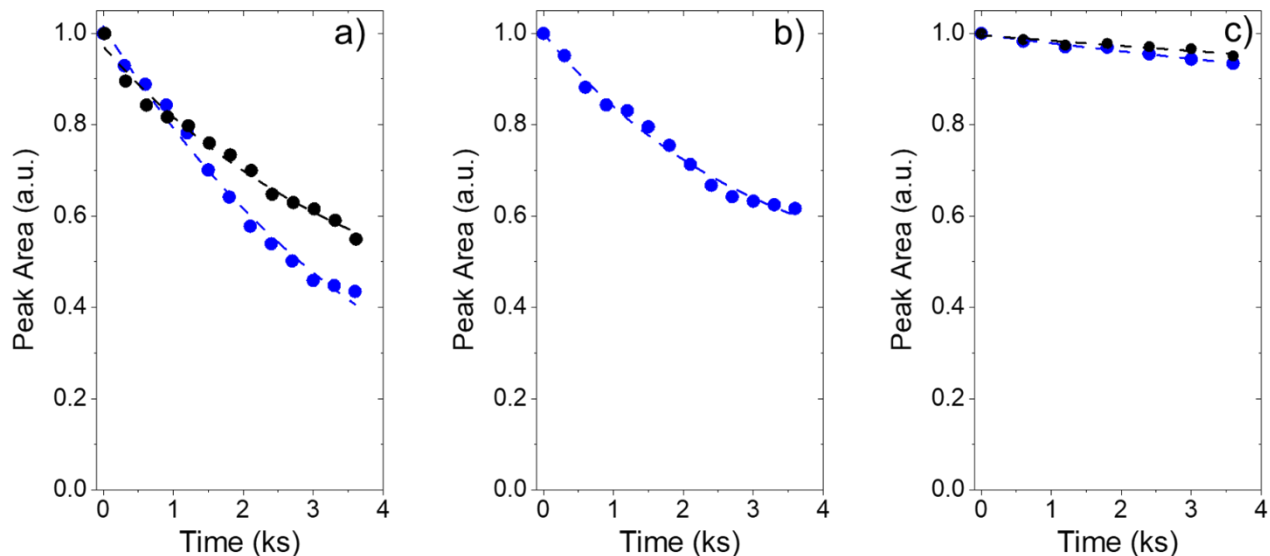


Figure B11. Normalized H_2O_2 -derived intermediate peak areas as a function of time after H_2O_2 activation (100 mM H_2O_2 (with 390 mM H_2O), 313 K, $1 \text{ cm}^3 \text{ min}^{-1}$) within continuously flowing neat a) H_2O , b) equimolar H_2O and $\text{C}_4\text{H}_6\text{O}_2$, c) and neat $\text{C}_4\text{H}_6\text{O}_2$ (313 K, $1 \text{ cm}^3 \text{ min}^{-1}$) over Ti-BEA-OH (blue) and Ti-BEA-F (black). The dashed lines represent fits to an exponential decay function for first-order kinetics.

B6. Derivation of Rate Expression for 1-Hexene Epoxidation over Ti-BEA Materials

Scheme 3.1 shows the elementary steps for 1-hexene (C_6H_{12}) epoxidation and H_2O_2 decomposition.³⁰ The mechanism begins with the quasi-equilibrated adsorption of a solvent molecule (step 0), C_6H_{12} (step 1), or H_2O_2 (step 2). H_2O_2 then irreversibly activates to form Ti-OOH (step 3).^{30, 32} The Ti-OOH intermediate may then react with another H_2O_2 molecule in H_2O_2 decomposition (step 6), react with a C_6H_{12} molecule in the kinetically relevant step for epoxidation (step 4), or desorb to re-form H_2O_2 (reverse of step 3). The epoxide that forms undergoes quasi-equilibrated desorption to form the 1,2-epoxyhexane ($\text{C}_6\text{H}_{12}\text{O}$) product.

Epoxidation turnover rates can be modeled with **Equation 3.3**:

$$r_{\text{epox}} = k_4[\text{Ti} - \text{OOH}][\text{C}_6\text{H}_{12}] \quad (\text{B9})$$

where r_{epox} is the epoxidation rate, k_4 is the rate constant for step 4 in **Scheme 3.1**, and $[\text{Ti-OOH}]$

and $[C_6H_{12}]$ represent the number of H_2O_2 -activated metal sites and C_6H_{12} molecules in the liquid phase. Applying the pseudo-steady state hypothesis to the Ti-OOH intermediate gives:

$$r_{epox} = \frac{k_3 k_4 K_2 [C_6H_{12}] [H_2O_2] [*]}{k_{-3} + k_4 [C_6H_{12}] + k_6 [H_2O_2]} \quad (B10)$$

The total number of Ti active sites ($[L]$) can be written as:

$$[L] = [S *] + [C_6H_{12} *] + [H_2O_2 *] + [OOH *] + [C_6H_{12}O *] \quad (B11)$$

where $[S*]$ is the number of sites occupied by a solvent molecule (S ; CH_3CN , CH_3OH , $C_4H_6O_2$, or H_2O) and the other terms represent the number of adsorbed reactants and products. Substituting rate constants, equilibrium constants, and reactant and product concentrations gives:

$$[L] = K_0 [S] + K_1 [C_6H_{12}] + K_2 [H_2O_2] + \frac{k_3 K_2 [H_2O_2]}{k_{-3} + k_4 [C_6H_{12}] + k_6 [H_2O_2]} + \frac{[C_6H_{12}O]}{K_5} \quad (B12)$$

Combining **Equations B10** and **B12** gives the full rate expression (**Equation 3.4**):

$$\frac{r_{epox}}{[L]} = \frac{\frac{k_3 k_4 K_2 [C_6H_{12}] [H_2O_2]}{k_{-3} + k_4 [C_6H_{12}] + k_6 [H_2O_2]}}{K_0 [S] + K_1 [C_6H_{12}] + K_2 [H_2O_2] + \frac{k_3 K_2 [H_2O_2]}{k_{-3} + k_4 [C_6H_{12}] + k_6 [H_2O_2]} + \frac{[C_6H_{12}O]}{K_5}} \quad (B13)$$

When molar ratios of H_2O_2 to C_6H_{12} exceed two, rates depend linearly on $[C_6H_{12}]$ and negligibly on $[H_2O_2]$ (**Figure 3.2** and **Figure B9**), indicating that Ti-OOH intermediates saturate Ti sites. The $[OOH*]$ term dominates in the denominator under these conditions, and all other terms can be canceled out. **Equation B13** then simplifies to the same form as **Equation 3.5**:

$$\frac{r_{epox}}{[L]} = k_4 [C_6H_{12}] \quad (B14)$$

Equation B14 describes the kinetic regime under which activation barriers were measured. Under conditions in which the active sites are saturated with the epoxide product, the $[C_6H_{12}O*]$ term dominates in the denominator of **Equation B13**, which instead simplifies to:

$$\frac{r_{epox}}{[L]} = \frac{k_3 k_4 K_2 K_5 [C_6H_{12}] [H_2O_2]}{[C_6H_{12}O] (k_{-3} + k_4 [C_6H_{12}] + k_6 [H_2O_2])} \quad (B15)$$

When materials show high H₂O₂ selectivities towards epoxidation (i.e., $S_{H_2O_2} > 90\%$), the rate of epoxidation far exceeds H₂O₂ decomposition (i.e., $k_4[C_6H_{12}] \gg k_6[H_2O_2]$). Combining this with a solvent that shows negligible re-formation rates of H₂O₂ from Ti-OOH (e.g., CH₃CN or C₄H₆O₂ with minimal quantities of H₂O), where the value of the quantity $k_4[C_6H_{12}]$ is much greater than k_{-3} , allows for further simplification of **Equation B15**:

$$\frac{r_{epox}}{[L]} = \frac{k_3 K_2 K_5 [H_2O_2]}{[C_6H_{12}O]} \quad (B16)$$

Equation B16 matches previous reports from our group in which rates of C₆H₁₂³⁰ and C₆H₁₀³¹ epoxidation over Ti-BEA in CH₃CN solvent depend negligibly on the concentration of the alkene substrate, linearly on the concentration of H₂O₂, and inversely on epoxide concentration when the alkene is present in significant excess to H₂O₂ (i.e., molar ratio of alkene to H₂O₂ greater than 50).

Equation 3.6 shows the expression for H₂O₂ decomposition rates:

$$-r_{decomp} = k_6[Ti-OOH][H_2O_2] \quad (B17)$$

Substituting terms for [Ti-OOH] and using the site balance for [L] leads to (**Equation 3.7**):

$$-\frac{r_{decomp}}{[L]} = \frac{\frac{k_3 k_4 K_2 [H_2O_2]^2}{k_{-3} + k_4 [C_6H_{12}] + k_6 [H_2O_2]}}{K_0 [S] + K_1 [C_6H_{12}] + K_2 [H_2O_2] + \frac{k_3 K_2 [H_2O_2]}{k_{-3} + k_4 [C_6H_{12}] + k_6 [H_2O_2]} + \frac{[C_6H_{12}O]}{K_5}} \quad (B18)$$

At the low ratios of [C₆H₁₂]:[H₂O₂] used when measuring activation barriers, Ti-OOH saturates the Ti-BEA surface and H₂O₂ decomposition rates increase linearly with [H₂O₂].³¹ This allows us to simplify **Equation B18** to:

$$-\frac{r_{decomp}}{[L]} = k_6 [H_2O_2] \quad (B19)$$

Activation parameter equations for H₂O₂ decomposition can be derived in an identical procedure as for C₆H₁₂ epoxidation in **Section 3.3.4**. The apparent activation free energy ($\Delta G_{app}^\ddagger$) equals the difference between the free energy of the transition state and reference state:

$$\Delta G_{app,decomp}^\ddagger = (G_{decomp}^{\ddagger,0} + G_{decomp}^{\ddagger,\varepsilon}) - (G_{Ti-OOH}^0 + G_{Ti-OOH}^\varepsilon) - (G_{H_2O_2}^0 + G_{H_2O_2}^\varepsilon) \quad (B20)$$

An apparent free energy term ($\Delta G_{app}^{\ddagger}$) excluding the activity coefficient of H_2O_2 corresponds to k_6^* introduced in **Equation 3.10**, which originates from the rate constant for H_2O_2 decomposition (k_6):

$$k_6^* = \frac{k_B T}{h} \exp\left(-\frac{\Delta G_{app,decomp}^{\ddagger}}{RT}\right) \quad (B21)$$

To obtain $\Delta G_{app,decomp}^{\ddagger}$, we add $G_{H_2O_2}^\varepsilon$ to each side of **Equation B20**:

$$\Delta G_{app,decomp}^{\ddagger} = \Delta G_{app,decomp}^{\ddagger} + G_{H_2O_2}^\varepsilon = (G_{decomp}^{\ddagger,0} + G_{decomp}^{\ddagger,\varepsilon}) - (G_{Ti-OOH}^0 + G_{Ti-OOH}^\varepsilon) - G_{H_2O_2}^0 \quad (B22)$$

B7. Excess Energies to Probe Changes in Fluid Phase C_6H_{12} and H_2O_2 Stability

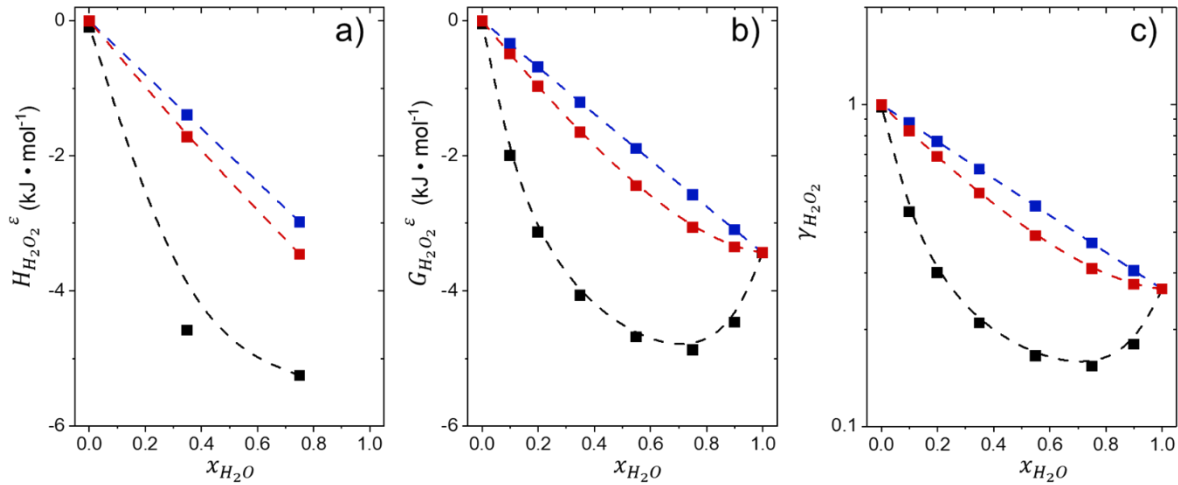


Figure B12. a) Excess enthalpies ($H_{H_2O_2}^\varepsilon$) (308 – 338 K), b) excess free energies ($G_{H_2O_2}^\varepsilon$) (313 K), and c) activity coefficients of H_2O_2 ($\gamma_{H_2O_2}$) (313 K) as a function of x_{H_2O} in mixtures of CH_3CN (■), CH_3OH (■), and $C_4H_6O_2$ (■) with H_2O . Activity coefficients for H_2O_2 were obtained with the NRTL method on ChemCAD.

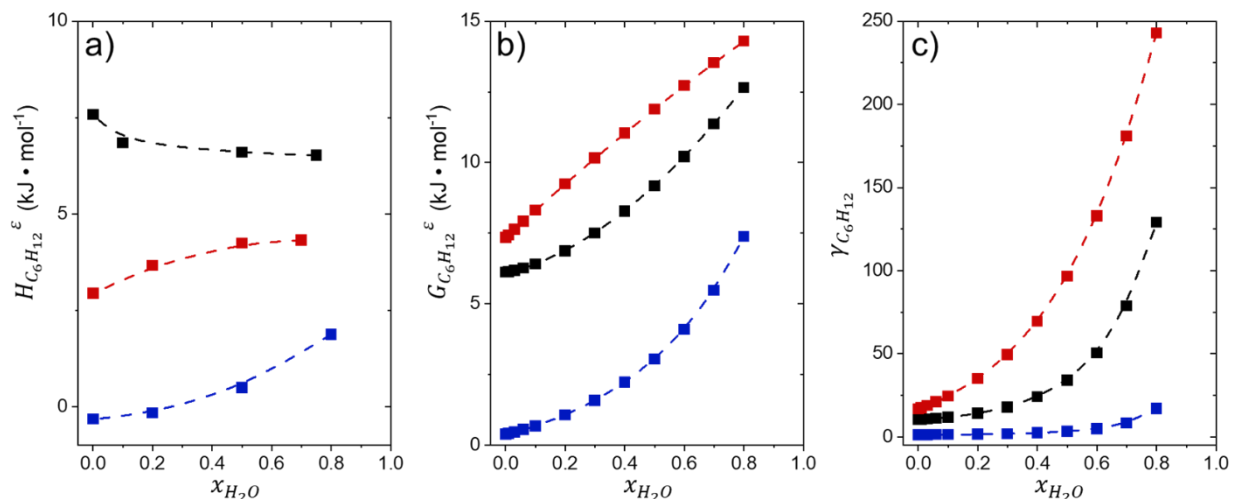


Figure B13. a) Excess enthalpies ($H_{C_6H_{12}}^\varepsilon$) (308 – 338 K), b) excess free energies ($G_{C_6H_{12}}^\varepsilon$) (313 K), and c) activity coefficients of C₆H₁₂ ($\gamma_{C_6H_{12}}$) (313 K) as a function of x_{H_2O} in mixtures of CH₃CN (■), CH₃OH (■), and C₄H₆O₂ (■) with H₂O. Activity coefficients for C₆H₁₂ were obtained with the Volume-Translated Peng-Robinson (VTPR) method on ChemCAD.

Figures B12 and B13 show excess energies and activity coefficients for C₆H₁₂ and H₂O₂, respectively. The equations to compute the excess energies from the activity coefficients are:

$$G_j^\varepsilon = RT * \ln(\gamma_j) \quad (B23)$$

$$H_j^\varepsilon = -RT^2 * \frac{d \ln(\gamma_j)}{dT} \quad (B24)$$

where j represents C₆H₁₂ or H₂O₂ here, R equals the ideal gas constant, and T is temperature. The differential term $\left(\frac{d \ln(\gamma_j)}{dT}\right)$ was obtained by calculating activity coefficients between 308-333 K by increments of 5 K. The natural log of the activity coefficients was plotted against temperature, and the slope of this line equaled the differential term (examples in **Figure B14**).

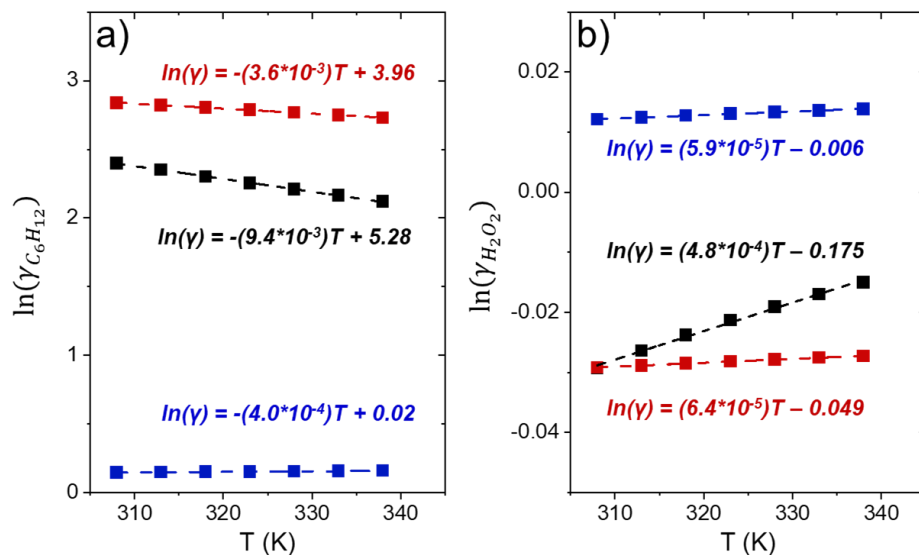


Figure B14. Natural logs of the activity coefficient of a) C₆H₁₂ and b) H₂O₂ as a function of temperature (308 – 338 K) in CH₃CN (■), CH₃OH (■), and C₄H₆O₂ (■) with 39 mM H₂O ($x_{H_2O} = 0.002$). Activity coefficients were obtained with the Volume-Translated Peng-Robinson (VTPR) method for C₆H₁₂ and the UNIQUAC method for H₂O₂ on ChemCAD.

B8. C₆H₁₂ Epoxidation and H₂O₂ Decomposition Rates Normalized by Reactant Activity Coefficients

Changing x_{H_2O} affects the stability of fluid phase C₆H₁₂, so rates were normalized by C₆H₁₂ activity coefficients to examine the effect of C₆H₁₂ stability on epoxidation rates (**Figure 3.3a**). An expression for normalized C₆H₁₂ epoxidation rates can be obtained by starting with the expression for epoxidation rates (**Equation B9**). Using transition state theory,^{39, 271} we can define an alternate rate expression for epoxidation, an equilibrium constant between the transition state and reference state (K^{*epox}), and a new expression for the rate constant k_4 :

$$r_{epox} = k_4[\ddagger_{epox}] \quad (B25)$$

$$K^{*epox} = \frac{a_{\ddagger}}{a_{C_6H_{12}} a_{Ti-OOH}} = \frac{\gamma_{\ddagger}[\ddagger_{epox}]}{\gamma_{C_6H_{12}}[C_6H_{12}] \gamma_{Ti-OOH}[Ti-OOH]} \quad (B26)$$

$$k_4 = \frac{k_B T}{h} K^{*epox} \quad (B27)$$

where $[‡_{epox}]$ is the concentration of transition state complexes, a_i is the activity of a component, and γ_i is the activity coefficient of a component. We can substitute the expressions for $K^{\ddagger_{epox}}$ and k_4 into **Equation B25**:

$$r_{epox} = \frac{k_B T}{h} K^{\ddagger_{epox}} \frac{\gamma_{C_6H_{12}} \gamma_{Ti-OOH} [C_6H_{12}] [Ti-OOH]}{\gamma_{\ddagger_{epox}}} \quad (B28)$$

Under conditions where Ti-OOH is the MARI, $[L] = [Ti-OOH]$. Substituting in $[L]$ and dividing by $[L]$ and $\gamma_{C_6H_{12}}$ yields the final expression for activity-normalized turnover rates:

$$\frac{r_{epox}}{[L] \gamma_{C_6H_{12}}} = \frac{k_B T}{h} K^{\ddagger_{epox}} \frac{\gamma_{Ti-OOH} [C_6H_{12}]}{\gamma_{\ddagger_{epox}}} \quad (B29)$$

Changing $[H_2O]$ also alters the stability of fluid phase H_2O_2 , so H_2O_2 decomposition rates were normalized by H_2O_2 activity coefficients (**Figure 3.3b**). Again, invoking transition theory, we obtain a normalized decomposition rate expression with an identical form to **Equation B28**:

$$-r_{decomp} = \frac{k_B T}{h} K^{\ddagger_{decomp}} \frac{\gamma_{H_2O_2} \gamma_{Ti-OOH} [H_2O_2] [Ti-OOH]}{\gamma_{\ddagger_{decomp}}} \quad (B30)$$

When Ti-OOH saturates the active sites, the expression simplifies to:

$$\frac{-r_{decomp}}{[L] \gamma_{H_2O_2}} = \frac{k_B T}{h} K^{\ddagger_{decomp}} \frac{\gamma_{Ti-OOH} [H_2O_2]}{\gamma_{\ddagger_{decomp}}} \quad (B31)$$

Several activity coefficients were examined for the rate normalizations, as shown in **Figures B15** and **B16**. The Wilson and NRTL methods give similar activity coefficients for H_2O_2 , while the Modified UNIFAC (Dortmund) and VTPR methods give similar activity coefficients for C_6H_{12} . NRTL and VTPR were chosen to report the normalized rates in **Figure 3.3** because of the agreement with another method. The UNIQUAC (**Figure B15a**) and UNIFAC LLE (**Figure B16a**) methods gave activity coefficients that did not agree closely with any available methods in ChemCAD.

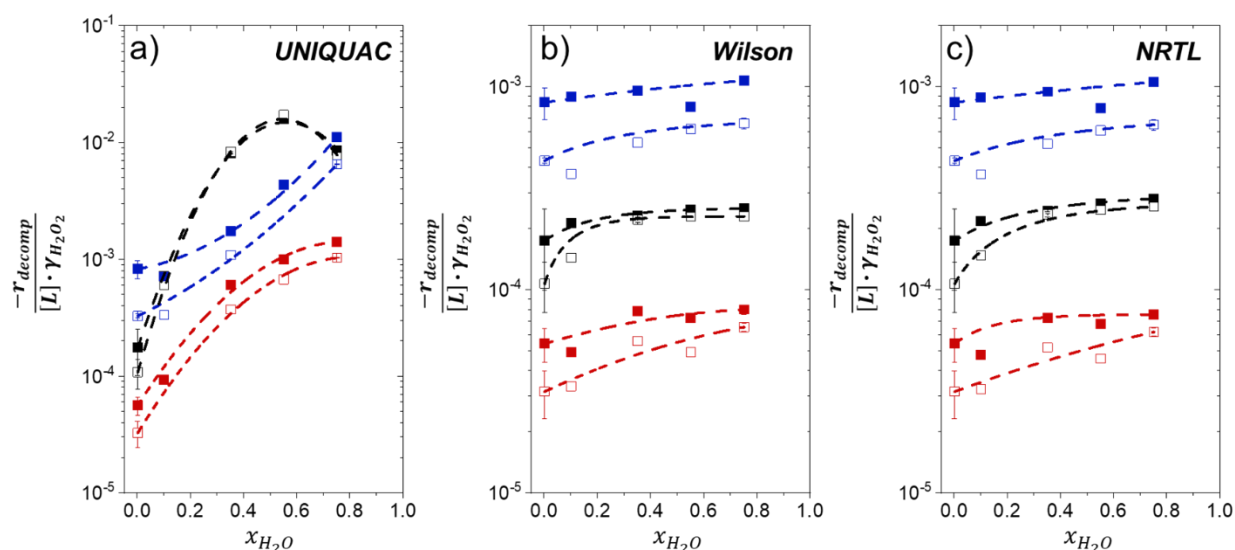


Figure B15. Turnover rates for H_2O_2 decomposition (1 mM H_2O_2 , 313 K) normalized by H_2O_2 activity coefficient and as a function of $x_{\text{H}_2\text{O}}$ in mixtures of CH_3CN (■,□), CH_3OH (■,□), and $\text{C}_4\text{H}_6\text{O}_2$ (■,□) with H_2O over Ti-BEA-OH (solid points) and Ti-BEA-F (hollow points). Activity coefficients of H_2O_2 were calculated using the methods listed in the plot area on ChemCAD.

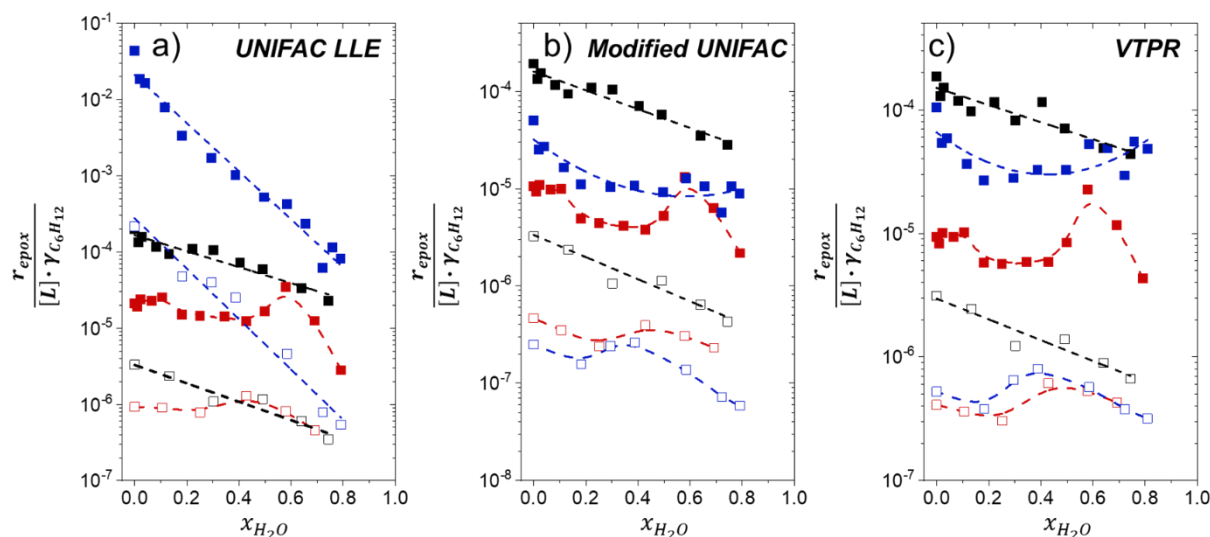


Figure B16. Turnover rates for C_6H_{12} epoxidation (1 mM C_6H_{12} , 10 mM H_2O_2 , 313 K) normalized by C_6H_{12} activity coefficient and as a function of $x_{\text{H}_2\text{O}}$ in mixtures of CH_3CN (■,□), CH_3OH (■,□), and $\text{C}_4\text{H}_6\text{O}_2$ (■,□) with H_2O over Ti-BEA-OH (solid points) and Ti-BEA-F (hollow points). Activity coefficients of C_6H_{12} were calculated using the methods listed in the plots on ChemCAD.

B9. Activation Enthalpies and Entropies for C₆H₁₂ Epoxidation and H₂O₂ Decomposition

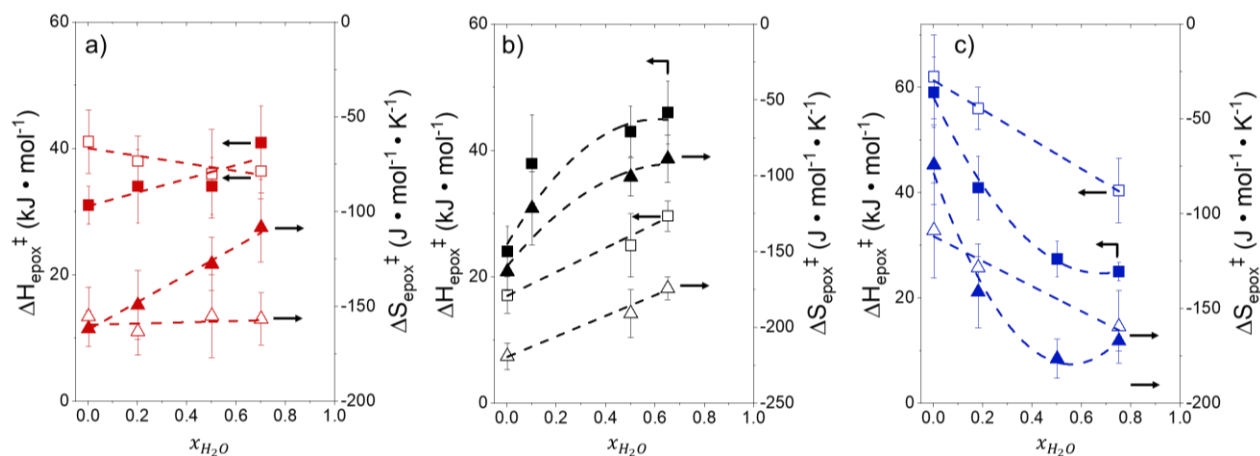


Figure B17. Apparent activation enthalpies (squares) and entropies (triangles) for H₂O₂ decomposition (1 mM H₂O₂, 313–343 K) as a function of $x_{\text{H}_2\text{O}}$ in mixtures of a) CH₃OH (red), b) CH₃CN (black), and c) C₄H₆O₂ (blue) with H₂O over Ti-BEA-OH (solid points) and Ti-BEA-F (hollow points).

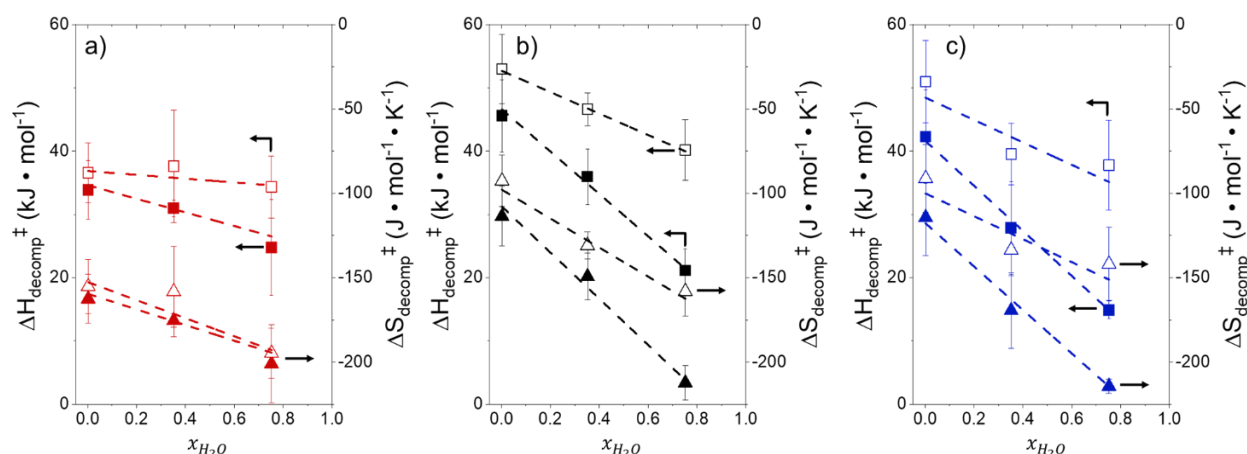


Figure B18. Apparent activation enthalpies (squares) and entropies (triangles) for C₆H₁₂ epoxidation (1 mM C₆H₁₂, 10 mM H₂O₂, 308–338 K) as a function of $x_{\text{H}_2\text{O}}$ in mixtures of a) CH₃OH (red), b) CH₃CN (black), and c) C₄H₆O₂ (blue) with H₂O over Ti-BEA-OH (solid points) and Ti-BEA-F (hollow points).

Figures B17 and B18 present $\Delta H_{\text{app}}^\ddagger$ and $\Delta S_{\text{app}}^\ddagger$ values for C₆H₁₂ epoxidation and H₂O₂ decomposition. $\Delta H_{\text{app}}^\ddagger$ and $\Delta S_{\text{app}}^\ddagger$ generally trend in the same direction for each reaction, organic solvent, and zeolite. Taken together with the values from **Figures 3.5 and 3.6**, the data in **Figure B16** indicate that changes in the enthalpy of the transition states and Ti-OOH intermediate from

interactions with solvent molecules couple with compensating changes in entropy. A decrease in enthalpy of a species from solvent interactions (e.g., hydrogen bonding) couples with a decrease in entropy from the same interactions, while solvent interactions that give an increase in enthalpy (e.g., disruption of hydrogen bonds) also give an increase in entropy of that species. However, the enthalpy and entropy changes generally do not offset, leading to differences in $\Delta G_{app}^\ddagger$ and rates between organic solvents and zeolites.

$\Delta H_{app}^\ddagger$ and $\Delta S_{app}^\ddagger$ values were calculated using van't Hoff analysis. Applying transition state theory and substituting an expression for the apparent free energy to **Equations 3.5** and **3.8** yields alternate rate expressions for C_6H_{12} epoxidation and H_2O_2 decomposition:

$$\frac{r_E}{[L]} = \frac{k_B T}{h} \cdot \exp\left(-\frac{\Delta G_{epox}^\ddagger}{RT}\right) \cdot [C_6H_{12}] \quad (B32)$$

$$\frac{r_D}{[L]} = \frac{k_B T}{h} \cdot \exp\left(-\frac{\Delta G_{decomp}^\ddagger}{RT}\right) \cdot [H_2O_2] \quad (B33)$$

Rearranging and substituting in the apparent activation enthalpy and entropy:

$$\ln\left(\frac{r_E}{[L]} \frac{h}{k_B T [C_6H_{12}]}\right) = \frac{1}{T} \left(\frac{-\Delta H_{epox}^\ddagger}{R}\right) + \frac{\Delta S_{epox}^\ddagger}{R} \quad (B34)$$

$$\ln\left(\frac{r_D}{[L]} \frac{h}{k_B T [H_2O_2]}\right) = \frac{1}{T} \left(\frac{-\Delta H_{decomp}^\ddagger}{R}\right) + \frac{\Delta S_{decomp}^\ddagger}{R} \quad (B35)$$

The natural log term on the left side of **Equations B34** and **B35** was plotted as the y-axis against inverse temperature as the x-axis. As depicted in **Figure B19**, a line was fit to this data, and the slope of this line equaled the negative of the apparent activation enthalpy divided by the ideal gas constant, while the y-intercept equaled the apparent activation entropy divided by the ideal gas constant (**Table B4**).

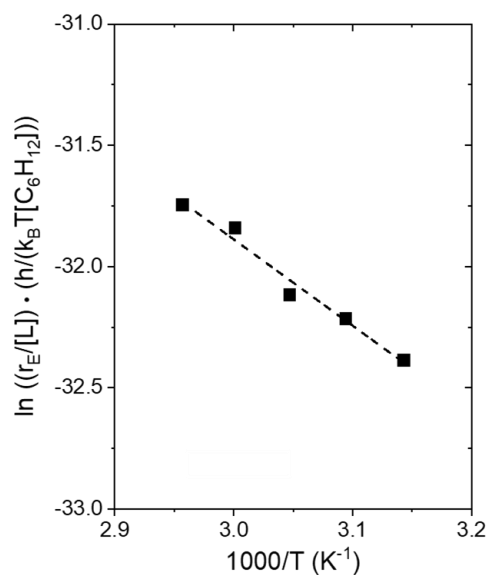


Figure B19. Representative Eyring plot for C₆H₁₂ epoxidation (1 mM C₆H₁₂, 10 mM H₂O₂, 318-338 K) in $x_{\text{CH}_3\text{CN}} = 0.35$ (11.7 M) with H₂O (21.6 M) over Ti-BEA-F.

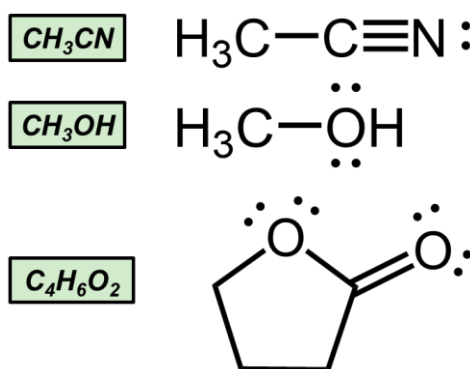
$\frac{-\Delta H_{epox}^{\ddagger}}{R}$	$\frac{\Delta S_{epox}^{\ddagger}}{R}$
-3.57 ± 0.32	-21.2 ± 1.0

Table B4. Activation enthalpy and entropy for C₆H₁₂ epoxidation divided by the ideal gas constant, obtained from the slope and intercept, respectively, of **Figure B19**.

B10. Solvent Properties

Solvent	α (Kamlet-Taft)	β (Kamlet-Taft)	E_T (Dimroth-Reichardt)	# of hydrogen bond donors	# of hydrogen bond acceptors
CH ₃ CN	0.19	0.40	45.6	0	1
C ₄ H ₆ O ₂	0	0.49	44.3	0	4
CH ₃ OH	0.98	0.66	55.4	1	2
H ₂ O	1.17	0.47	63.1	2	2

Table B5. Hydrogen bonding donating ability (α), hydrogen bond accepting ability (β), Dimroth-Reichardt parameter (E_T), and the number of hydrogen bond donors and acceptors for each solvent used in the study. The Kamlet-Taft and Reichardt parameters are previously tabulated values.³⁷⁰



Scheme B1. Structures of the organic solvents used in the study.

The Kamlet-Taft and Dimroth-Reichardt parameters are determined from the energies of the longest wavelength absorption peaks of probe solutes into each solvent. The Kamlet-Taft parameters, number of hydrogen bond donors and acceptors (see **Scheme B1** for illustration), and excess enthalpies of mixing (**Figure B20**) provide measures of the strength of interactions between the three organic solvents and H₂O. The Dimroth-Reichardt parameter provides a measure of the ionizing power of a solvent.³⁷¹ Overall, the information from **Table B5**, **Scheme B1**, and **Figure B20** provides evidence that among the organic solvents in this study, H₂O hydrogen bonds most strongly with CH₃OH and least strongly with CH₃CN.

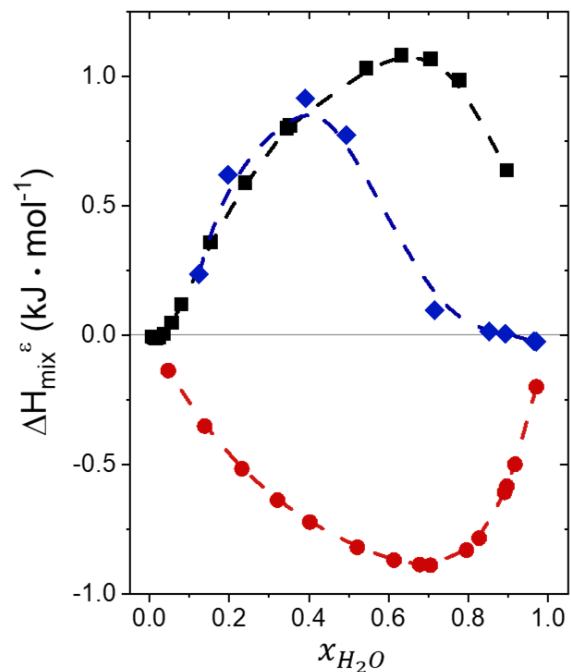


Figure B20. Excess enthalpy of mixing ($\Delta H_{mix}^{\varepsilon}$) as a function of x_{H_2O} in mixtures of CH₃OH (●), b) CH₃CN (■), and c) C₄H₆O₂ (◆) with H₂O, obtained from previous reports.³⁷²⁻³⁷⁴

B11. Isothermal Titration Calorimetry Thermograms and Heats per Injection

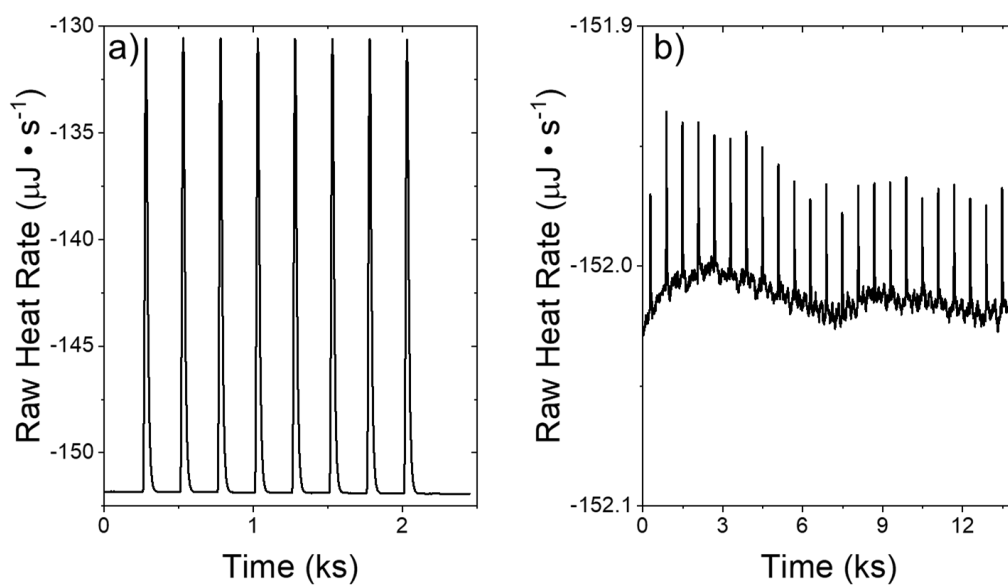


Figure B21. a) ITC thermogram from the electrical calibration of the NanoITC. b) ITC thermogram from the water-water adsorption to check the cleanliness of the ITC cell.

The plots in **Figure B21** were obtained during the cleaning and calibration procedures for isothermal titration calorimetry (ITC), as discussed in **Section 3.2.5**. **Figure B21a** shows the heat released from the sequential pulses during the electrical calibration. The instrument gave a calibration factor after completion, for which values greater than 0.98 were assumed to be satisfactory. **Figure B21b** shows the heat released during the water-water injection, during which each 1 μL injection led to a peak with an area between -3 and +3 μJ .

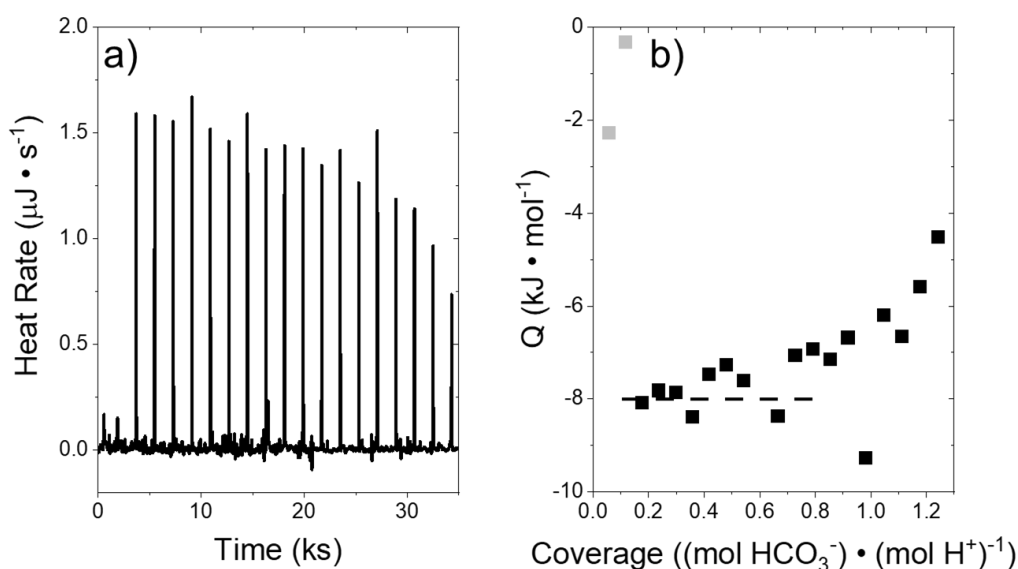


Figure B22. a) ITC thermogram from the acid-base titration of HNO_3 (0.0005 M in 0.1 M NaCl) with NaHCO_3 (0.0052 M in 0.1 M NaCl), b) the corresponding heats released as a function of bicarbonate ion coverage.

Figure B22 shows an acid-base titration of NaHCO_3 into HNO_3 , which was used as a standard to verify the ITC results obtained. The adsorption enthalpy calculated from **Figure B22b** was $-8.1 \pm 1.2 \text{ kJ mol}^{-1}$. This agrees well with the reported enthalpy of -9.1 kJ mol^{-1} .³⁵³⁻³⁵⁴

The ITC thermogram and heat release plots for all ITC experiments (other than that in **Figure 3.8**) are shown below. As discussed in **Section 3.3.6**, early injections often show lower heat released than expected due to the evaporation of liquid from the syringe needle. Although less

common, some of the experiments below show outlier points at later injections, which may result from an inconsistent volume or epoxide concentration in those injections.

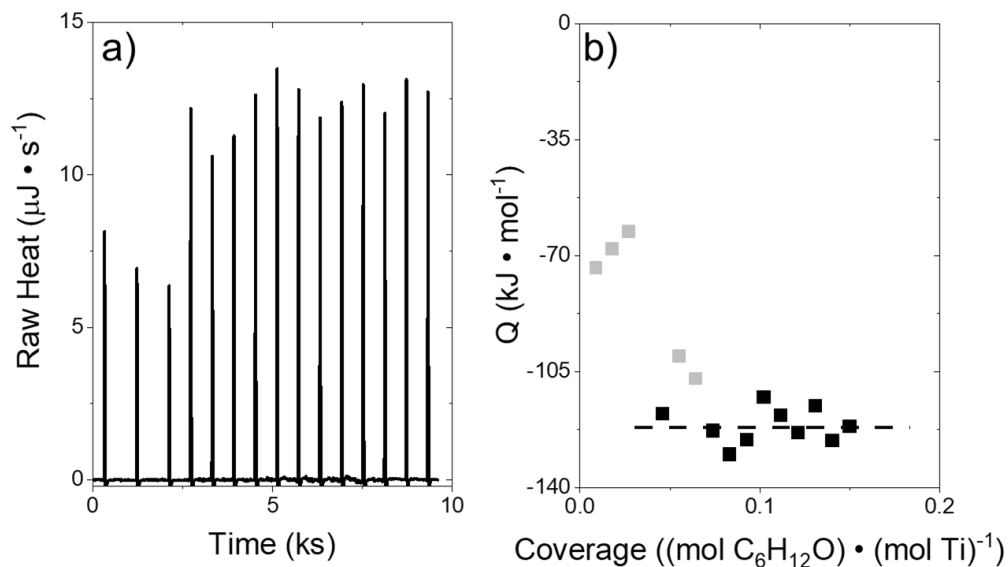


Figure B23. a) ITC thermogram from the titration of Ti-BEA-OH with 1,2-epoxyhexane (5 mM $\text{C}_6\text{H}_{12}\text{O}$ in CH_3CN with 39 mM H_2O ($x_{\text{H}_2\text{O}} = 0.002$), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

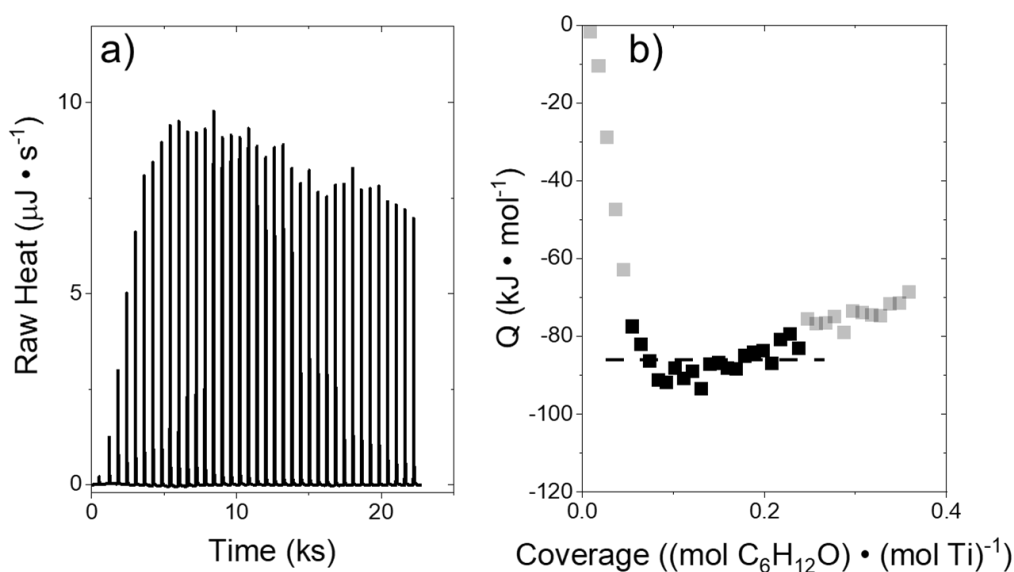


Figure B24. a) ITC thermogram from the titration of Ti-BEA-OH with 1,2-epoxyhexane (5 mM $\text{C}_6\text{H}_{12}\text{O}$ in $x_{\text{CH}_3\text{CN}} = 0.9$ (18.4 M) with H_2O (2.1 M), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

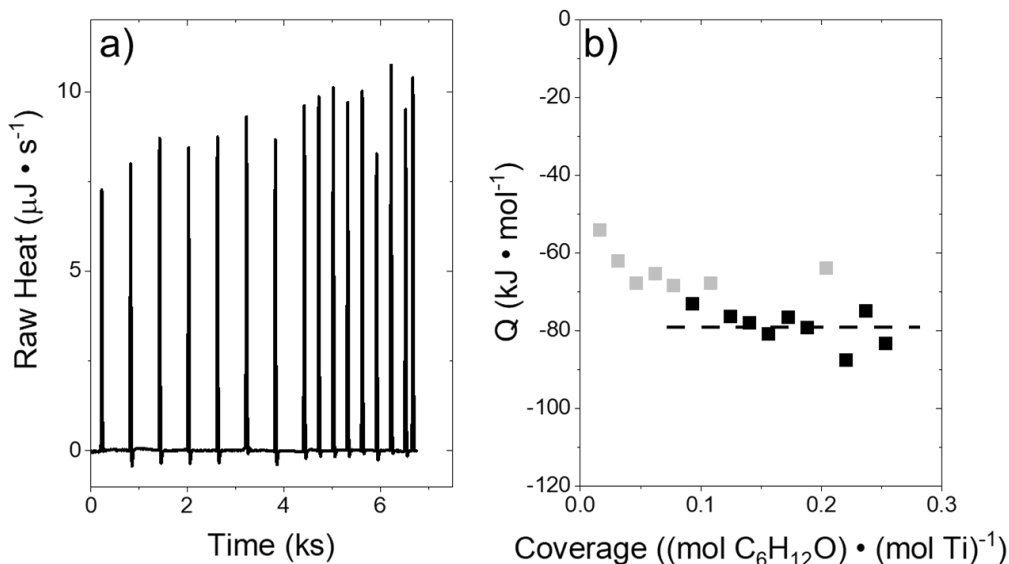


Figure B25. a) ITC thermogram from the titration of Ti-BEA-OH with 1,2-epoxyhexane (5 mM $\text{C}_6\text{H}_{12}\text{O}$ in $x_{\text{CH}_3\text{CN}} = 0.35$ (11.7 M) with H_2O (21.6 M), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

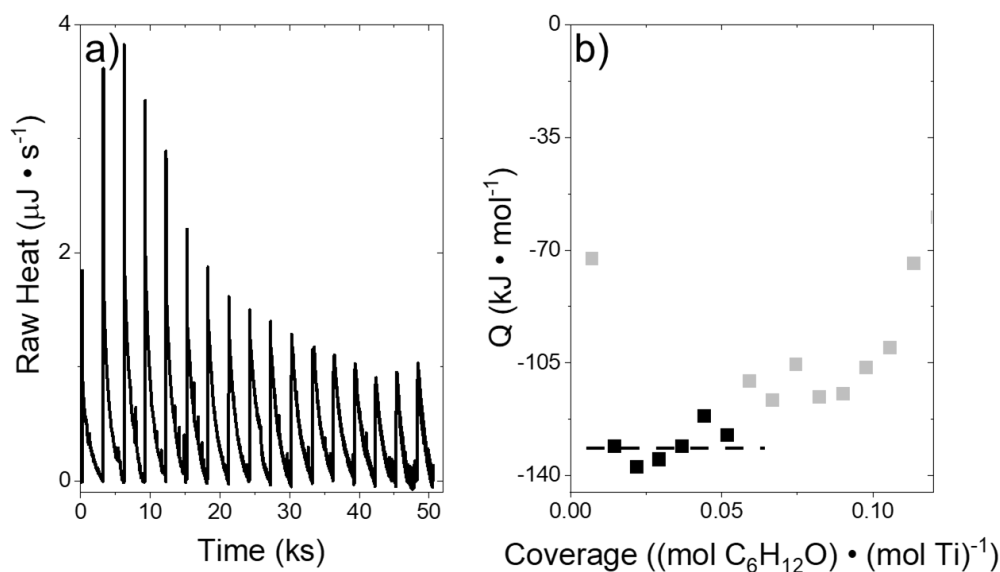


Figure B26. a) ITC thermogram from the titration of Ti-BEA-F with 1,2-epoxyhexane (5 mM $\text{C}_6\text{H}_{12}\text{O}$ in CH_3CN with 39 mM H_2O ($x_{\text{H}_2\text{O}} = 0.002$), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

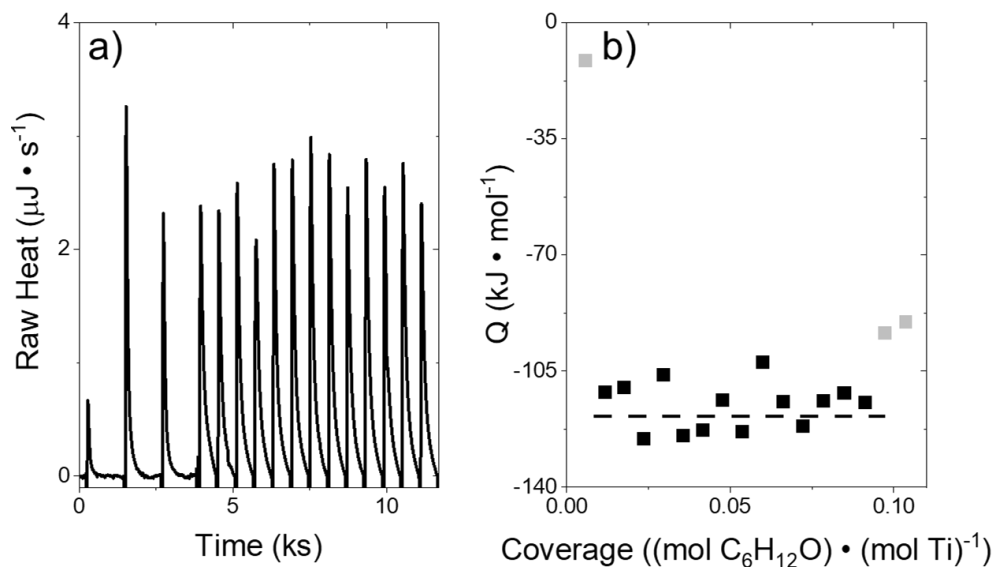


Figure B27. a) ITC thermogram from the titration of Ti-BEA-F with 1,2-epoxyhexane (5 mM $\text{C}_6\text{H}_{12}\text{O}$ in $x_{\text{CH}_3\text{CN}} = 0.9$ (18.4 M) with H_2O (2.1 M), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

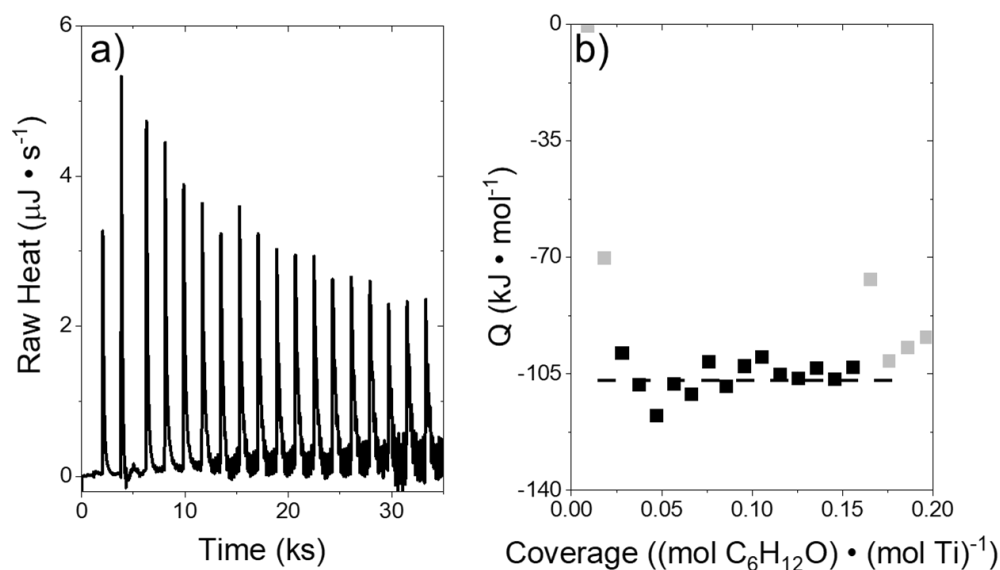


Figure B28. a) ITC thermogram from the titration of Ti-BEA-F with 1,2-epoxyhexane (5 mM $\text{C}_6\text{H}_{12}\text{O}$ in $x_{\text{CH}_3\text{CN}} = 0.35$ (11.7 M) with H_2O (21.6 M), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

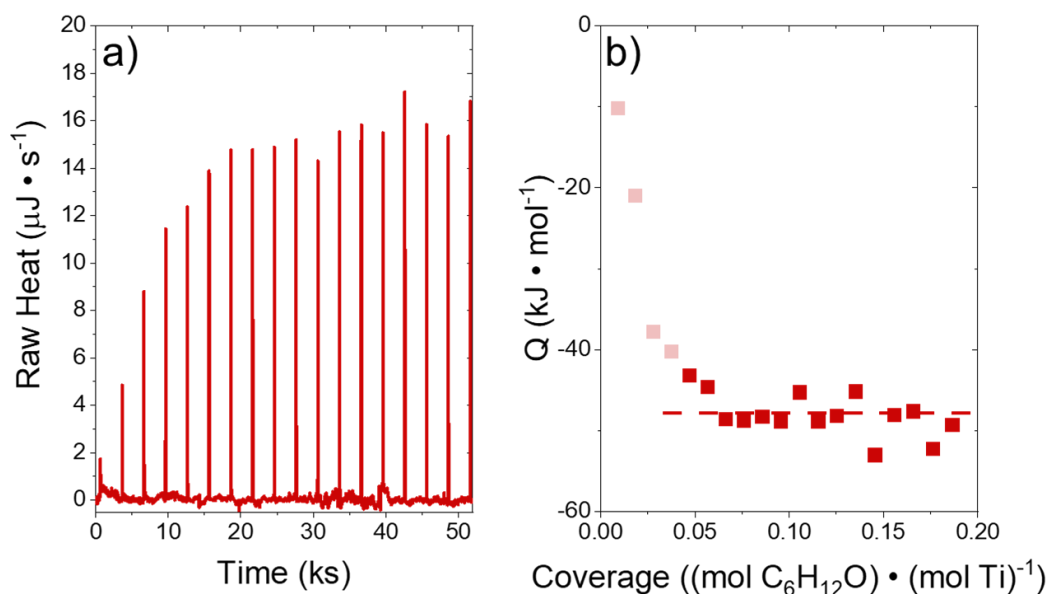


Figure B29. a) ITC thermogram from the titration of Ti-BEA-OH with 1,2-epoxyhexane (10 mM $\text{C}_6\text{H}_{12}\text{O}$ in CH_3OH with 39 mM H_2O ($x_{\text{H}_2\text{O}} = 0.002$), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

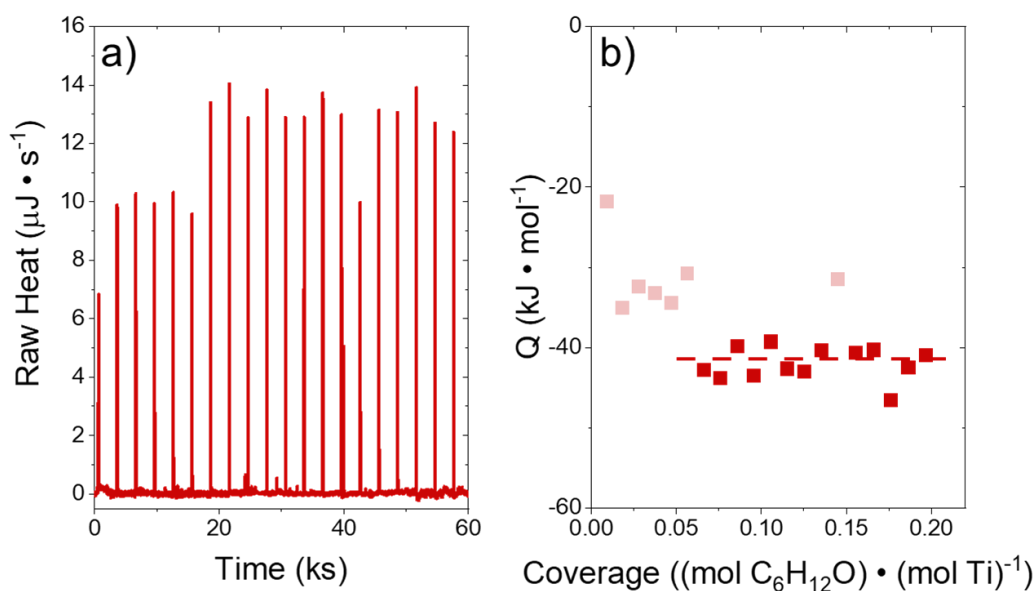


Figure B30. a) ITC thermogram from the titration of Ti-BEA-OH with 1,2-epoxyhexane (10 mM $\text{C}_6\text{H}_{12}\text{O}$ in $x_{\text{CH}_3\text{OH}} = 0.8$ (22.2 M) with H_2O (5.6 M), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

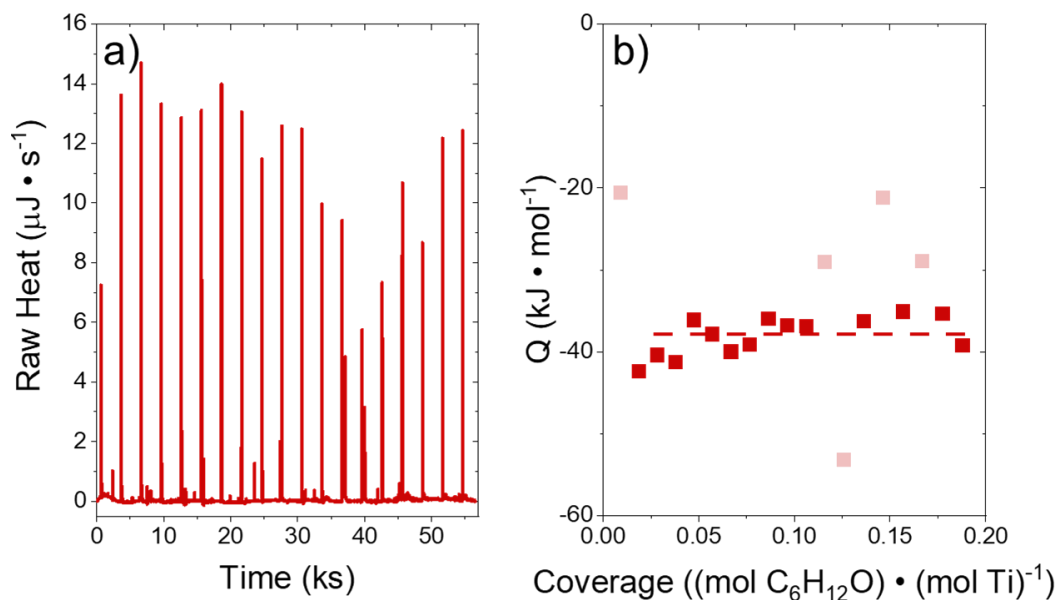


Figure B31. a) ITC thermogram from the titration of Ti-BEA-OH with 1,2-epoxyhexane (10 mM $\text{C}_6\text{H}_{12}\text{O}$ in $x_{\text{CH}_3\text{OH}} = 0.5$ (17.1 M) with H_2O (17.1 M), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

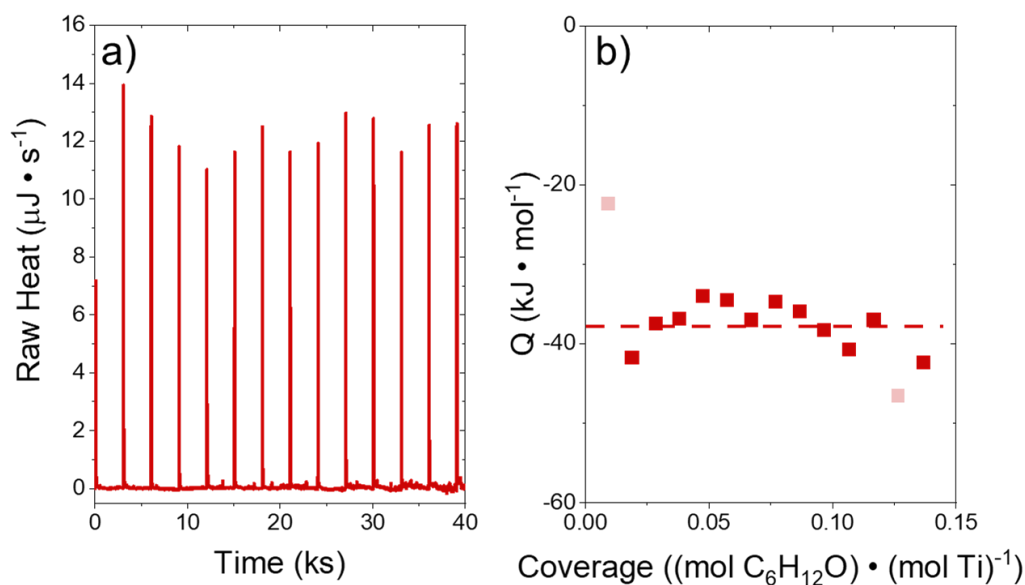


Figure B32. a) ITC thermogram from the titration of Ti-BEA-OH with 1,2-epoxyhexane (10 mM $\text{C}_6\text{H}_{12}\text{O}$ in $x_{\text{CH}_3\text{OH}} = 0.3$ (12.1 M) with H_2O (28.3 M), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

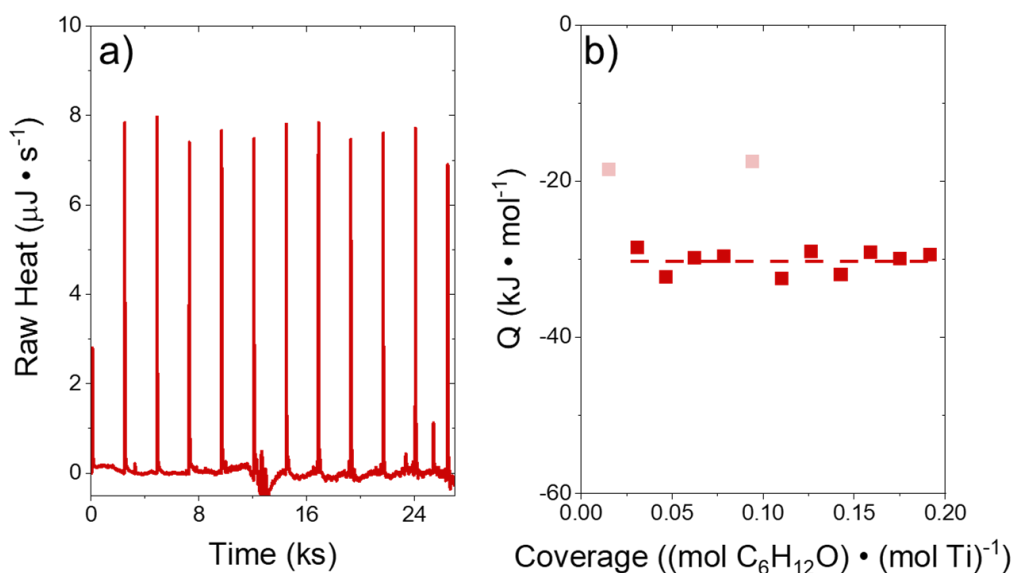


Figure B33. a) ITC thermogram from the titration of Ti-BEA-F with 1,2-epoxyhexane (10 mM $\text{C}_6\text{H}_{12}\text{O}$ in CH_3OH with 39 mM H_2O ($x_{\text{H}_2\text{O}} = 0.002$), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

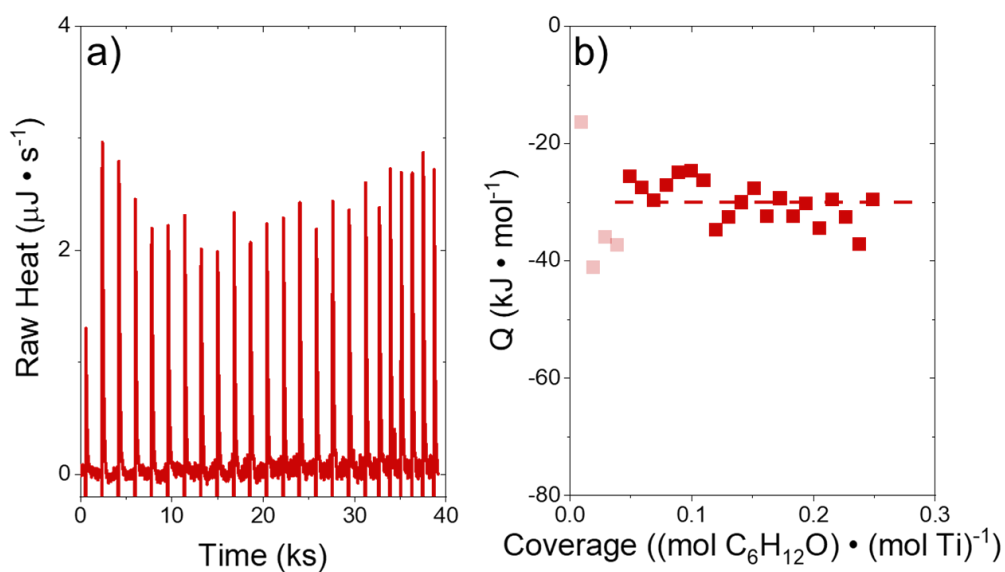


Figure B34. a) ITC thermogram from the titration of Ti-BEA-F with 1,2-epoxyhexane (10 mM $\text{C}_6\text{H}_{12}\text{O}$ in $x_{\text{CH}_3\text{OH}} = 0.5$ (17.1 M) with H_2O (17.1 M), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

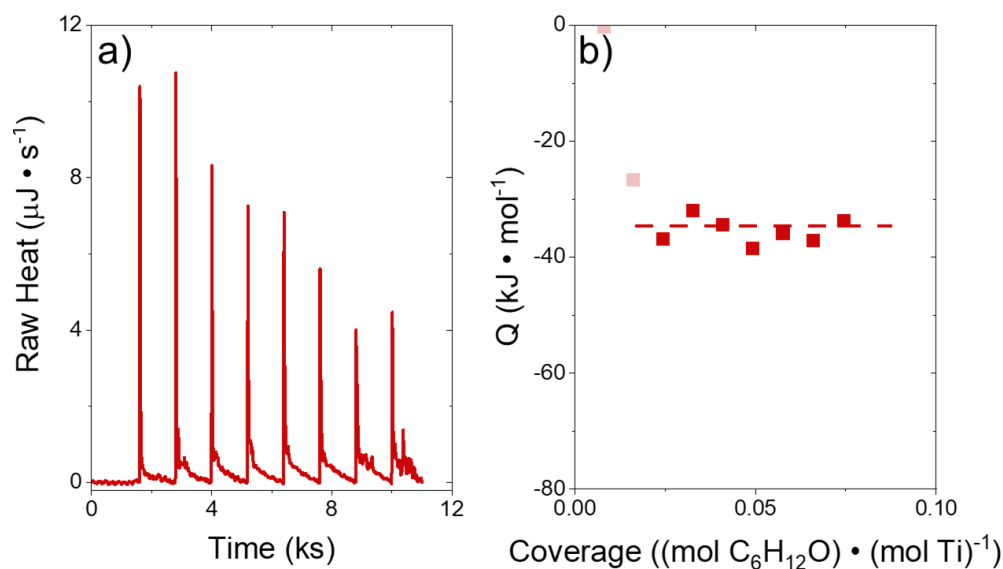


Figure B35. a) ITC thermogram from the titration of Ti-BEA-F with 1,2-epoxyhexane (10 mM $\text{C}_6\text{H}_{12}\text{O}$ in $x_{\text{CH}_3\text{OH}} = 0.3$ (12.1 M) with H_2O (28.3 M), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

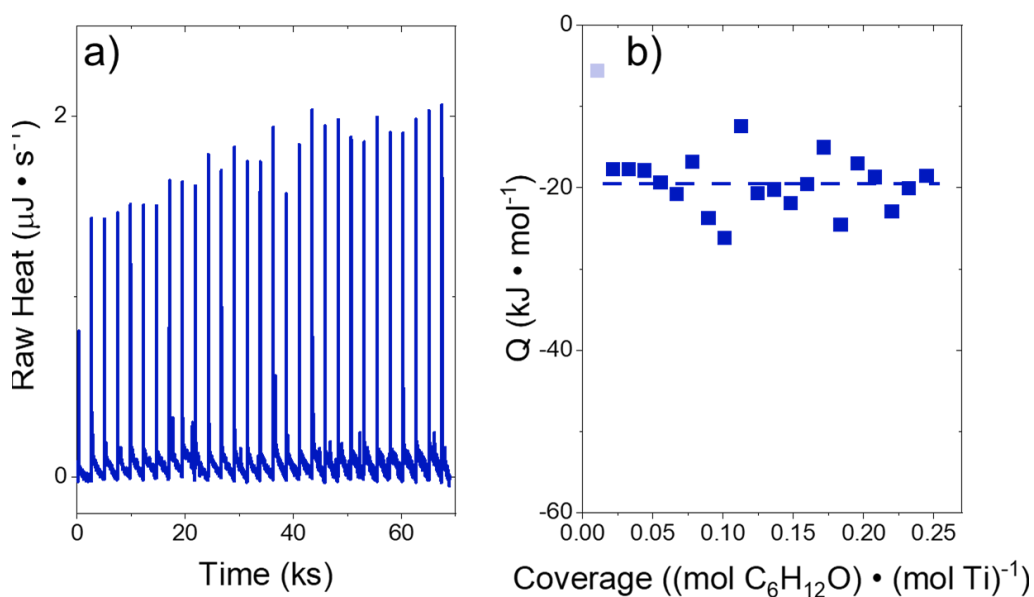


Figure B36. a) ITC thermogram from the titration of Ti-BEA-OH with 1,2-epoxyhexane (10 mM $\text{C}_6\text{H}_{12}\text{O}$ in $\text{C}_4\text{H}_6\text{O}_2$ with 39 mM H_2O ($x_{\text{H}_2\text{O}} = 0.002$), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

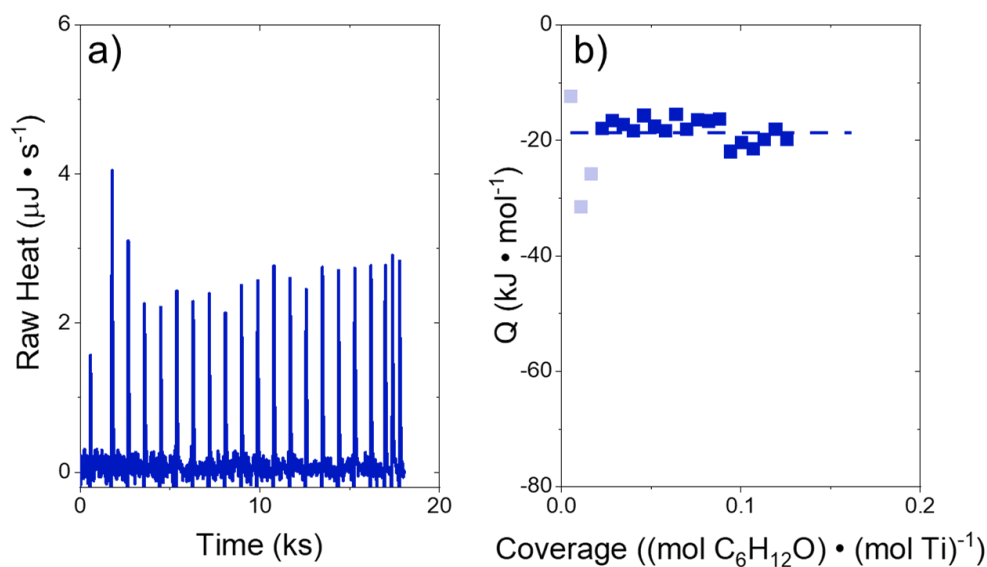


Figure B37. a) ITC thermogram from the titration of Ti-BEA-F with 1,2-epoxyhexane (10 mM $\text{C}_6\text{H}_{12}\text{O}$ in $\text{C}_4\text{H}_6\text{O}_2$ with 39 mM H_2O ($x_{\text{H}_2\text{O}} = 0.002$), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

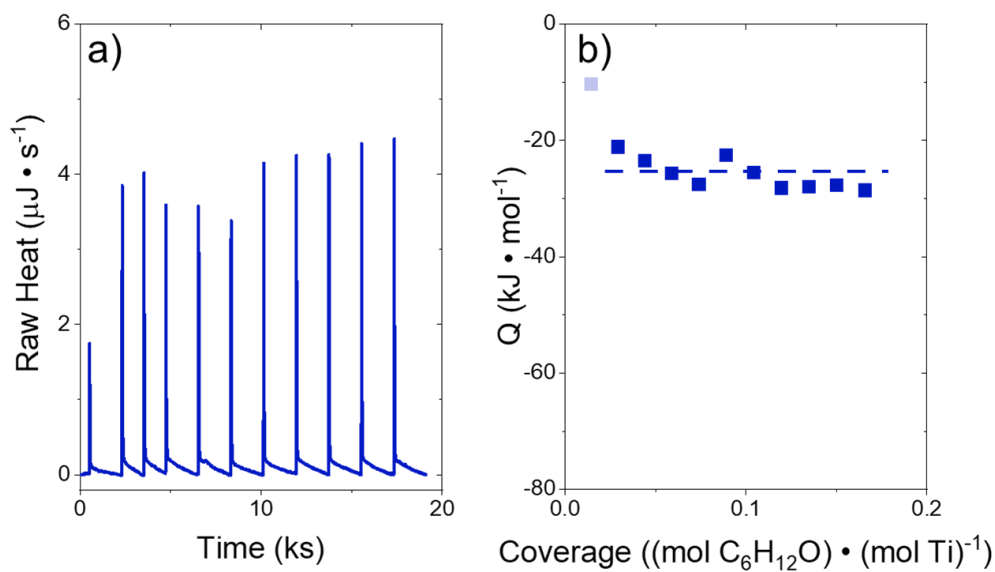


Figure B38. a) ITC thermogram from the titration of Ti-BEA-F with 1,2-epoxyhexane (10 mM $\text{C}_6\text{H}_{12}\text{O}$ in $x_{\text{C}_4\text{H}_6\text{O}_2} = 0.8$ (12.4 M) with H_2O (3.1 M), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

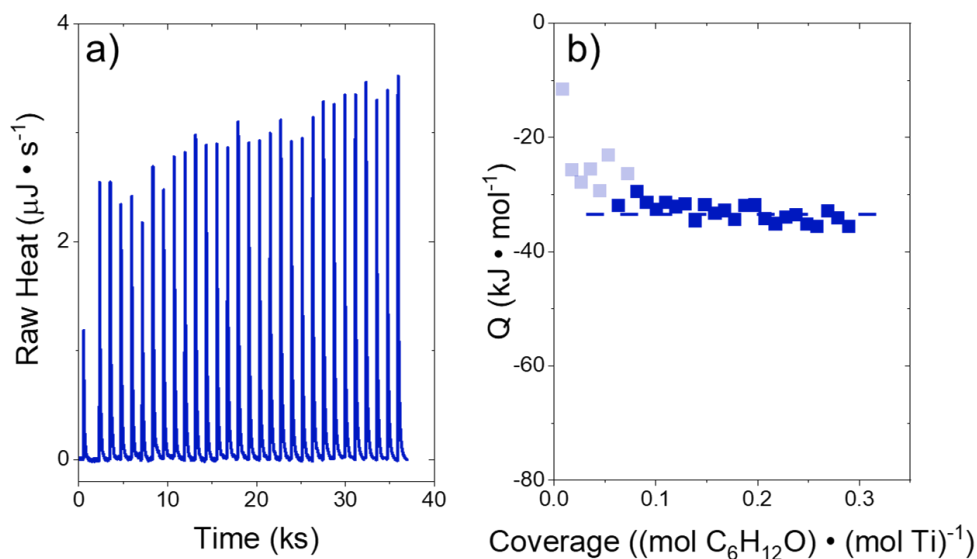


Figure B39. a) ITC thermogram from the titration of Ti-BEA-OH with 1,2-epoxyhexane (10 mM $\text{C}_6\text{H}_{12}\text{O}$ in $x_{\text{C}_4\text{H}_6\text{O}_2} = 0.8$ (12.4 M) with H_2O (3.1 M), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

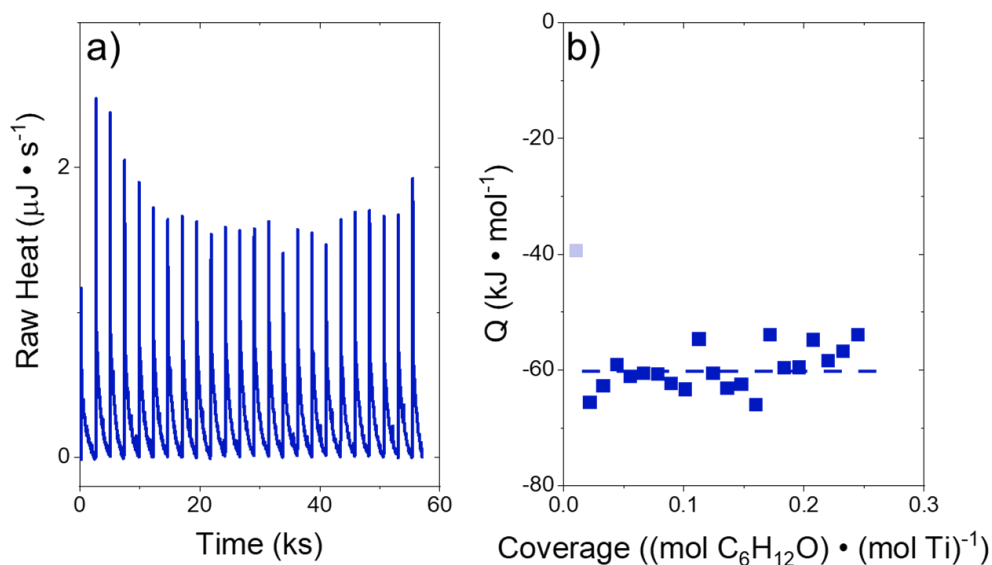


Figure B40. a) ITC thermogram from the titration of Ti-BEA-F with 1,2-epoxyhexane (5 mM $\text{C}_6\text{H}_{12}\text{O}$ in $x_{\text{C}_4\text{H}_6\text{O}_2} = 0.25$ (7.6 M) with H_2O (22.8 M), 313 K, 1 μL per injection), b) the corresponding heats released as a function of 1,2-epoxyhexane coverage.

APPENDIX C

SUPPLEMENTAL DATA AND ANALYSIS FOR CHAPTER 4

C1. Catalyst Characterization

C1.1 Diffuse Reflectance UV-Vis Spectra to Infer Metal Atom Dispersity

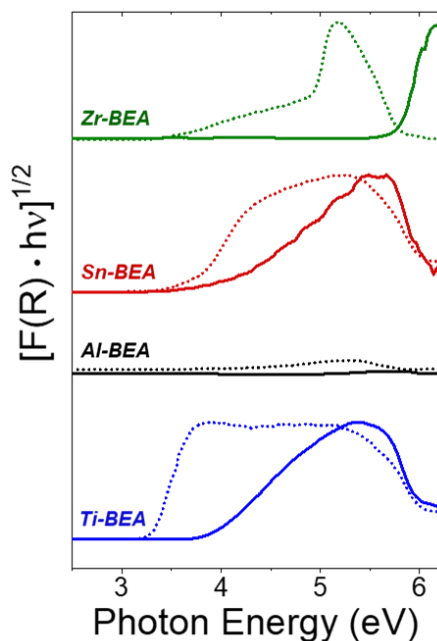


Figure C1. Tauc plots obtained with a UV-Vis spectrophotometer at ambient conditions for M-BEA (solid lines; Ti (—), Al (—), Sn (—), Zr (—)) and the respective metal oxides (dotted lines; anatase TiO₂ (---), γ -Al₂O₃ (---), SnO₂ (---), ZrO₂ (---)). Spectra were obtained from 200 to 800 nm. The Tauc plots were normalized to the most intense features and are vertically offset for clarity.

The band gaps for each M-BEA and the respective metal oxides were obtained by extrapolating the linear absorbance region of the Tauc plot in **Figure C1** to the baseline. The intersection of the baseline and linear region represents the band gap photon energy. Both Al-BEA and γ -Al₂O₃ show negligible features within the region of photon energies examined, consistent with reported band gaps greater than 7 eV for γ -Al₂O₃.³⁷⁵⁻³⁷⁶ **Table C1** reveals that the band gaps for Sn-, Ti-, and Zr-BEA are greater than the band gaps for the metal oxides, providing evidence that the metal atoms are well dispersed in the *BEA framework.

Metal	M-BEA Band Gap (eV)	Metal Oxide Band Gap (eV)
Al	--	--
Ti	4.1	3.4
Sn	4.7	3.9
Zr	5.8	4.9

Table C1. Calculated band gaps for M-BEA and metal oxide materials. The band gaps for Al materials likely exceed the regime of wavelengths possible to measure on the spectrophotometer.

The photon energy E in electron volts (eV) was obtained from the wavelength as follows:

$$E = \frac{3 * 10^8 \frac{m}{s}}{\text{Wavelength (nm)} * \frac{1 m}{10^9 nm}} * h * \left(6.242 * 10^{18} \frac{eV}{J} \right)$$

where h equals the Planck constant. The ordinate from **Figure C1** was obtained from the ordinate of the raw spectra, the percent reflectance (% R). The Kubelka-Munk function ($F(R)$) was calculated from % R:

$$F(R) = \frac{\left(1 - \frac{\%R}{100} \right)^2}{2 * \left(\frac{\%R}{100} \right)}$$

$F(R)$ was then multiplied by the photon energy, and taking the square root of the resulting quantity yielded the ordinate for **Figure C1**.

C1.2 X-Ray Diffraction to Observe Crystallinity of M-BEA Catalysts

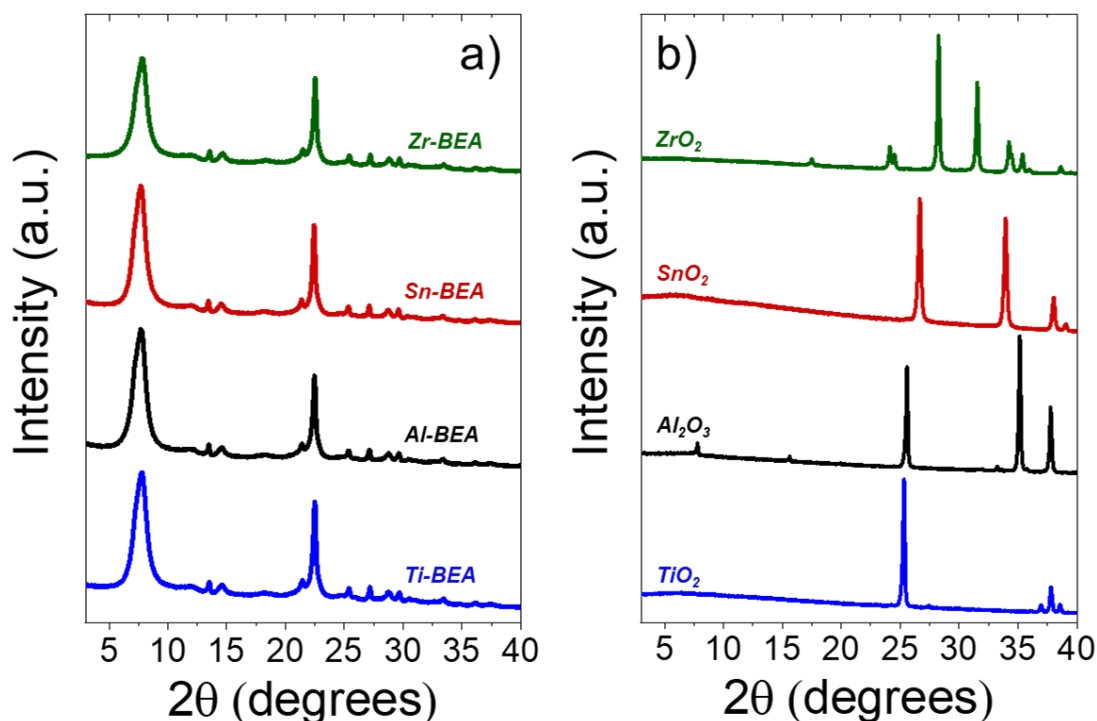


Figure C2. Powder X-ray diffractograms obtained with Cu K α radiation (0.15418 nm) under ambient conditions for a) M-BEA (Ti (blue), Al (black), Sn (red), Zr (green)), and b) the corresponding bulk metal oxides (TiO₂ (blue), γ -Al₂O₃ (black), SnO₂ (red), ZrO₂ (green)). Spectra are vertically offset for clarity.

The crystallographic features for each M-BEA are representative of the *BEA framework.¹⁵¹ As displayed in **Figure C2a**, each M-BEA material shows weak features around 25.5, 27, 29, and 33 degrees. **Figure C2b** reveals that each peak location coincides with strong features in the diffractograms of at least one of the metal oxides. However, the presence of the weak features in all M-BEA suggests that the features are characteristic of the *BEA framework rather than originating from the presence of metal oxide. Overall, the XRD patterns in **Figure C2** support that each M-BEA possesses the crystalline *BEA framework, with minimal to no detectable metal oxide crystallites present.

C1.3 Ex situ Raman Spectra of M-BEA Materials to Confirm Metal Coordination

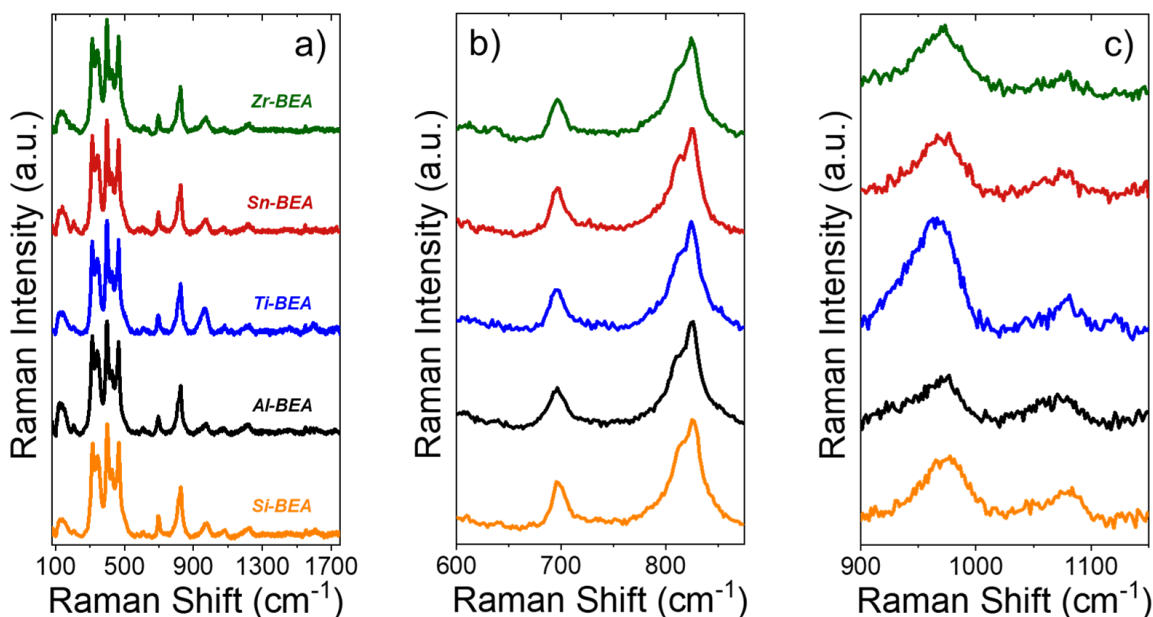


Figure C3. Ex situ Raman spectra of M-BEA (Zr (green), Sn (red), Ti (blue), Al (black), Si (orange)) at (a) the full range of Raman shifts examined, (b) magnified view of 600-875 cm^{-1} , and (c) magnified view of 900-1150 cm^{-1} . The spectra are an average of 10 scans with an exposure time of 20 s. Spectra are normalized by the maximum feature at $\sim 400 \text{ cm}^{-1}$ and are vertically offset for clarity. The spectra were taken at ambient conditions with a Raman spectrometer (Renishaw, InVia) equipped with a 532 nm laser and a power density of $\sim 2 \text{ mW } \mu\text{m}^{-2}$.

Figure C3a reveals that each M-BEA and a dealuminated *BEA material (Si-BEA) possess similar Raman spectra, with features characteristic of the *BEA framework. The intense peaks between 250 and 550 cm^{-1} represent features of the *BEA framework: the peaks at 315 and 345 cm^{-1} are assigned to six-membered rings, the peaks at 400 and 425 cm^{-1} are assigned to five-membered rings, and the peak at 465 cm^{-1} represents four-membered rings characteristic of the *BEA framework.³³³⁻³³⁴ The peak at $\sim 695 \text{ cm}^{-1}$ has previously been reported on Raman spectra of crystalline *BEA zeolites, suggesting the feature may be characteristic of the *BEA framework.³³⁵⁻³³⁶ The peak at $\sim 820 \text{ cm}^{-1}$ represents a symmetric skeletal mode of microporous silicates.³³⁷⁻³³⁸

TiO_2 shows an intense E_g vibration peak at 144 cm^{-1} ,^{254, 332, 377} a region where all M-BEA show a weak feature. The peak in this region in Ti-BEA shows a similar intensity to all other M-

BEA. Furthermore, the feature is also present in Si-BEA, which supports that the feature results from a mode inherent to the *BEA framework instead of TiO₂. Alternatively, the feature may be an artifact of the Raman filter used to suppress signal from Rayleigh scattering. **Figure C3b** zooms into a region in which Al₂O₃ (640, 751 cm⁻¹)³⁷⁸⁻³⁸⁰, SnO₂ (632, 773 cm⁻¹)³⁸¹⁻³⁸³, TiO₂ (610, 633 cm⁻¹)^{254, 332, 377}, and ZrO₂ (610, 640 cm⁻¹)³⁸⁴⁻³⁸⁶ have been reported to show Raman features. All M-BEA materials show nearly identical spectra in this region, with no notable features in the regions where the respective metal oxides contain features. These data support that all M-BEA materials do not contain oligomeric metal oxide structures.

Figure C3c shows that each M-BEA possesses features at ~960 and ~1080 cm⁻¹. The feature at ~960 cm⁻¹ has been commonly attributed to silanol defects^{150, 333, 339} and Ti atoms incorporated at tetrahedral positions in zeolite frameworks.^{150, 254, 339-343} Notably, Ti-BEA shows a more intense feature at ~960 cm⁻¹ than any other material. Silanol defects likely contribute to this peak in each material, but the presence of framework Ti atoms likely leads to the most intense feature in Ti-BEA. The peak at ~1080 cm⁻¹ plausibly originates from the *BEA framework. Ti-BEA also contains a weak feature at ~1125 cm⁻¹, where the other materials do not. This may represent an additional feature of Ti atoms within the framework; previous studies assign the ~960 and ~1125 cm⁻¹ peaks to antisymmetric and symmetric Ti-O-Si vibrations, respectively.^{254, 342-344} While Ti-O-Si features have been commonly reported in the literature, similar features have not been well reported for Al-, Sn-, or Zr-containing zeolites. Therefore, the presence of each metal in the framework cannot be confirmed with Raman spectra but is indirectly supported by the absence of metal oxide features.

The Raman spectra in **Figure C3** suggest that the Al, Ti, Sn, and Zr atoms within M-BEA predominately reside at tetrahedral framework positions within the *BEA zeolite framework.

C1.4 ATR-FTIR Spectra to Confirm Heteroatom Incorporation Into *BEA Framework

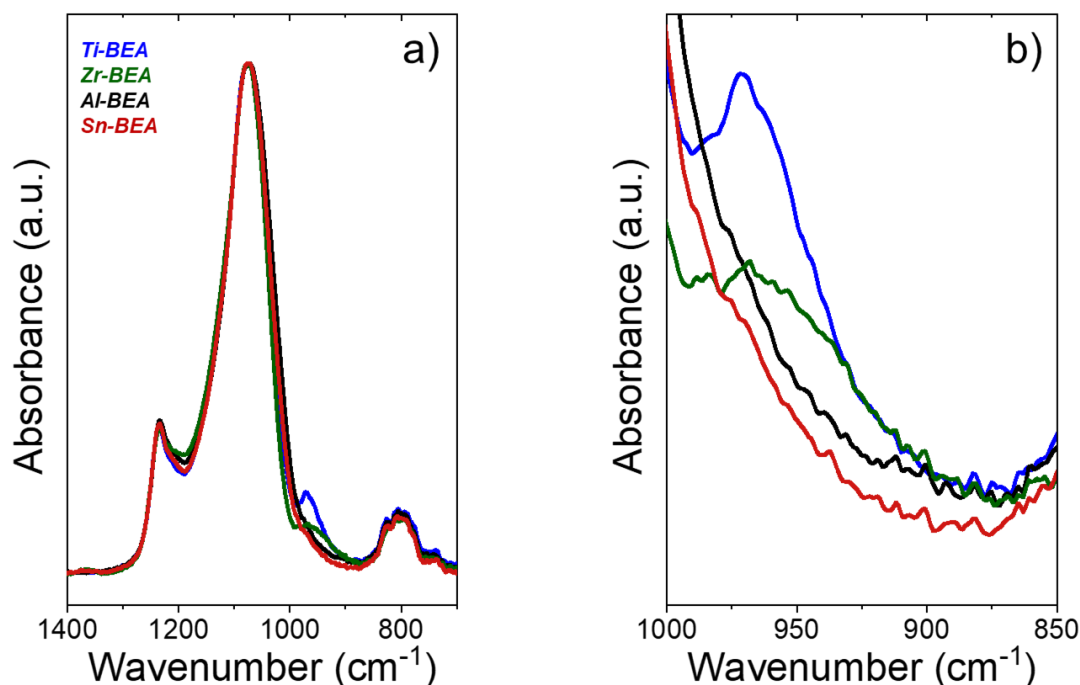


Figure C4. Infrared spectra collected at ambient conditions for M-BEA (Ti (blue), Al (black), Sn (red), Zr (green)) in a) the zeolite framework stretching region and b) zoomed in to show the Si-O-M feature at $\sim 960\text{ cm}^{-1}$. All spectra are normalized to the framework vibration at 1080 cm^{-1} .

All M-BEA possess very similar spectra in the framework stretching region (**Figure C4a**). Notably, Ti- and Zr-BEA show a weak feature at $\sim 960\text{ cm}^{-1}$, while Al- and Sn-BEA do not (**Figure C4b**). This feature has been attributed to $\nu(\text{Si-O-M})$ from framework heteroatoms (i.e., not Si or Al), most commonly for Ti-containing silicates,^{31, 134, 343, 387-389} in which the 960 cm^{-1} peak intensity has been shown to correlate with Ti concentration.³⁴³ Some publications have also claimed that the presence of the feature supports the presence of framework Zr within silicates.^{31, 390-391} A feature at 960 cm^{-1} has also been observed on Sn-containing zeolites but disappeared on a freshly calcined material.³⁹² The authors argue the feature instead arises from internal Si-OH groups formed upon interaction with water,³⁹² consistent with previous works that argued that Si-OH groups could also contribute to features at 960 cm^{-1} .³⁹³⁻³⁹⁴

Overall, **Figure C4** provides evidence that Ti atoms are located at framework positions within *BEA, in line with a wide body of previous literature on Ti-silicates. The presence of a peak at 960 cm^{-1} may also support that Zr atoms are incorporated into the framework. However, **Figure C4** and previous literature demonstrate that infrared techniques cannot be used as a reliable method to confirm the positioning of Al, Sn, or Zr atoms within zeolites.

C1.5 Infrared Spectra of M-BEA Materials to Measure Silanol Density

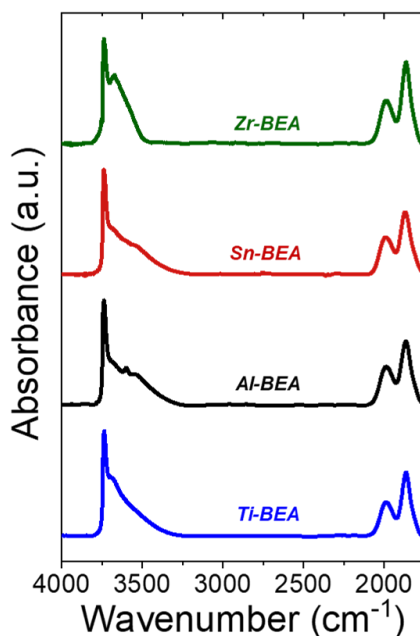


Figure C5. Infrared spectra of dehydrated samples of M-BEA (Ti (blue), Al (black), Sn (red), Zr (green)). The samples were dehydrated under flowing He (101 kPa He , $50\text{ cm}^3\text{ min}^{-1}$) at 573 K prior to measurement. Spectra are vertically offset for clarity.

The similar $\nu(\text{O-H})$ areas ($3300\text{--}3750\text{ cm}^{-1}$) for each M-BEA, with respect to the $\nu(\text{Si-O-Si})$ area ($1800\text{--}2100\text{ cm}^{-1}$), shows that each M-BEA possesses a similar density of $(\text{SiOH})_x$ groups. The Φ_{IR} values in **Table 4.1** were calculated by peak fitting on Origin 2021 (OriginLab Corporation). The peak areas for $\nu(\text{O-H})$ and $\nu(\text{Si-O-Si})$ were calculated with Gaussian fits (example shown in **Figure C6**).

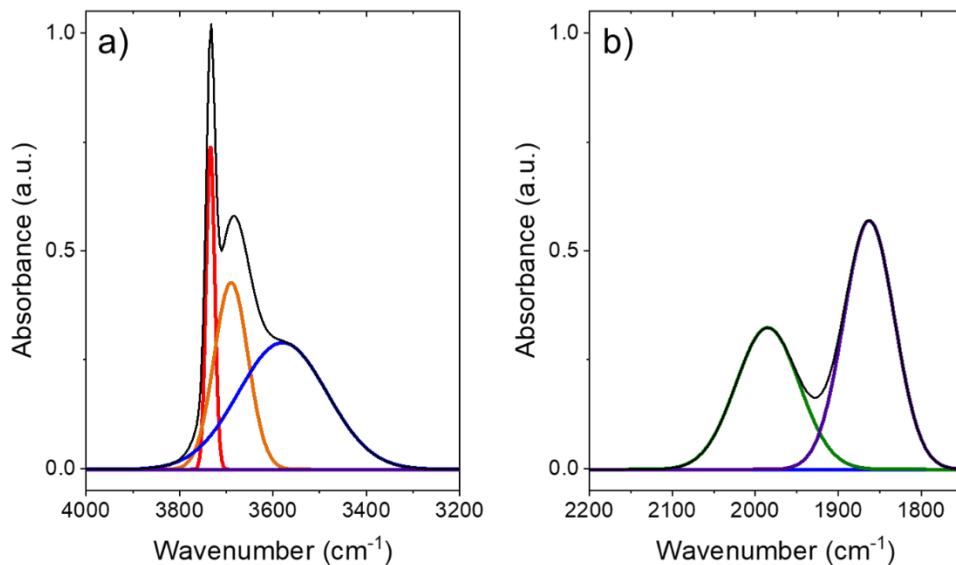


Figure C6. Fitted peaks for the (a) networked (blue, orange) Si-OH region and (b) Si-O-Si overtones at 1865 (purple) and 2000 cm^{-1} (green) for Ti-BEA.

As shown in **Equation 4.1**, the equation to calculate Φ_{IR} is:

$$\Phi_{\text{IR}} = \frac{A_{\nu(\text{O-H})}}{A_{\nu(\text{Si-O-Si})}} \quad (\text{C1})$$

The blue and orange peaks represent networked SiOH features which are summed to determine $A_{\nu(\text{O-H})}$. The green and purple peaks in the Si-O-Si region were summed together to get $A_{\nu(\text{Si-O-Si})}$. The red peak in $\nu(\text{O-H})$ represents isolated SiOH features, so these peak areas were excluded from the Φ_{IR} calculations.

C1.6 Calculation of $(\text{SiOH})_x$ (unit cell) $^{-1}$ in M-BEA

The density of $(\text{SiOH})_x$ per unit cell in M-BEA was estimated based on the initial quantity of Al present in the commercial zeolite (Si:Al = 20). A *BEA unit cell contains 64 T atoms (i.e., Si, Al, Sn, Ti, or Zr), so the initial quantity of Al per unit cell equals 3.047:

$$\text{Si} + \text{Al} = 64$$

$$20\text{Al} + \text{Al} = 64$$

$$Al = 3.047 \text{ per unit cell}$$

Assuming all Al atoms are removed in the thorough dealumination treatment for the Lewis acids, the dealumination produces $3.047 (\text{SiOH})_x (\text{unit cell})^{-1}$. The metal weight loading allows for the calculation of the Si:M ratio for each M-BEA:

$$Si + M = 64$$

$$(Si: M)M + M = 64$$

This can be used to calculate the number of metal atoms per unit cell incorporated into the formed $(\text{SiOH})_x$. The final $(\text{SiOH})_x (\text{unit cell})^{-1}$ for the Lewis acids is equal to the initial amount of Al (assumed that all Al is removed) subtracted by the added M. In contrast, the $(\text{SiOH})_x (\text{unit cell})^{-1}$ for the Brønsted acid equals the initial quantity of Al subtracted by the amount of Al removed:

$$(\text{SiOH})_{x, \text{Lewis acids}} = 3.047 - \text{added } M$$

$$(\text{SiOH})_{x, \text{Lewis acids}} = 3.047 - \text{removed } Al$$

Table C2 reports metal loadings per unit cell from ICP and calculated $(\text{SiOH})_x$ per unit cell. The calculated values predict a wider range of zeolite hydrophilicity than the Φ_{IR} calculations in **Section C1.5**. However, rate measurements as a function of metal loading (**Section C4**, *vide infra*) demonstrate a weak rate dependence on metal loading, and therefore $(\text{SiOH})_x (\text{unit cell})^{-1}$, within the range of loadings examined here. The effect of a wider range of $(\text{SiOH})_x (\text{unit cell})^{-1}$ will be explored in a future study.

Catalyst	M (unit cell) ⁻¹	(SiOH) _x (unit cell) ⁻¹
Al-BEA	0.94	2.11
Sn-BEA	0.42	2.62
Ti-BEA	0.66	2.38
Zr-BEA	0.45	2.59

Table C2. Metal loadings and $(\text{SiOH})_x$ per unit cell, determined from metal loadings from ICP and estimated Al removed by dealumination treatments.

C1.7 Infrared Spectra of C₅H₅N and CD₃CN Adsorption to Probe Active Site Character

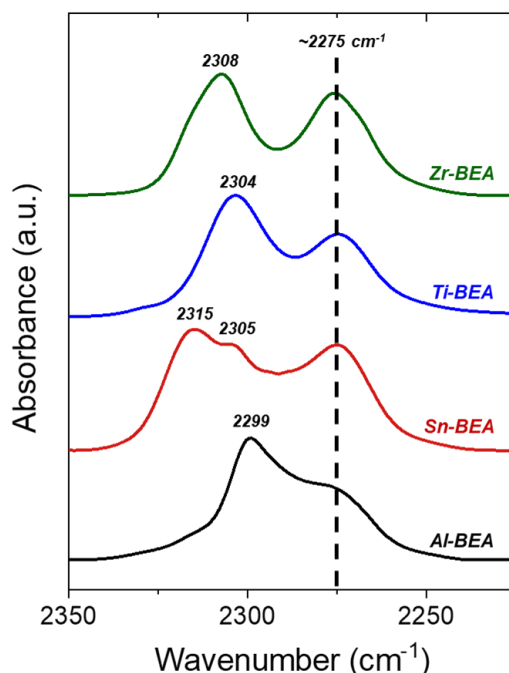


Figure C7. Infrared spectra of deuterated acetonitrile (CD₃CN) bound to Lewis acid (2302 – 2313 cm⁻¹), Brønsted acid (2299 cm⁻¹), and silanol sites (~2275 cm⁻¹) on Al-BEA (black), Sn-BEA (red), Zr-BEA (green), and Ti-BEA (blue) (0.03 kPa CD₃CN, 101 kPa Ar, 303 K). All spectra are normalized to the area of the Si-O-Si region of the zeolite from 1750-2100 cm⁻¹. Spectra are vertically offset for clarity.

After adsorption of deuterated acetonitrile (CD₃CN), all M-BEA show an absorbance feature at ~2275 cm⁻¹ from CD₃CN coordinated to Si-OH groups within *BEA.³⁹⁵⁻³⁹⁶ The feature at ~2299 cm⁻¹ for Al-BEA is consistent with previous assignments for Brønsted acidic Al sites.³⁹⁶⁻³⁹⁷ Lewis acid Al species³⁹⁶⁻³⁹⁷ show features at ~2310 and ~2325 cm⁻¹ that do not appear for Al-BEA, supporting that all Al sites within Al-BEA have Brønsted acid character. Ti-BEA and Zr-BEA possess single peaks at ~2304 and ~2308 cm⁻¹, respectively, in agreement with previous assignments of Lewis acid-bound CD₃CN within Ti-^{74, 398} and Zr-incorporated³⁹⁹⁻⁴⁰⁰ zeolites.

CD₃CN adsorption on Sn-BEA gives rise to a feature at ~2315 cm⁻¹ and a shoulder at ~2305 cm⁻¹. These regions correspond to previous assignments for open and closed Lewis acid sites within Sn-incorporated zeolites, respectively.^{137, 282, 401} While Ti- and Zr-BEA only show a single

Lewis acid feature in **Figure C7**, each material likely contains both open and closed sites. Previous work demonstrated the presence of two Lewis acid features over Zr-incorporated zeolites from the infrared spectra of CO adsorption under cryogenic conditions, which the authors attributed to the presence of both open and closed Zr sites.³⁹⁹ Evidence for open Ti sites has also been reported with EXAFS measurements,⁴⁰²⁻⁴⁰³ among other techniques. Several publications also argue that closed Lewis acid sites may open in the presence of protic molecules such as H₂O^{392, 404-405} and alcohols,⁴⁰⁶⁻⁴⁰⁷ meaning that Lewis acid sites in M-BEA could open in the presence of CH₃OH and convolute *ex situ* comparisons of site distributions. Collectively, the spectra of adsorbed CD₃CN in **Figure C7** demonstrate the presence of Lewis and Brønsted acid sites within M-BEA and confirm the existence of both open and closed Sn sites in Sn-BEA.

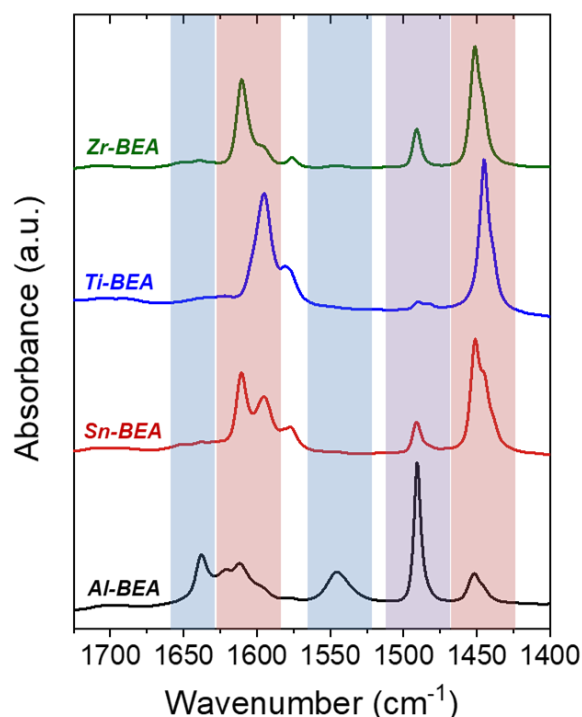


Figure C8. Infrared spectra of pyridine (C₅H₅N) bound to Lewis and Brønsted acid sites on Al-BEA (black), Sn-BEA (red), Zr-BEA (green), and Ti-BEA (blue) (1.4 kPa C₅H₅N, 101 kPa Ar, 393 K). All spectra are normalized to the area of the Si-O-Si region of the zeolite from 1750-2100 cm⁻¹. The highlighted regions on the plot represent the tabulated regions for C₅H₅N absorbance features coordinated to only Brønsted acid sites (blue), only Lewis acid sites (red), and either Lewis or Brønsted acid sites (purple). Spectra are vertically offset for clarity.

After pyridine ($\text{C}_5\text{H}_5\text{N}$) adsorption, all M-BEA materials possess features at $\sim 1490\text{ cm}^{-1}$, corresponding to $\text{C}_5\text{H}_5\text{N}$ bound to Lewis or Brønsted acid sites.⁴⁰⁸⁻⁴⁰⁹ Each material also possesses a feature at $\sim 1450\text{ cm}^{-1}$ that has been attributed to $\text{C}_5\text{H}_5\text{N}$ bound to only Lewis acid sites.^{408, 410-412} Each material also possesses features in the region of $1580\text{-}1625\text{ cm}^{-1}$, commonly attributed to Lewis-bound $\text{C}_5\text{H}_5\text{N}$.⁴¹³⁻⁴¹⁵ The presence of these features in Al-BEA may signal the presence of some fraction of extraframework Lewis acidic Al species, in contrast with the absence of Lewis acid Al features on the CD_3CN spectra. Al-BEA also shows features at ~ 1550 and $\sim 1640\text{ cm}^{-1}$, which solely originate from protonated $\text{C}_5\text{H}_5\text{N}$ at Brønsted acid sites.⁴⁰⁸⁻⁴¹² None of the Lewis acid materials contain features in this region, suggesting that all active sites within Sn-, Ti-, and Zr-BEA are Lewis acidic. Each material also shows a feature at $\sim 1575\text{ cm}^{-1}$ of varying intensity, which has been attributed to physisorbed $\text{C}_5\text{H}_5\text{N}$.^{408, 412, 416}

Notably, Sn-BEA shows two distinct features between 1580 to 1625 cm^{-1} (~ 1595 and ~ 1610) and a shoulder on the feature at $\sim 1450\text{ cm}^{-1}$, centered at $\sim 1445\text{ cm}^{-1}$. The peak at $\sim 1610\text{ cm}^{-1}$ has previously been assigned to $\text{C}_5\text{H}_5\text{N}$ coordinated to Lewis acidic Sn sites.^{137, 417-418} However, the peak at $\sim 1595\text{ cm}^{-1}$ and shoulder at $\sim 1445\text{ cm}^{-1}$ reside in positions previously assigned to $\text{C}_5\text{H}_5\text{N}$ hydrogen-bonded to $-\text{OH}$ groups.^{409, 411-412, 414} These may arise from $\text{C}_5\text{H}_5\text{N}$ coordinated to the $-\text{OH}$ group from Sn-OH or the adjacent Si-OH in open sites within Sn-BEA. Zr-BEA also shows a weak feature at $\sim 1595\text{ cm}^{-1}$, which may arise from $\text{C}_5\text{H}_5\text{N}$ coordinated at open sites in Zr-BEA. However, a feature at $\sim 1595\text{ cm}^{-1}$ has also been attributed to gas-phase $\text{C}_5\text{H}_5\text{N}$, which convolutes the assignment of that feature for Sn- and Zr-BEA. Overall, the spectra of adsorbed $\text{C}_5\text{H}_5\text{N}$ in **Figure C8** provide insight into the distribution of active sites within each M-BEA.

C2. Calculation of Epoxide and Product Sensitivity Factors

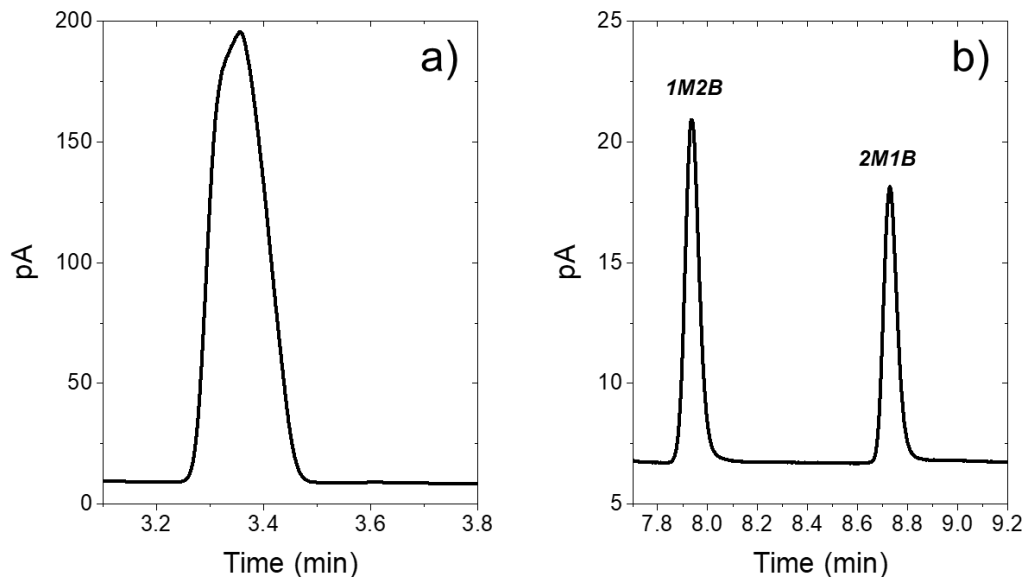


Figure C9. Raw GC chromatograms zoomed in to show peaks corresponding to (a) C_4H_8O , and (b) 1-methoxy-2-butanol and 2-methoxy-1-butanol formed by reaction of C_4H_8O with CH_3OH over Zr-BEA for 1 h (0.005 M C_4H_8O , 6 M CH_3OH , CH_3CN , 308 K).

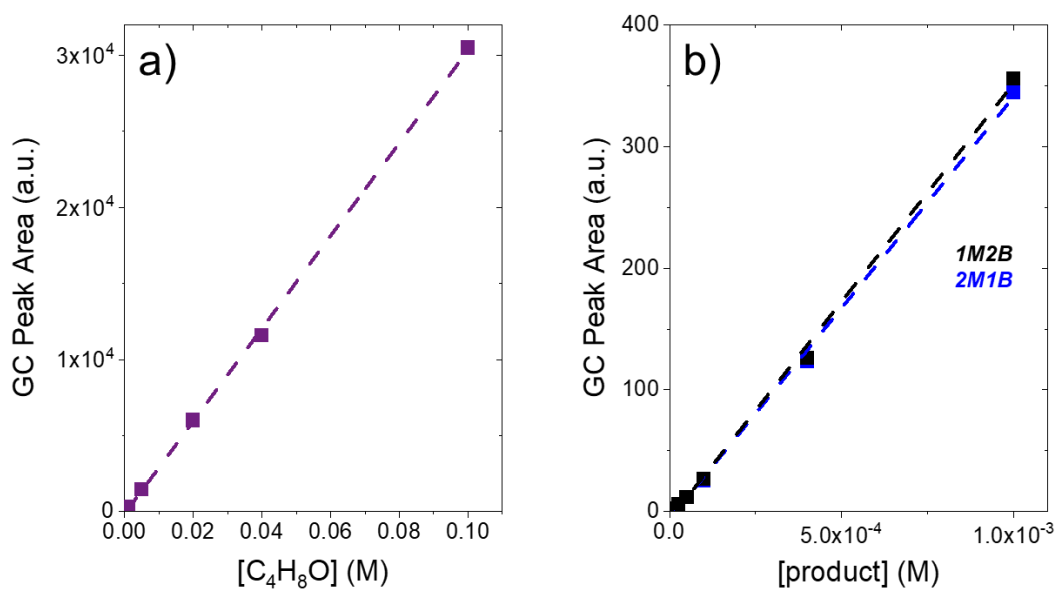


Figure C10. Integrated GC peak areas as a function of concentration for (a) C_4H_8O , and (b) 1-methoxy-2-butanol (black) and 2-methoxy-1-butanol (blue) in CH_3CN .

Figure C9 demonstrates the high signal-to-noise ratio of the epoxide and product peaks from the GC chromatograms, as well as the peak separation between the ring-opening products. GC chromatograms were collected as a function of concentrations (**Figure C10**) to determine the sensitivity factors of the epoxide and products using the as-purchased chemicals (see **Sections 4.2.3** and **4.2.4** for sources and purities). **Table C3** reports the sensitivity factors, which equal the slope of the calibration curve fit lines in **Figure C10**.

Compound	Sensitivity Factor (peak area M ⁻¹)
C ₄ H ₈ O	302810
1M2B	349380
2M1B	338550

Table C3. Sensitivity factors determined from calibration curves in **Figure C11**.

During reactions, the concentration of the products was calculated with the integrated peak areas and measured sensitivity factors:

$$[product] = \frac{GC \text{ Peak Area}}{Sensitivity \text{ Factor}} \quad (C2)$$

C3. Hot Filtrations and Madon-Boudart Criterion Tests to Identify Active Centers for Ring-Opening

Figure C11 displays the results of the hot filtration tests for all M-BEA. For all M-BEA, product formation ceases after separating the solution from the catalyst (hollow points). This result provides evidence that metal atoms do not leach from the *BEA framework, and the active sites remain within the framework during catalysis.

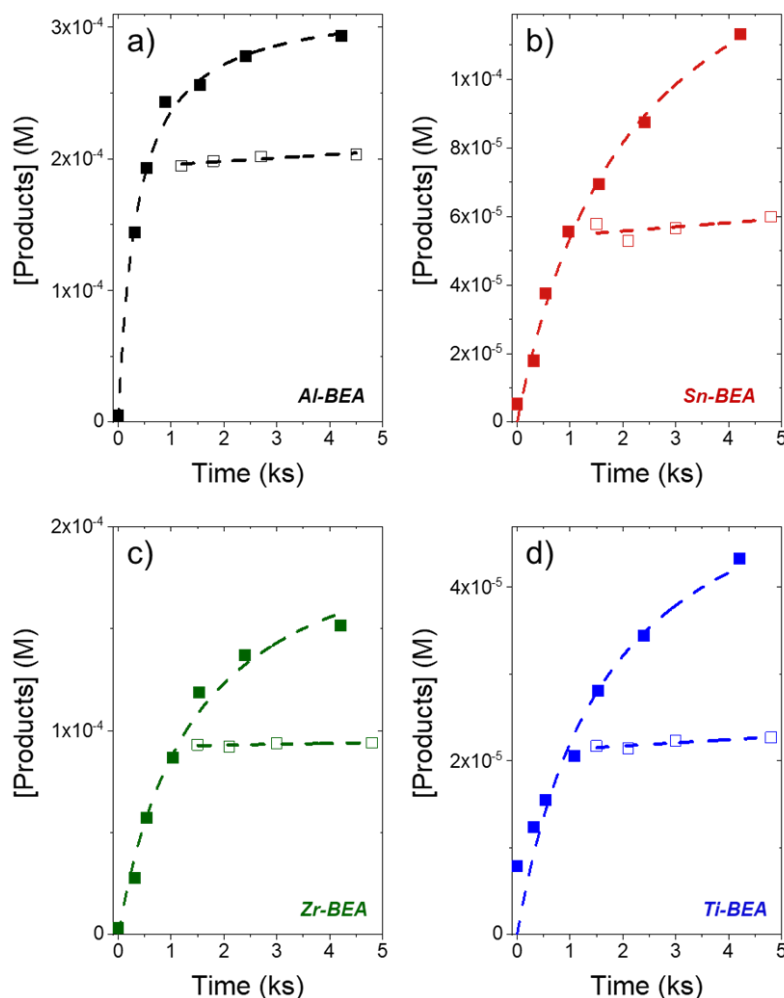


Figure C11. Measured total product concentrations (sum of [1M2B] and [2M1B]) as functions of time during hot filtration tests (0.005 M C_4H_8O , 6 M CH_3OH , CH_3CN solvent, 308 K) over (a) Al-BEA (black), (b) Sn-BEA (red), (c) Zr-BEA (green), and (d) Ti-BEA (blue). The hollow points represent epoxide concentrations from aliquots that were separated from the catalyst after ~10-15 min, while solid points indicate concentrations from aliquots that were kept in contact with the catalyst over the course of the reaction.

Figure C12 presents turnover rates as a function of metal loading for each M-BEA. Rates depend negligibly on metal loading within the range of loadings examined for all materials, ruling out contributions from intrapore mass transfer to turnover rate measurements. When normalized by residual Al content from ICP, turnover rates for the dealuminated *BEA material used in the synthesis of Sn-, Zr-, and Ti-BEA are more than seven times lower than all M-BEA materials, ruling out contributions from residual Al to measured rates over the Lewis acids.

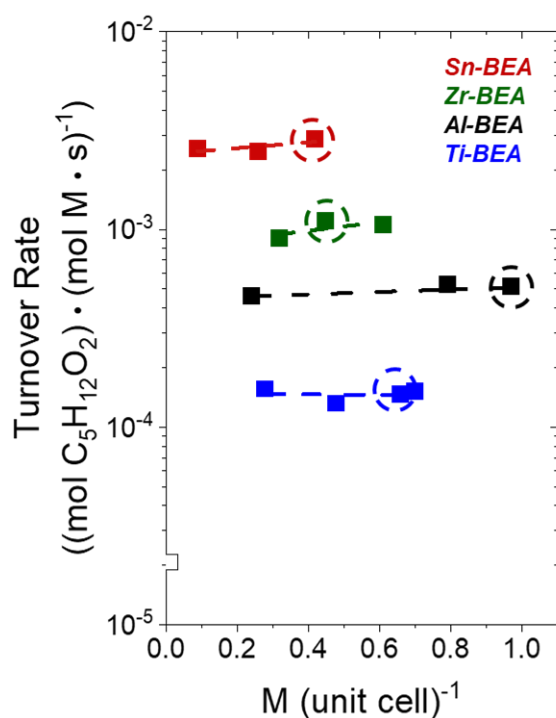


Figure C12. Total product formation rates from C₄H₈O ring-opening with CH₃OH (0.02 M C₄H₈O, 0.4 M CH₃OH, CH₃CN solvent, 308 K) as a function of active metal loading over Al-BEA (black, solid point), Sn-BEA (red), Zr-BEA (green), Ti-BEA (blue), and a dealuminated *BEA (black, hollow point, Si:Al ~ 3900 from ICP). The circled points signify the catalyst used for this study.

C4. Site Counting with 1,2-Diphenyl-1,2-Ethylenediamine Titrations

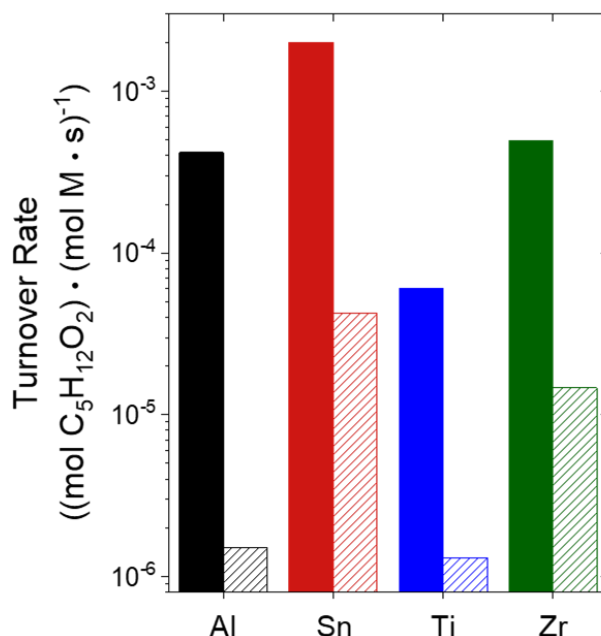


Figure C13. Total product formation rates from C_4H_8O ring-opening with CH_3OH (0.005 M C_4H_8O , 0.4 M CH_3OH , CH_3CN solvent, 308 K) over Al-BEA (black), Sn-BEA (red), Zr-BEA (green), and Ti-BEA (blue) in the absence (solid bars) and presence (patterned bars) of 1,2-diphenyl-1,2-ethylenediamine (DPED). The ratio of DPED to M atoms was 2:1 for each M-BEA.

Recently, phosphonic acids^{30, 32, 419-420} have been employed as titrants during liquid phase reactions to count or distinguish acid sites in Lewis acid materials. Amines have been used to probe both Lewis acid^{214, 421} and Brønsted acid sites⁴²²⁻⁴²³ for similar purposes. Therefore, we selected 1,2-diphenyl-1,2-ethylenediamine (DPED) as a titrant that could poison active sites in both Lewis and Brønsted acidic M-BEA. Upon adding an excess of DPED (2:1 to active site quantity), rates decrease by more than 97% or greater for all M-BEA. This result indicates that DPED binds to both Lewis and Brønsted sites and suppresses the ring-opening of C_4H_8O with CH_3OH .

The change in concentration of DPED during the reactions in **Figure C13** was used to estimate the number of active sites in each material. A GC calibration curve was developed for DPED, from which the moles of DPED in the liquid phase before and at the completion of the reaction was determined with GC peak areas. A separate DPED adsorption measurement was

carried out in a dealuminated *BEA catalyst (Si-BEA) to estimate contributions from DPED bound to (SiOH)_x and pore walls (i.e., Si-O-Si). The difference in DPED adsorbed between Si-BEA and the M-BEA materials was taken as a measure of the amount of DPED adsorbed to the catalytically active sites in M-BEA. From there, an active site density was calculated with the assumption that each active site binds one DPED molecule. **Table C4** shows the results of this analysis, in which an active metal percentage was determined by taking the ratio of the DPED-measured site density to the theoretical site density from ICP. The calculated percentages of active metal range from 92 % to 115 %. Variations in the quantity of DPED adsorption to (SiOH)_x and Si-O-Si between experiments may introduce errors in the calculated percentages, along with competitive adsorption between DPED and the ring-opening reactants over M-BEA that was not present in the Si-BEA measurement performed in the absence of the reactants. Nevertheless, these measurements provide evidence that the large majority of metal atoms within M-BEA are active for ring-opening catalysis.

Catalyst	DPED adsorbed (mol) ^a	Theoretical Active Site Density (mol g ⁻¹) ^b	Measured Active Site Density (mol g ⁻¹) ^c	Measured Active Metal % ^d
Al-BEA	5.44 x 10 ⁻⁵	2.37 x 10 ⁻⁴	2.72 x 10 ⁻⁴	115
Sn-BEA	2.56 x 10 ⁻⁵	1.04 x 10 ⁻⁴	9.59 x 10 ⁻⁵	92
Ti-BEA	3.58 x 10 ⁻⁵	1.67 x 10 ⁻⁴	1.55 x 10 ⁻⁴	93
Zr-BEA	2.86 x 10 ⁻⁵	1.13 x 10 ⁻⁴	1.10 x 10 ⁻⁴	97
Si-BEA	1.09 x 10 ⁻⁵	--	--	--

Table C4. ^aMeasured from the difference in DPED peak area on GC before and after contact with M-BEA. ^bCalculated from metal weight loadings from ICP. ^cCalculated from the amount of DPED assumed to bind to active sites rather than (SiOH)_x or Si-O-Si. ^dRatio of measured to theoretical active site density.

C5. Measurements of Intrapore Solvent Composition

The liquid-phase concentrations of mixtures of CH₃OH and CH₃CN were quantified by GC before and after contact with M-BEA to determine the intrapore solvent composition. The ratio of the GC peak areas for each component was calculated for each sample before ($A_{CH_3OH:CH_3CN,initial}$) and after ($A_{CH_3OH:CH_3CN,final}$) adding the catalyst to the mixture. Then, the known initial mole fraction of CH₃OH ($x_{CH_3OH,bulk,initial}$) was used to calculate the final bulk solvent fractions:

$$x_{CH_3OH,bulk,final} = x_{CH_3OH,bulk,initial} * \frac{A_{CH_3OH:CH_3CN,final}}{A_{CH_3OH:CH_3CN,initial}} \quad (C3)$$

$$x_{CH_3CN,bulk,final} = 1 - x_{CH_3OH,bulk,final} \quad (C4)$$

The fraction of the initial solvent volume remaining in the bulk solvent after adsorption ($x_{bulk,final}$) was then calculated by estimating the fraction of solvent adsorbed from the bulk solvent ($V_{solvent,ads}$):

$$V_{solvent,ads} = m_{zeolite} * V_{pore,*BEA} \quad (C5)$$

$$x_{bulk,final} = 1 - \left(\frac{V_{solvent,ads}}{V_{solvent,total}} \right) \quad (C6)$$

where $m_{zeolite}$ is the mass of M-BEA added to the solvent and $V_{pore,*BEA}$ is the pore volume of *BEA, measured for a Ti-BEA material in a previous study by Ar physisorption²¹¹ and assumed to be identical for all M-BEA here. From there, the intrapore molar ratio ($\frac{n_{CH_3OH,pore}}{n_{CH_3CN,pore}}$) and CH₃OH fraction ($x_{CH_3OH,pore}$) can be calculated:

$$\frac{n_{CH_3OH,pore}}{n_{CH_3CN,pore}} = \frac{x_{CH_3OH,bulk,initial} - (x_{bulk,final} * x_{CH_3OH,bulk,final})}{x_{CH_3CN,bulk,initial} - (x_{bulk,final} * x_{CH_3CN,bulk,final})} \quad (C7)$$

$$x_{CH_3OH,pore} = \frac{\frac{n_{CH_3OH,pore}}{n_{CH_3CN,pore}}}{1 + \frac{n_{CH_3OH,pore}}{n_{CH_3CN,pore}}} \quad (C8)$$

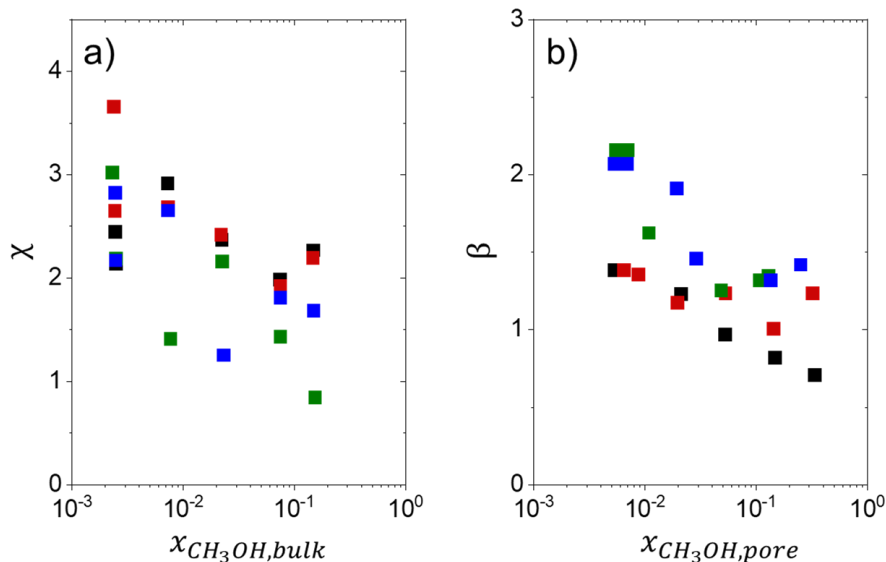


Figure C14. a) χ values as a function of $x_{CH_3OH,bulk}$ at 308 K in a mixture of CH_3OH and CH_3CN and b) β values for C_4H_8O ring-opening from **Figure 4.7** as a function of $x_{CH_3OH,pore}$ over Sn- (red), Zr- (green), Al- (black), and Ti-BEA (blue).

Figure C14a reports $x_{CH_3OH,bulk}$ as a function of the ratio of $x_{CH_3OH,pore}$ to $x_{CH_3OH,bulk}$, defined as χ :

$$\chi = \frac{x_{CH_3OH,pore}}{x_{CH_3OH,bulk}} \quad (C9)$$

χ values decrease with increasing $x_{CH_3OH,bulk}$ and approach values of 1, indicating that the solvent structure becomes more similar between the bulk and intrapore environments at higher $[CH_3OH]$. The larger χ values at lower $x_{CH_3OH,bulk}$ values signify a more non-ideal intrapore solvent environment, which may contribute to larger differences in β values between metals at low $[CH_3OH]$ (**Figure 4.7**). More generally, **Figure C14b** demonstrates that β values decrease at greater $x_{CH_3OH,pore}$ for all M-BEA, providing evidence that the solvent structure surrounding active sites may strongly influence regioselectivities for C_4H_8O ring-opening through changes in $G_{2M1B}^{\ddagger,\varepsilon}$ and $G_{1M2B}^{\ddagger,\varepsilon}$. Of note, this result demonstrates that the choice of active metal not only influences G^0 values of reactive species through covalent interactions, but also can indirectly affect G^ε values by influencing the surrounding solvent structure. The choice of active metal leads to a span of β values

even at nearly identical $x_{\text{CH}_3\text{OH},\text{pore}}$, showing that differences in G^0 stemming from the properties of the active site contribute to differences in β .

C6. Formation Rates of Individual Products of $\text{C}_4\text{H}_8\text{O}$ Ring-Opening with CH_3OH

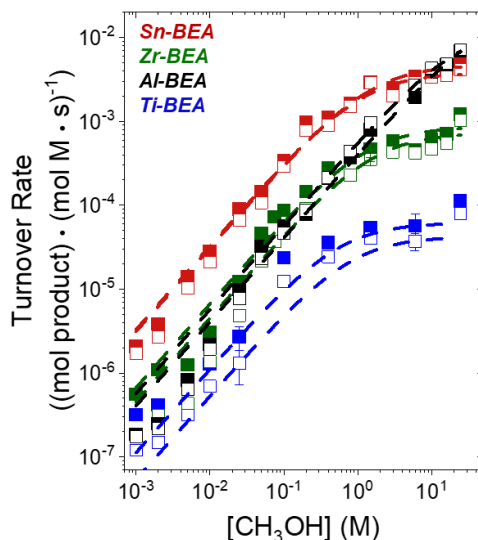


Figure C15. Formation rates of 1-methoxy-2-butanol (solid points) and 2-methoxy-1-butanol (hollow points) products from $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH as functions of CH_3OH concentration over Sn- (red), Zr- (green), Al- (black), and Ti-BEA (blue) (0.005 M $\text{C}_4\text{H}_8\text{O}$, CH_3CN solvent, 308 K).

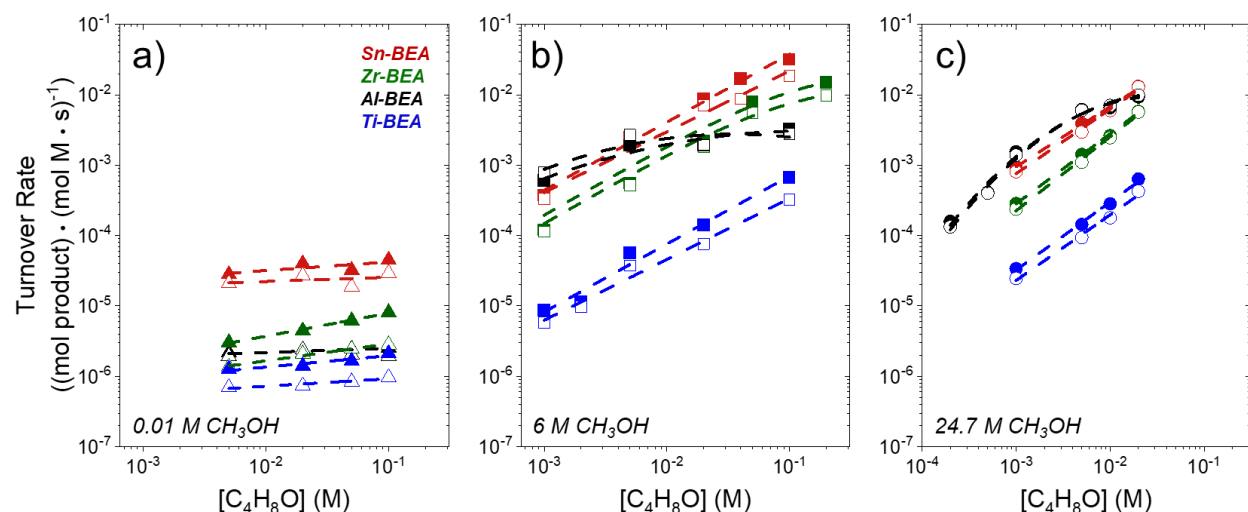


Figure C16. Formation rates of 1-methoxy-2-butanol (solid points) and 2-methoxy-1-butanol (hollow points) products from $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH as functions of $\text{C}_4\text{H}_8\text{O}$ concentration at a) 0.01 M CH_3OH , b) 6 M CH_3OH , or c) neat (24.7 M) CH_3OH (CH_3CN solvent, 308 K) over Sn- (red), Zr- (green), Al- (black), and Ti-BEA (blue).

Figures C15 and C16 present the formation rates of the individual products from C_4H_8O ring-opening over M-BEA (total ring-opening rates shown in **Figures 4.1 and 4.2**). In all M-BEA and solvent composition combinations, both products show nearly identical formation rate dependences on $[C_4H_8O]$ and $[CH_3OH]$. The similar rate dependences provide compelling evidence that each product forms from identical reaction pathways and reactive intermediates, and differences in transition state stabilities between the products drive changes in regioselectivities.

The reaction orders for the individual products (and for overall product formation in **Figures 4.1 and 4.2**) were quantified by taking the slope of a linear fit between the turnover rate and concentration. The product formation rate is proportional to the reactant concentrations raised to the reaction orders, shown as “a” and “b” here:

$$r_{RO} \sim [C_4H_8O]^a [CH_3OH]^b \quad (C10)$$

Taking the natural log of this expression converts the equation into slope-intercept form:

$$\ln r_{RO} \sim (a * \ln [C_4H_8O]) + (b * \ln [CH_3OH]) \quad (C11)$$

When we hold $[C_4H_8O]$ constant in **Figure 4.1**, we equate the reaction order of CH_3OH (“b”) to the slope of the linear fits at low $[CH_3OH]$ for the Lewis acids and at all $[CH_3OH]$ for the Brønsted acid, as demonstrated in **Figure C17**. The slopes for the metals in this example range from 0.94 to 1.13, which agrees within the uncertainty to a linear dependence of rates on $[CH_3OH]$. We apply similar linear fits to calculate the reaction orders in the plots in **Figures 4.2, C15, and C16** as well. All claims of linear rate dependences in these figures stem from the calculation of similar slopes as shown in **Figure C17**, within an error of uncertainty for a linear correlation.

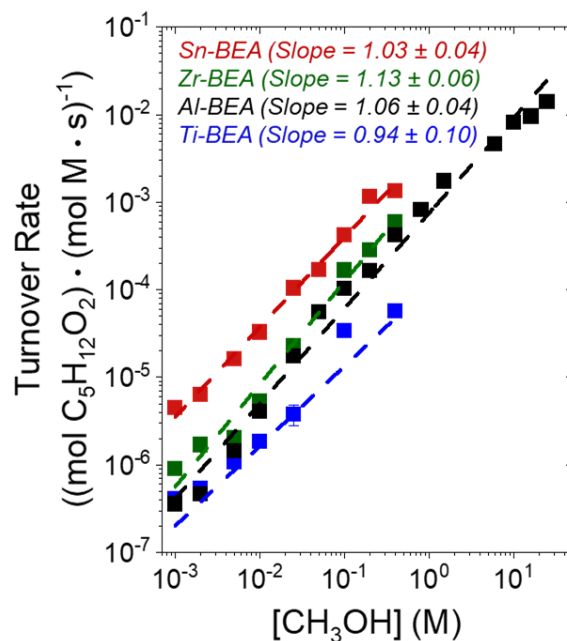


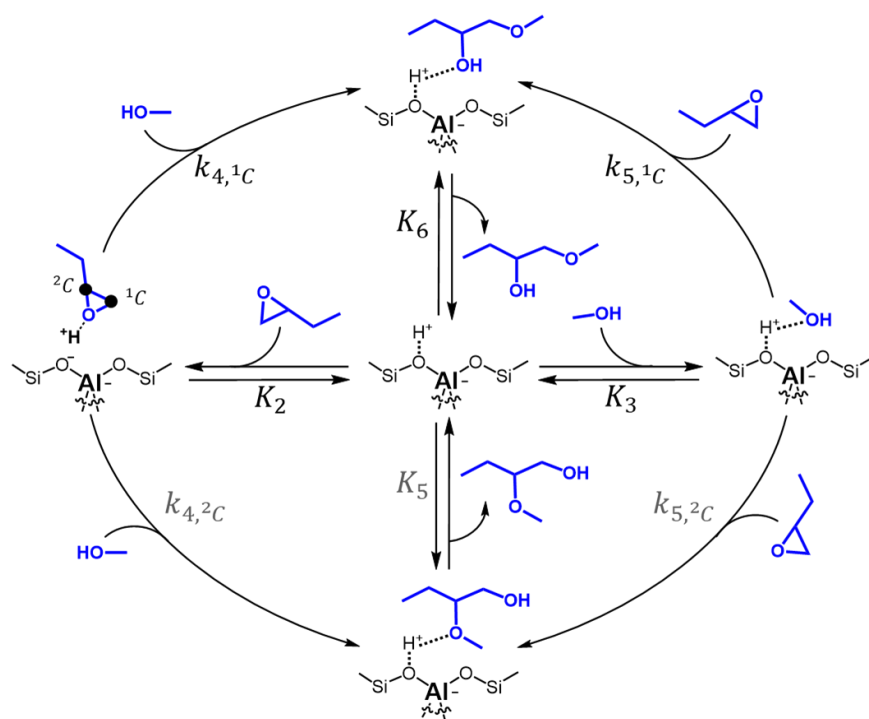
Figure C17. Turnover rates for C₄H₈O ring-opening with CH₃OH as functions of [CH₃OH], within the [CH₃OH] regime in which rates are argued to correlate linearly with [CH₃OH], over Al- (black), Sn- (red), Zr- (green), and Ti-BEA (blue) (0.005 M C₄H₈O, CH₃CN solvent, 308 K).

Catalyst	[CH ₃ OH]:[C ₄ H ₈ O] < 100		[CH ₃ OH]:[C ₄ H ₈ O] > 500	
	TE	TA	TE	TA
Al-BEA	[CH ₃ OH] ^{1.11} [C ₄ H ₈ O] ^{0.05}	[CH ₃ OH] ^{1.07} [C ₄ H ₈ O] ^{0.01}	[CH ₃ OH] ^{0.79} [C ₄ H ₈ O] ^{0.23}	[CH ₃ OH] ^{0.72} [C ₄ H ₈ O] ^{0.28}
Sn-BEA	[CH ₃ OH] ^{0.99} [C ₄ H ₈ O] ^{0.12}	[CH ₃ OH] ^{1.06} [C ₄ H ₈ O] ^{0.06}	[CH ₃ OH] ^{0.17} [C ₄ H ₈ O] ^{1.03}	[CH ₃ OH] ^{0.13} [C ₄ H ₈ O] ^{0.94}
Zr-BEA	[CH ₃ OH] ^{1.02} [C ₄ H ₈ O] ^{0.22}	[CH ₃ OH] ^{1.17} [C ₄ H ₈ O] ^{0.14}	[CH ₃ OH] ^{0.13} [C ₄ H ₈ O] ^{1.05}	[CH ₃ OH] ^{0.16} [C ₄ H ₈ O] ^{0.98}
Ti-BEA	[CH ₃ OH] ^{0.93} [C ₄ H ₈ O] ^{0.16}	[CH ₃ OH] ^{1.03} [C ₄ H ₈ O] ^{0.11}	[CH ₃ OH] ^{0.19} [C ₄ H ₈ O] ^{0.97}	[CH ₃ OH] ^{0.16} [C ₄ H ₈ O] ^{0.91}

Table C5. Formation Rate Orders of TE and TA from **Figures C15** and **C16**.

Table C5 reports the formation rate orders for the TE and TA products in regimes of high and low $[\text{CH}_3\text{OH}]:[\text{C}_4\text{H}_8\text{O}]$. While regioselectivities do vary with reactant concentrations (**Figure 4.7**), the product formation rate orders never differ by more than 0.15 for a given catalyst in each regime. The similarity in rate orders suggests that the products form by similar reaction mechanisms and regioselectivity differences with reactant concentrations instead originate from changes in the free energy of the transition states to form the products.

C7. Derivation of Rate Expression for $\text{C}_4\text{H}_8\text{O}$ Ring-Opening with CH_3OH over M-BEA



Scheme C1. Proposed catalytic cycle for $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH in CH_3CN solvent over Brønsted acidic M-BEA zeolites. All adsorption steps are currently assumed as reversible. Steps to form 1M2B and 2M1B are denoted as ^1C or ^2C , to signify nucleophilic attack on the primary and secondary carbons in the epoxide ring, respectively. For brevity, we do not show the reversible adsorption of CH_3CN molecules (step 1) in this cycle.

Scheme 4.2 and **Scheme C1** above present proposed catalytic cycles for the ring-opening of $\text{C}_4\text{H}_8\text{O}$ with CH_3OH over Lewis and Brønsted acidic M-BEA materials, respectively. Each mechanism begins with the adsorption of CH_3CN (step 1), $\text{C}_4\text{H}_8\text{O}$ (step 2), or CH_3OH (step 3).

The 1M2B or 2M1B products may then form through one of two plausible kinetically relevant steps (4 and 5), where a liquid-phase CH₃OH or C₄H₈O molecule may then react with adsorbed C₄H₈O or CH₃OH, respectively. The products then desorb in a reversible step to complete the cycle, with steps 6 and 7 accounting for the individual products that can form. Epoxide ring-opening rates for the two possible reaction paths can be modeled with **Equation 4.2**:

$$r_{RO} = r_4 + r_5 = k_4[C_4H_8O^*][CH_3OH] + k_5[C_4H_8O][CH_3OH^*] \quad (C12)$$

where k_4 and k_5 are the sum of the rate constants to form each product in steps 4 ($k_{4,1C}$, $k_{4,2C}$) and 5 ($k_{5,1C}$, $k_{5,2C}$) in **Scheme C1**, and $[C_4H_8O^*]$ and $[CH_3OH^*]$ represent the number of bound intermediates from each reactant. We apply the pseudo-state hypothesis to the respective bound intermediates, which gives:

$$r_{RO,C_4H_8O^*} = \frac{k_2 k_4 [C_4H_8O][CH_3OH][*]}{k_{-2} + k_4 [CH_3OH]} + \frac{k_3 k_5 [C_4H_8O][CH_3OH][*]}{k_{-3} + k_5 [C_4H_8O]} \quad (C13)$$

The total number of active sites in each M-BEA ([L]) can be written as:

$$[L] = [*] + [CH_3CN^*] + [CH_3OH^*] + [C_4H_8O^*] + [1M2B^*] + [2M1B^*] \quad (C14)$$

Where $[*]$ is the number of unoccupied active sites and the other terms represent the number of adsorbed solvent, reactant, and product molecules. Substituting in terms for the solvent, product, and reactant concentrations, rate constants, and equilibrium constants yields:

$$[L] = [*] \left(1 + K_1 [CH_3CN] + \frac{k_2 [C_4H_8O]}{k_{-2} + k_4 [CH_3OH]} + \frac{k_3 [CH_3OH]}{k_{-3} + k_5 [C_4H_8O]} + \frac{k_4 [CH_3OH] + k_5 [C_4H_8O] + k_{-6} [1M2B]}{k_6} + \frac{k_4 [CH_3OH] + k_5 [C_4H_8O] + k_{-7} [2M1B]}{k_7} \right) \quad (C15)$$

Using **Equation C15** to substitute an expression for $[*]$ in **Equation C13** yields a full rate expression (**Equation 4.3**):

$$\frac{r_{RO}}{[L]} = \frac{\frac{k_2 k_4 [C_4H_8O][CH_3OH]}{k_{-2} + k_4 [CH_3OH]} + \frac{k_3 k_5 [C_4H_8O][CH_3OH]}{k_{-3} + k_5 [C_4H_8O]}}{1 + K_1 [CH_3CN] + \frac{k_2 [C_4H_8O]}{k_{-2} + k_4 [CH_3OH]} + \frac{k_3 [CH_3OH]}{k_{-3} + k_5 [C_4H_8O]} + \frac{k_4 [CH_3OH] + k_5 [C_4H_8O] + k_{-6} [1M2B]}{k_6} + \frac{k_4 [CH_3OH] + k_5 [C_4H_8O] + k_{-7} [2M1B]}{k_7}} \quad (C16)$$

Rates depend linearly on $[CH_3OH]$ and weakly on $[C_4H_8O]$ at ratios of $[CH_3OH]$ to $[C_4H_8O]$ less than 40 over each M-BEA, implicating active sites saturated with a C_4H_8O -derived species. In this case, the $[C_4H_8O^*]$ term dominates in the denominator of **Equation C16**, allowing all other terms to be canceled out and simplifying the equation to **Equation 4.4**:

$$\frac{r_{RO}}{[L]} = \frac{k_2 k_4 [CH_3OH] (k_{-3} + k_5 [C_4H_8O]) + k_3 k_5 [CH_3OH] (k_{-2} + k_4 [CH_3OH])}{k_2 (k_{-3} + k_5 [C_4H_8O])} \quad (C17)$$

At sufficiently high ratios of $[CH_3OH]$ to $[C_4H_8O]$ (> 500 for Lewis acids and > 5000 for Al-BEA), ring-opening rates shift to a weak dependence on $[CH_3OH]$ and linear dependence on $[C_4H_8O]$. The $[CH_3OH^*]$ term now dominates in the denominator of **Equation C16**, such that the equations condense to **Equation 4.6**:

$$\frac{r_{RO}}{[L]} = \frac{k_2 k_4 [C_4H_8O] (k_{-3} + k_2 k_4 k_5 [C_4H_8O]) + k_3 k_5 [C_4H_8O] (k_{-2} + k_4 [CH_3OH])}{k_3 (k_{-2} + k_4 [CH_3OH])} \quad (C18)$$

The assumptions outlined in **Section 4.3.1** allow us to simplify these expressions to simple forms under a C_4H_8O - (**Equation C19**) and CH_3OH -derived MARI (**Equation C20**) that match **Equations 4.5** and **4.7**:

$$\frac{r_{RO}}{[L]} = k_4 [CH_3OH] \quad (C19)$$

$$\frac{r_{RO}}{[L]} = k_5 [C_4H_8O] \quad (C20)$$

The rate expressions in **Equations C19** and **C20** account for all kinetic regimes observed as functions of reactant concentrations in **Figures 4.1** and **4.2**.

C8. Adsorption Enthalpies of C₄H₈O and CH₃OH to M-BEA in CH₃CN

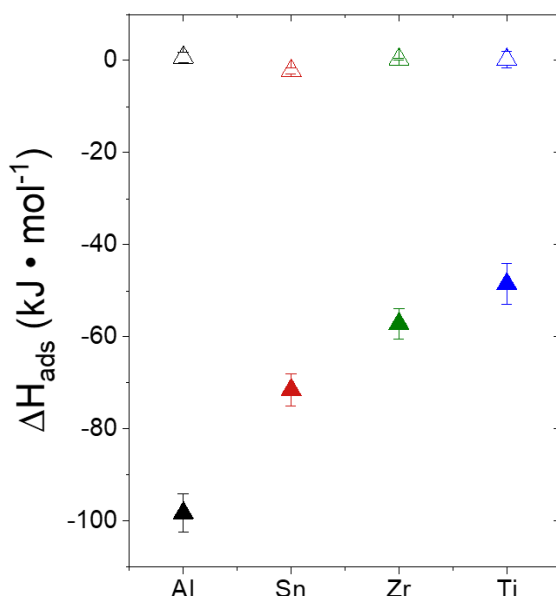


Figure C18. Adsorption enthalpies of C₄H₈O (solid points, 0.005 M C₄H₈O, 308 K) and CH₃OH (hollow points, 0.1 M CH₃OH, 308 K) as a function of active metal in CH₃CN over Sn- (red), Zr- (green), Ti- (blue), and Al-BEA (black).

The adsorption enthalpies of C₄H₈O and CH₃OH were obtained with isothermal titration calorimetry (see **Section C9** for thermograms). For all M-BEA, C₄H₈O shows an adsorption enthalpy at least 50 kJ mol⁻¹ more exothermic than CH₃OH. These values suggest that C₄H₈O adsorbs more readily to the active sites in M-BEA and likely explains why CH₃OH only saturates active sites under large excesses of CH₃OH ([CH₃OH]:[C₄H₈O] > 500, see **Section 4.3.1**).

C9. Activation Enthalpy and Entropy Calculations and Supplemental Data

$\Delta H^\ddagger$ and $\Delta S^\ddagger$ values to form each ring-opening product were calculated using van't Hoff analysis. Applying transition state theory and substituting an expression for the apparent free energy to **Equations C19** and **C20** yields alternate rate expressions for ring-opening through either the bound C₄H₈O path (C₄H₈O MARI) or bound CH₃OH route (CH₃OH MARI):

$$\frac{r_x}{[L]} = \frac{k_B T}{h} \cdot \exp\left(-\frac{\Delta G_x^\ddagger}{RT}\right) \cdot [CH_3OH] \quad (C21)$$

$$\frac{r_x}{[L]} = \frac{k_B T}{h} \cdot \exp\left(-\frac{\Delta G_x^\ddagger}{RT}\right) \cdot [C_4H_8O] \quad (C22)$$

Where x represents the two possible products, 1M2B and 2M1B. Rearranging and substituting in the apparent activation enthalpy and entropy:

$$\ln\left(\frac{r_x}{[L]} \frac{h}{k_B T [CH_3OH]}\right) = \frac{1}{T} \left(\frac{-\Delta H_x^\ddagger}{R}\right) + \frac{\Delta S_x^\ddagger}{R} \quad (C23)$$

$$\ln\left(\frac{r_x}{[L]} \frac{h}{k_B T [C_4H_8O]}\right) = \frac{1}{T} \left(\frac{-\Delta H_x^\ddagger}{R}\right) + \frac{\Delta S_x^\ddagger}{R} \quad (C24)$$

The natural log term on the left side of **Equations C23** and **C24** was plotted against the inverse temperature for each product. A line was fit to this data (**Figure C19**), where the slope of this line equaled the negative of the apparent activation enthalpy divided by the ideal gas constant, and the y-intercept equaled the apparent activation entropy divided by the ideal gas constant (**Table C6**).

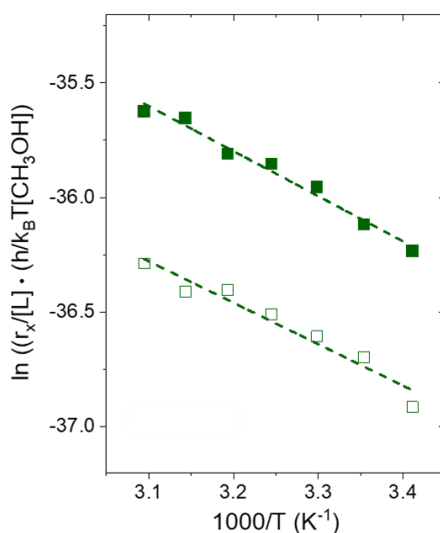


Figure C19. Representative Eyring plot for C_4H_8O ring-opening (5 mM C_4H_8O , 25 mM CH_3OH , CH_3CN solvent, 293-323 K) over Zr-BEA to form 1-methoxy-2-butanol (solid points) and 2-methoxy-1-butanol (hollow points).

$\frac{-\Delta H_{1M2B}^{\ddagger}}{R}$	$\frac{\Delta S_{1M2B}^{\ddagger}}{R}$	$\frac{-\Delta H_{2M1B}^{\ddagger}}{R}$	$\frac{\Delta S_{2M1B}^{\ddagger}}{R}$
-2.0 ± 0.1	-29.5 ± 1.0	-1.8 ± 0.2	-30.7 ± 0.6

Table C6. Activation enthalpy and entropy to form each product in C₄H₈O ring-opening divided by the ideal gas constant, obtained from the slope and intercept, respectively, of **Figure C19**.

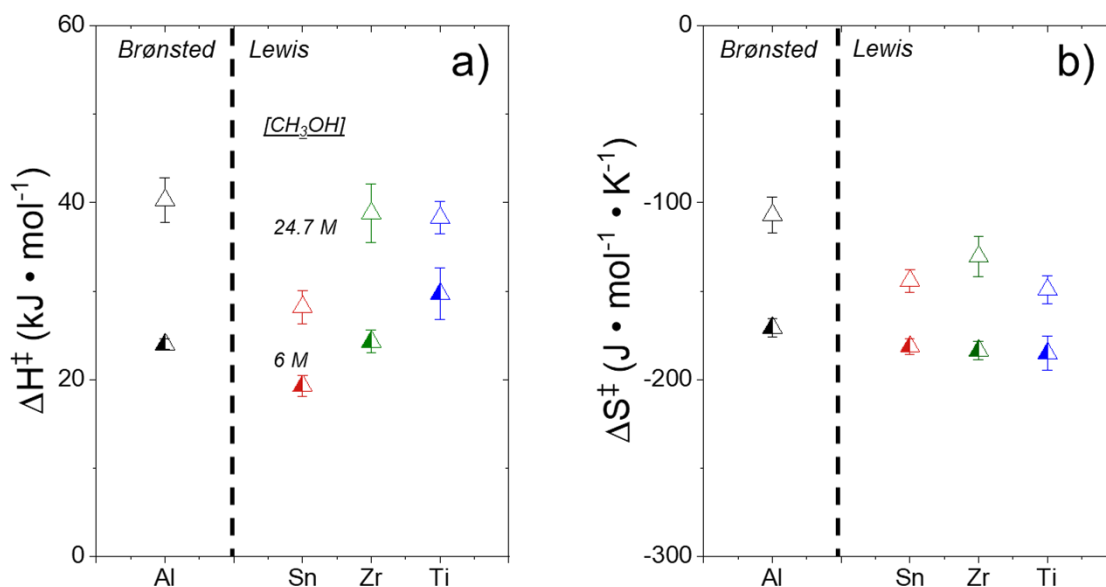


Figure C20. Activation a) enthalpies and b) entropies for C₄H₈O ring-opening with CH₃OH (0.0002 M (black) or 0.005 M (red, green, and blue) C₄H₈O, 6 M (half-solid points) or 24.7 M (hollow points) CH₃OH in CH₃CN, 293-323 K) over Al- (black), Sn- (red), Zr- (green), and Ti-BEA (blue).

Figure C20 reports activation barriers under conditions in which a CH₃OH-derived species saturates active sites. At the same [CH₃OH], $\Delta H^{\ddagger}$ values differ by less than 5 kJ mol⁻¹ when changing from a CH₃OH-derived to a C₄H₈O-derived MARI species (**Figure 4.3**). This trend also holds over Al-BEA at 6 M CH₃OH, but values differ between MARI species by ~15 kJ mol⁻¹ at 24.7 M CH₃OH. The greater difference may result from the solvation of the active proton by CH₃OH within Al-BEA at sufficiently high [CH₃OH], leading to greater differences in intermediate stability under conditions of a CH₃OH- or C₄H₈O-derived MARI.

Nevertheless, similar conclusions hold for the data in **Figure C20** as for **Figure 4.3**. A lower $\Delta H^\ddagger$ value corresponds to greater ring-opening rates for the Lewis acids, while $\Delta S^\ddagger$ changes weakly between metals. For all metals, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values increase with $[\text{CH}_3\text{OH}]$, supporting that a CH_3OH -rich environment drives rate increases through entropic gains. **Figure C20** provides compelling evidence that inner and outer sphere interactions influence $\text{C}_4\text{H}_8\text{O}$ ring-opening over M-BEA similarly under conditions of a CH_3OH - or $\text{C}_4\text{H}_8\text{O}$ -derived MARI.

C10. Kinetic Measurements Under $\text{C}_4\text{H}_8\text{O}$ -Covered Active Sites at High $[\text{C}_4\text{H}_8\text{O}]$

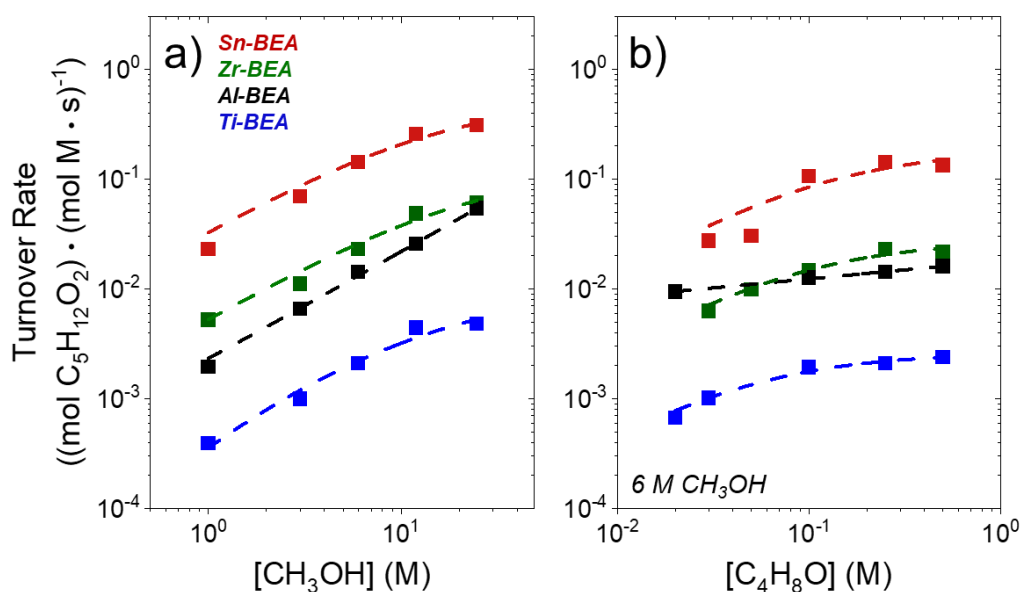


Figure C21. Turnover rates for $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH as functions of a) CH_3OH concentration at 0.25 M $\text{C}_4\text{H}_8\text{O}$ (CH_3CN solvent, 308 K) and b) $\text{C}_4\text{H}_8\text{O}$ concentration at 6 M CH_3OH (CH_3CN solvent, 308 K) over Sn- (red), Zr- (green), Al- (black), and Ti-BEA (blue).

Figures C21 and **C22** present turnover rates for $\text{C}_4\text{H}_8\text{O}$ ring-opening as a function of $[\text{CH}_3\text{OH}]$ and $[\text{C}_4\text{H}_8\text{O}]$ at high concentrations of $[\text{C}_4\text{H}_8\text{O}]$. All materials show a regime of first-order rate dependence on $[\text{CH}_3\text{OH}]$, under which rates were then measured at varying $[\text{C}_4\text{H}_8\text{O}]$. Under this regime, materials show a corresponding zero-order rate dependence on $[\text{C}_4\text{H}_8\text{O}]$, suggesting that $\text{C}_4\text{H}_8\text{O}$ saturates active sites even at these high concentrations of $[\text{C}_4\text{H}_8\text{O}]$. The

activation barriers reported in **Figure 4.3** were made under these conditions to ensure C_4H_8O -covered active sites at each $[CH_3OH]$.

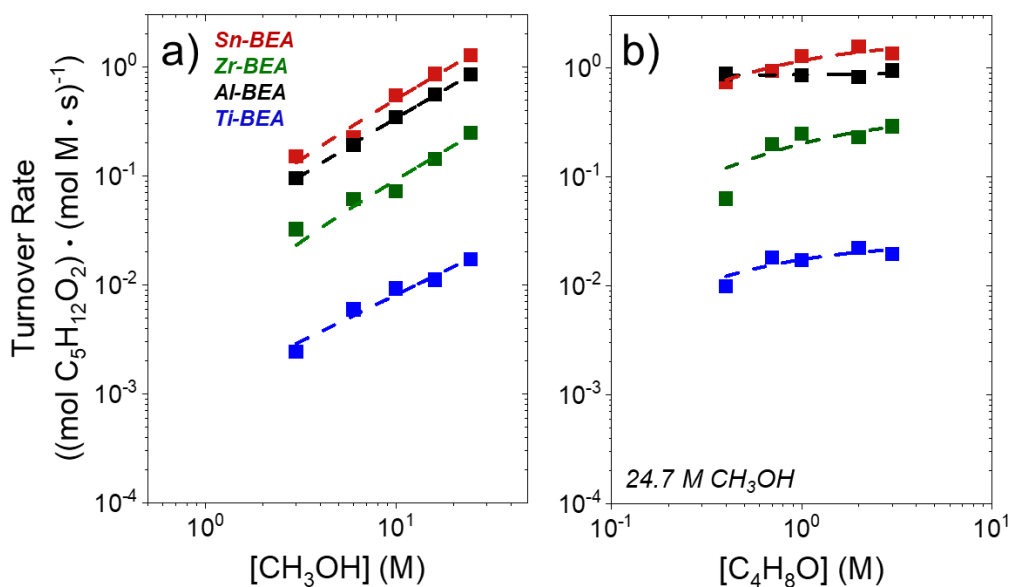


Figure C22. Turnover rates for C_4H_8O ring-opening with CH_3OH as functions of a) CH_3OH concentration at 1 M C_4H_8O (CH_3CN solvent, 308 K) and b) C_4H_8O concentration at 24.7 M CH_3OH (308 K) over Sn- (red), Zr- (green), Al- (black), and Ti-BEA (blue).

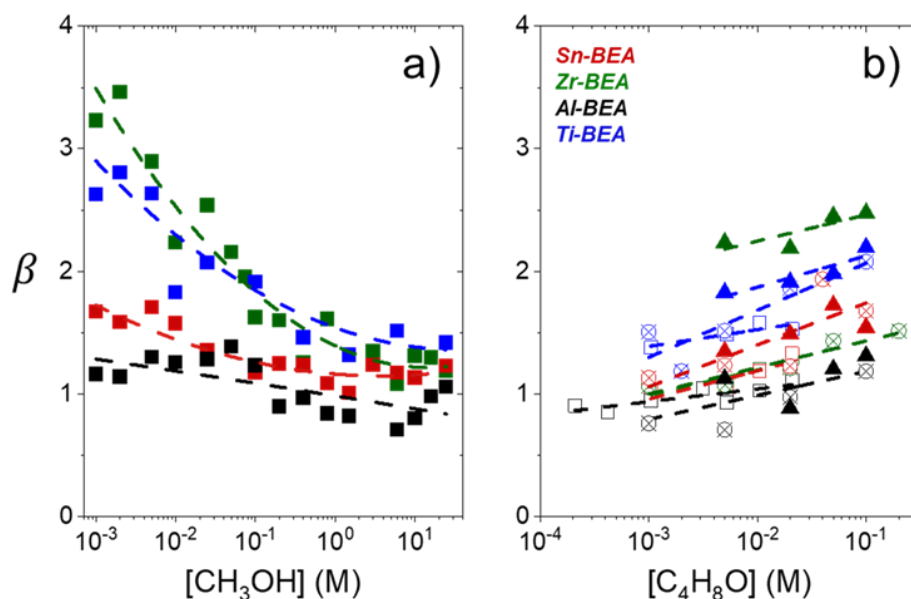


Figure C23. Values of β for C_4H_8O ring-opening with CH_3OH as a function of a) CH_3OH concentration (0.005 M C_4H_8O , CH_3CN solvent, 308 K), and b) C_4H_8O concentration at 0.01 M (solid triangles), 6 M (crossed circles), or 24.7 M CH_3OH (hollow squares) (CH_3CN , 308 K) over Sn- (red), Zr- (green), Al- (black), and Ti-BEA (blue).

Figure C23a shows β values for C₄H₈O ring-opening as a function of [CH₃OH] when C₄H₈O is held constant at 0.005 M. **Figure C23b** presents the β values as a function of [CH₃OH] under the lower range of [C₄H₈O] measurements from **Figures 4.1** and **4.2**. These ranges of conditions lead to a combination of C₄H₈O to CH₃OH-saturated active sites in each plot.

Notably, **Figure C23** shows very similar trends to **Figure 4.7** (which presents β values only when C₄H₈O covers active sites), where greater [CH₃OH] leads to lower β values and greater [C₄H₈O] provides higher β values. The similarity among the trends demonstrates that the shift from C₄H₈O to CH₃OH-saturated active sites at high [CH₃OH] in **Figure C23** does not strongly affect trends in β , supporting that the differences in β in both **Figure 4.7** and **Figure C23** stem from changes in the intrapore solvent environment rather than any changes in dominant surface intermediate.

C11. Excess Energies to Probe Liquid-Phase C₄H₈O and CH₃OH Stability

Table C7 presents the excess energies and activity coefficients for C₄H₈O and CH₃OH in mixtures of CH₃OH and CH₃CN at 308 K. The equations used to compute the excess energies from the activity coefficients are as follows:

$$G_j^\varepsilon = RT * \ln(\gamma_j) \quad (C25)$$

$$H_j^\varepsilon = -RT^2 * \frac{d \ln(\gamma_j)}{dT} \quad (C26)$$

where j represents C₄H₈O or CH₃OH here, R equals the ideal gas constant, and T represents temperature. The differential term $\left(\frac{d \ln(\gamma_j)}{dT}\right)$ was obtained by calculating activity coefficients between 303-323 K by increments of 5 K. The natural log of the activity coefficients was plotted against the temperature, and the slope of this line equaled the differential term.

Notably, γ values vary by factors of less than 2 and 3 for $\text{C}_4\text{H}_8\text{O}$ and CH_3OH , respectively, across the range of solvent compositions examined for ring-opening and $\text{C}_4\text{H}_8\text{O}$ adsorption. Furthermore, both H^ε and G^ε values span a range of less than 3 kJ mol^{-1} across solvent compositions. The weak dependences of these values on the mixing ratios of CH_3OH and CH_3CN support that the stability of reactive species and adsorbates in the liquid phase does not drive changes in ring-opening rates, activation enthalpies for ring-opening, and enthalpies of adsorption for $\text{C}_4\text{H}_8\text{O}$.

Solvent	$\text{C}_4\text{H}_8\text{O}$			CH_3OH		
	γ	$H^\varepsilon (\text{kJ mol}^{-1})$	$G^\varepsilon (\text{kJ mol}^{-1})$	γ	$H^\varepsilon (\text{kJ mol}^{-1})$	$G^\varepsilon (\text{kJ mol}^{-1})$
CH_3CN	2.23	1.01	2.08	2.64	2.39	2.53
6 M CH_3OH (in CH_3CN)	2.91	3.52	2.78	1.77	2.43	1.48
12 M CH_3OH (in CH_3CN)	2.85	3.20	2.72	1.29	0.9	0.66
CH_3OH	3.62	1.70	3.35	1	0	0

Table C7. Activity coefficients (γ), excess enthalpies (H^ε), and excess free energies (G^ε) calculated at 308 K in mixtures of CH_3CN and CH_3OH . Activity coefficients were obtained with the UNIFAC method on ChemCAD.

C12. Isothermal Titration Calorimetry Thermograms and Heats per Injection

The plots in **Figure C24** were obtained during the cleaning and calibration procedures for isothermal titration calorimetry (ITC), as discussed in **Section 4.2.4**. **Figure C24a** shows the heat released from the sequential pulses during the electrical calibration. The instrument gave a calibration factor after the calibration was completed, for which values greater than 0.98 were assumed to be satisfactory. **Figure C24b** shows the heat released during the water-water injection, during which each $1 \mu\text{L}$ injection led to a peak with an area between -3 and $+3 \mu\text{J}$.

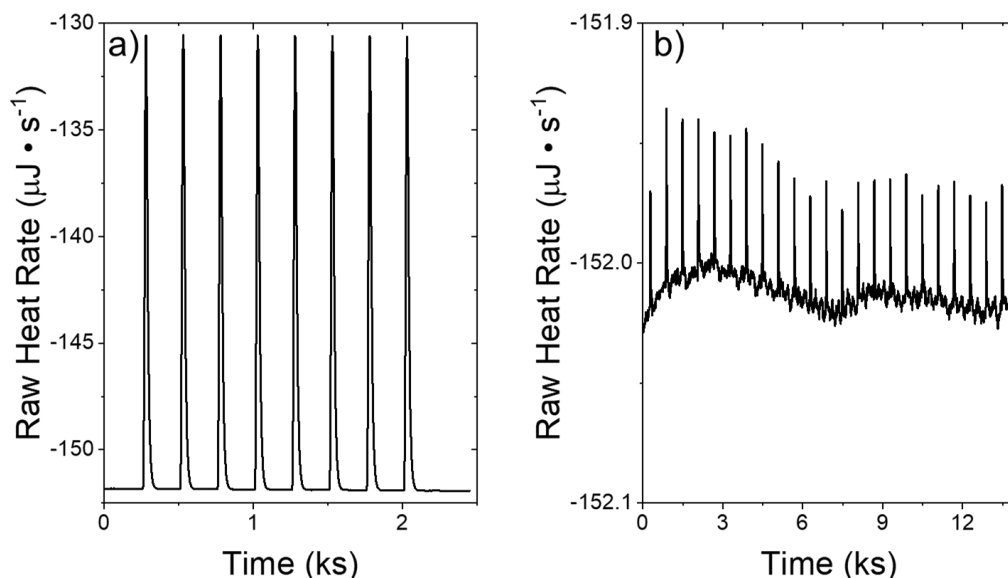


Figure C24. a) ITC thermogram from the electrical calibration of the NanoITC. b) ITC thermogram from the water-water adsorption to check the cleanliness of the ITC cell.

Figure C25 shows an acid-base titration of NaHCO_3 into HNO_3 , which was used as a standard to verify the ITC results obtained. The adsorption enthalpy calculated from **Figure C25b** was $-8.1 \pm 1.2 \text{ kJ mol}^{-1}$, which agrees well with the reported enthalpy of -9.1 kJ mol^{-1} .³⁵³⁻³⁵⁴

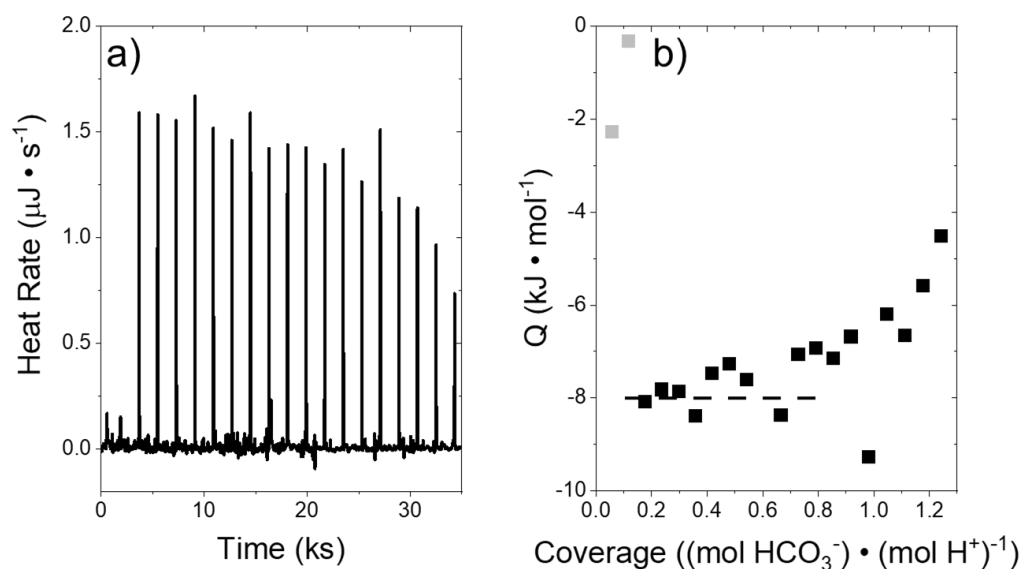


Figure C25. a) ITC thermogram from the acid-base titration of HNO_3 (0.0005 M in 0.1 M NaCl) with NaHCO_3 (0.0052 M in 0.1 M NaCl), b) the corresponding heats released as a function of bicarbonate ion coverage.

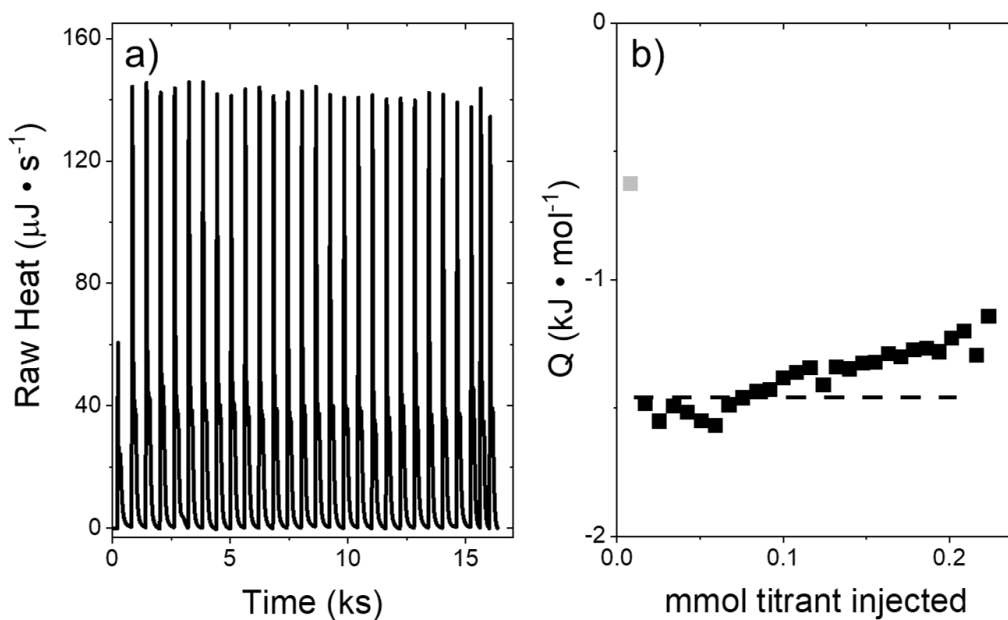


Figure C26. a) ITC thermogram from the titration of CH_3OH with neat 1M2B (8.7 M 1M2B, 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

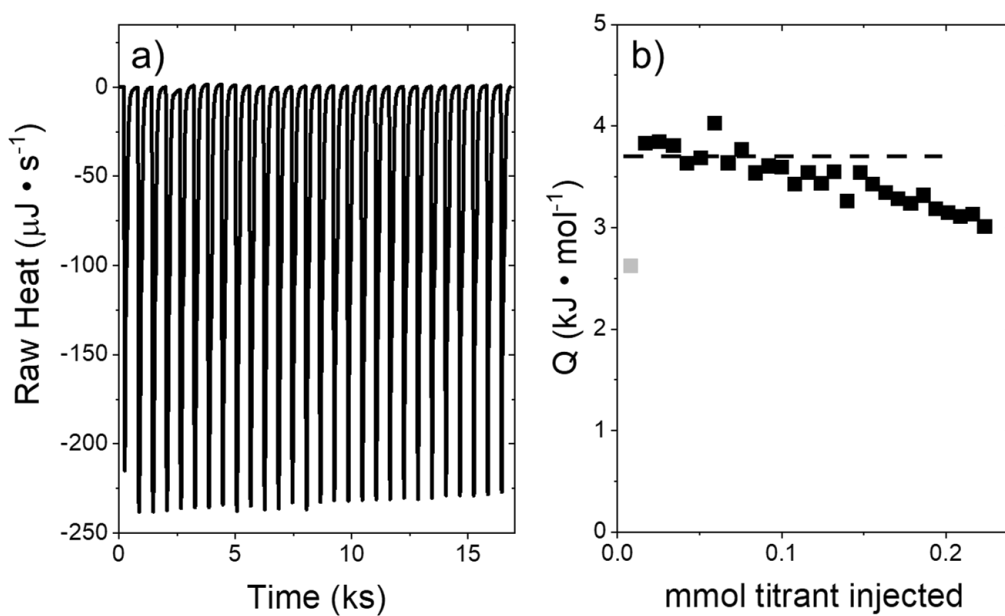


Figure C27. a) ITC thermogram from the titration of CH_3CN with neat 1M2B (8.7 M 1M2B, 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

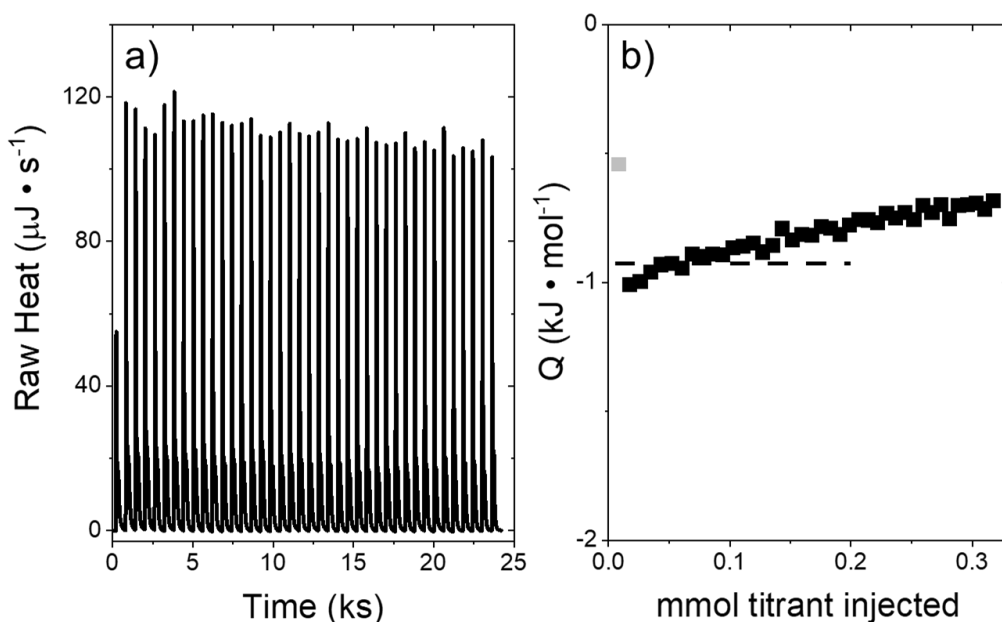


Figure C28. a) ITC thermogram from the titration of CH_3OH with neat 2M1B (8.9 M 2M1B, 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

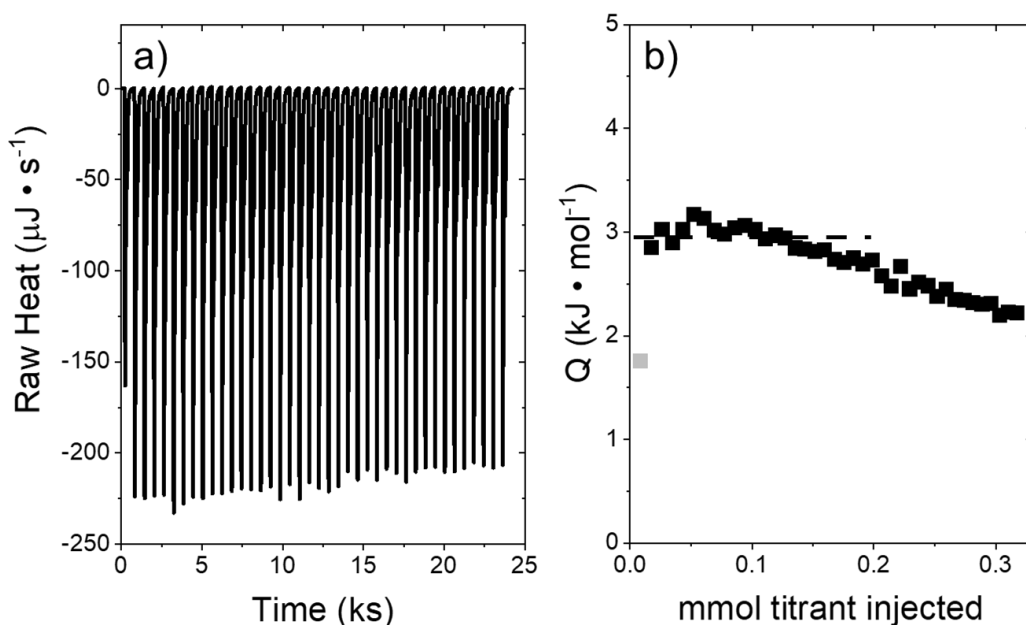


Figure C29. a) ITC thermogram from the titration of CH_3CN with neat 2M1B (8.9 M 2M1B, 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

Figures C26 to C29 report the heat changes from the injection of the neat ring-opening products into CH_3OH or CH_3CN . Each product adsorbs exothermically into CH_3OH and endothermically into CH_3CN . 1M2B shows a more exothermic enthalpy of mixing into CH_3OH

than 2M1B, but 2M1B shows a less endothermic enthalpy of mixing into CH₃CN than 1M2B. While these measurements provide insight into the stability of the products in CH₃OH and CH₃CN-rich solvents, they do not correlate with the trends of β values or $\Delta H_{ads,prod.}$ values into each solvent, indicating that the active metal and solvating environment within the pores of M-BEA govern these differences.

Figure C30 presents an ITC thermogram and heat release plot from the adsorption of C₄H₈O into Al-BEA at high coverages, to test if lateral interactions between nearby active sites play a role in the adsorption enthalpy of C₄H₈O. The integrated heat begins to decrease sharply near an epoxide coverage of 1, which supports that the Brønsted acid sites bind 1 epoxide molecule on average. Furthermore, the integrated heats change negligibly as the epoxide coverage approaches 1, which suggests that lateral interactions do not play a strong role between proximal active sites. The absence of these effects in the material with Al-BEA, which shows the highest density of active sites (Si:M ~70), also indicates that lateral interactions will not play a role in Ti-, Sn-, or Zr-BEA (Si:M > 90).

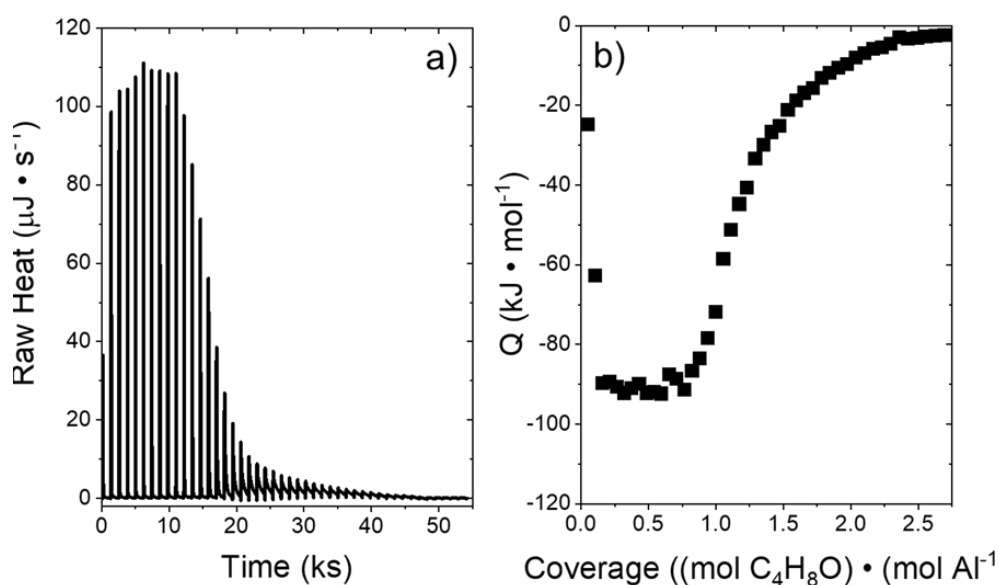


Figure C30. a) ITC thermogram from the titration of Al-BEA with C₄H₈O (0.05 M C₄H₈O in CH₃OH, 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

The ITC thermogram and heat release plots for all ITC experiments used to calculate the adsorption enthalpies of C_4H_8O into M-BEA (other than that in **Figure 4.4**), which were run at low coverages as compared to **Figure C30**, are shown below. ITC measurements for CH_3OH adsorption into M-BEA are also shown below, although these were performed at higher titrant concentrations (and thus higher coverages) because CH_3OH adsorbs weakly and higher concentrations are needed to observe sufficiently large peaks in the thermogram.

As discussed in **Section 4.3.3**, early injections often show lower heat released than expected due to the evaporation of liquid from the syringe needle. Although less common, some of the experiments below show outlier points at later injections, which may result from an inconsistent volume or epoxide concentration in those injections.

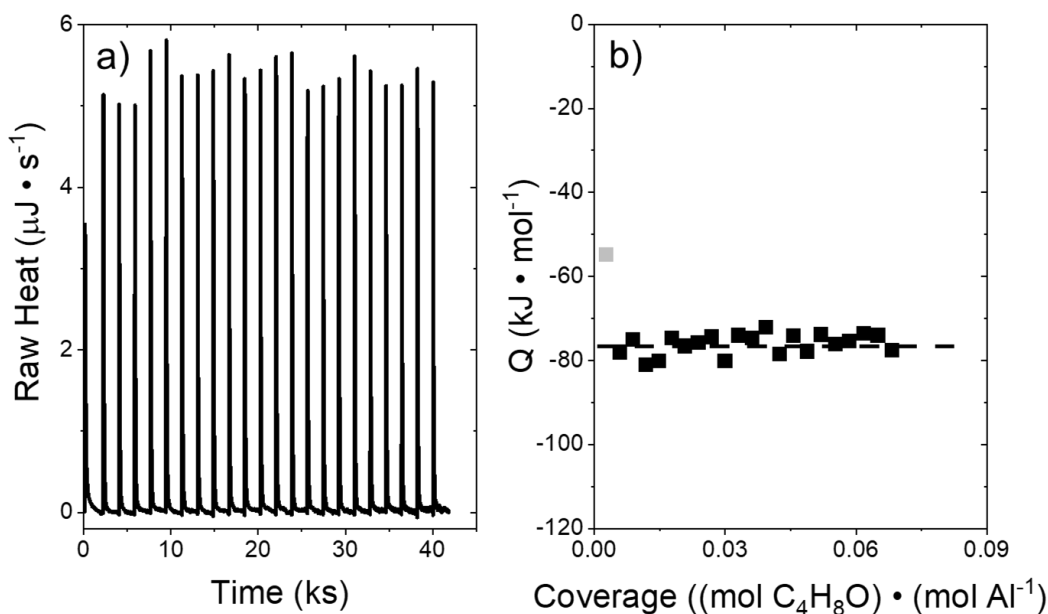


Figure C31. a) ITC thermogram from the titration of Al-BEA with C_4H_8O (0.005 M C_4H_8O in CH_3OH , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

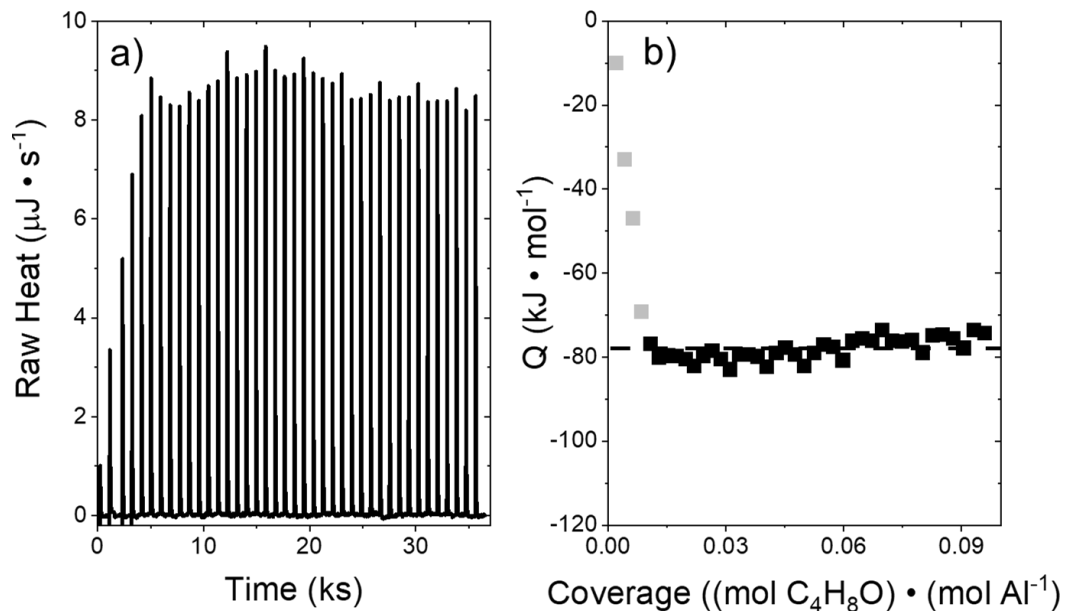


Figure C32. a) ITC thermogram from the titration of Al-BEA with $\text{C}_4\text{H}_8\text{O}$ (0.005 M $\text{C}_4\text{H}_8\text{O}$ in CH_3OH , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected. This point was repeated to ensure accuracy and reproducibility of measurements.

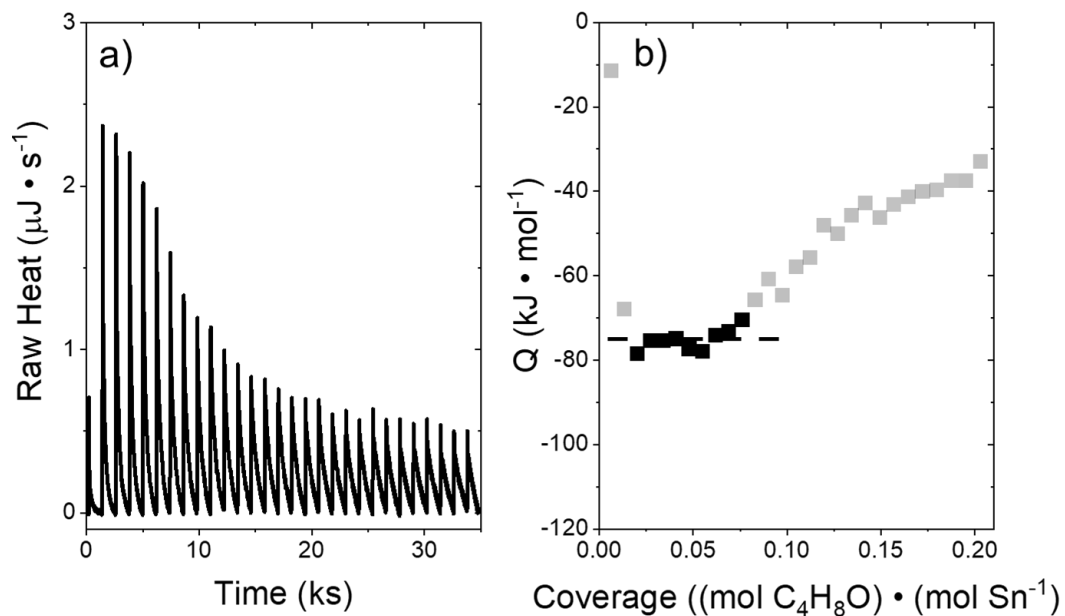


Figure C33. a) ITC thermogram from the titration of Sn-BEA with $\text{C}_4\text{H}_8\text{O}$ (0.005 M $\text{C}_4\text{H}_8\text{O}$ in CH_3OH , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected. This point was repeated to ensure accuracy and reproducibility of measurements (other measurement in **Figure 4.4**).

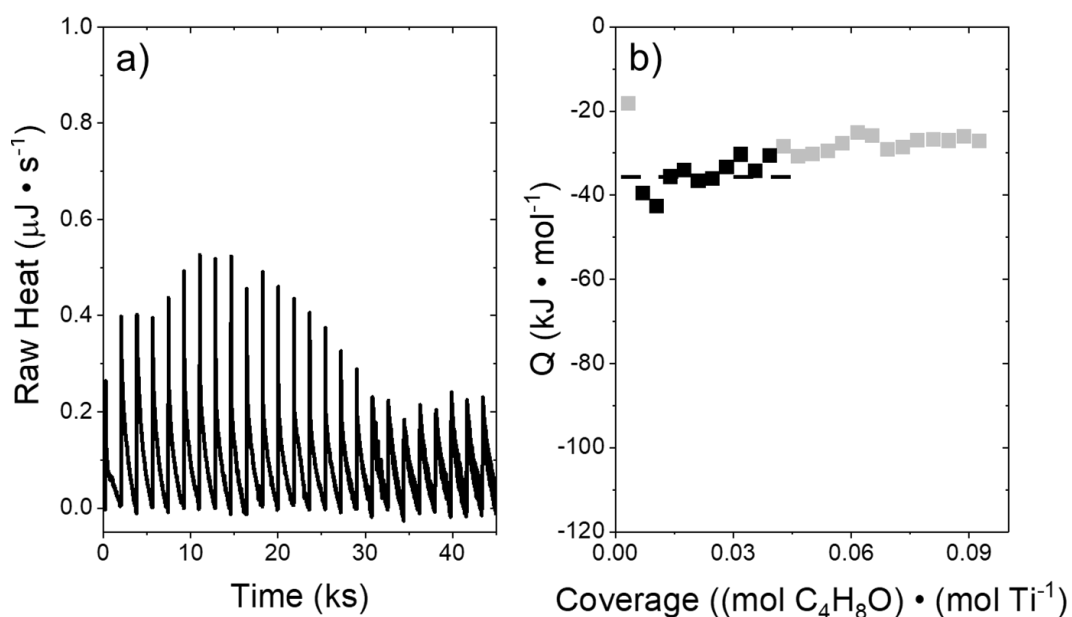


Figure C34. a) ITC thermogram from the titration of Ti-BEA with $\text{C}_4\text{H}_8\text{O}$ (0.005 M $\text{C}_4\text{H}_8\text{O}$ in CH_3OH , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

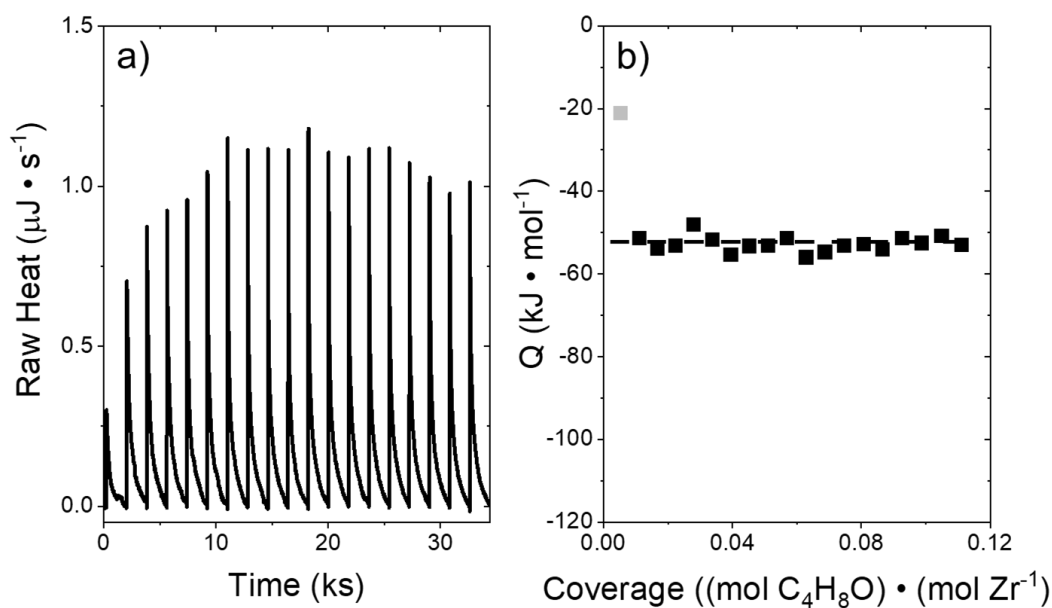


Figure C35. a) ITC thermogram from the titration of Zr-BEA with $\text{C}_4\text{H}_8\text{O}$ (0.005 M $\text{C}_4\text{H}_8\text{O}$ in CH_3OH , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

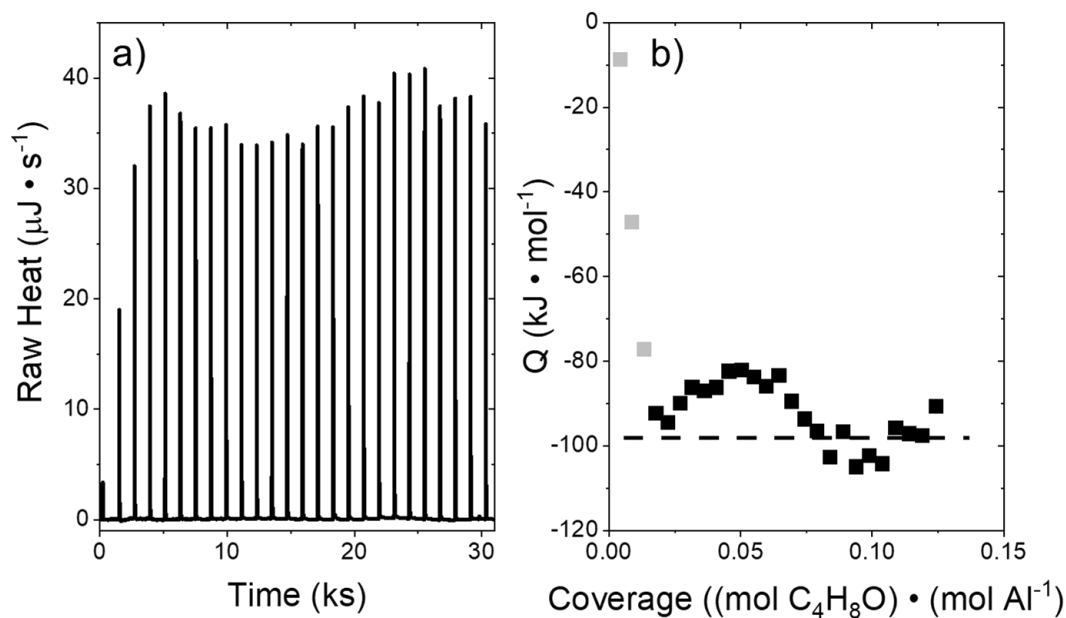


Figure C36. a) ITC thermogram from the titration of Al-BEA with $\text{C}_4\text{H}_8\text{O}$ (0.005 M $\text{C}_4\text{H}_8\text{O}$ in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

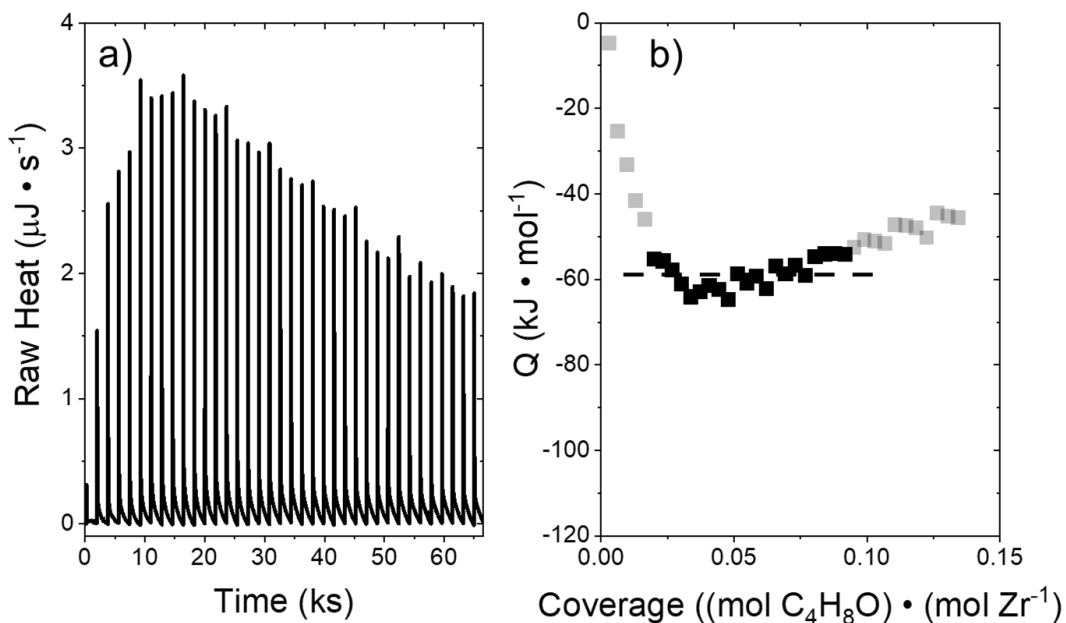


Figure C37. a) ITC thermogram from the titration of Zr-BEA with $\text{C}_4\text{H}_8\text{O}$ (0.005 M $\text{C}_4\text{H}_8\text{O}$ in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

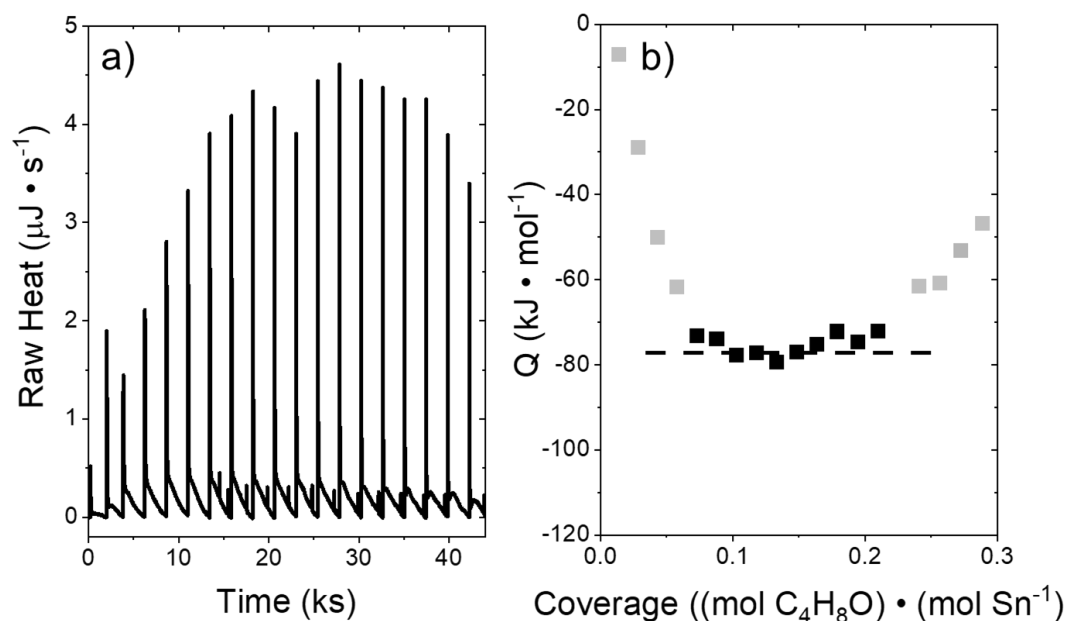


Figure C38. a) ITC thermogram from the titration of Sn-BEA with $\text{C}_4\text{H}_8\text{O}$ (0.005 M $\text{C}_4\text{H}_8\text{O}$ in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

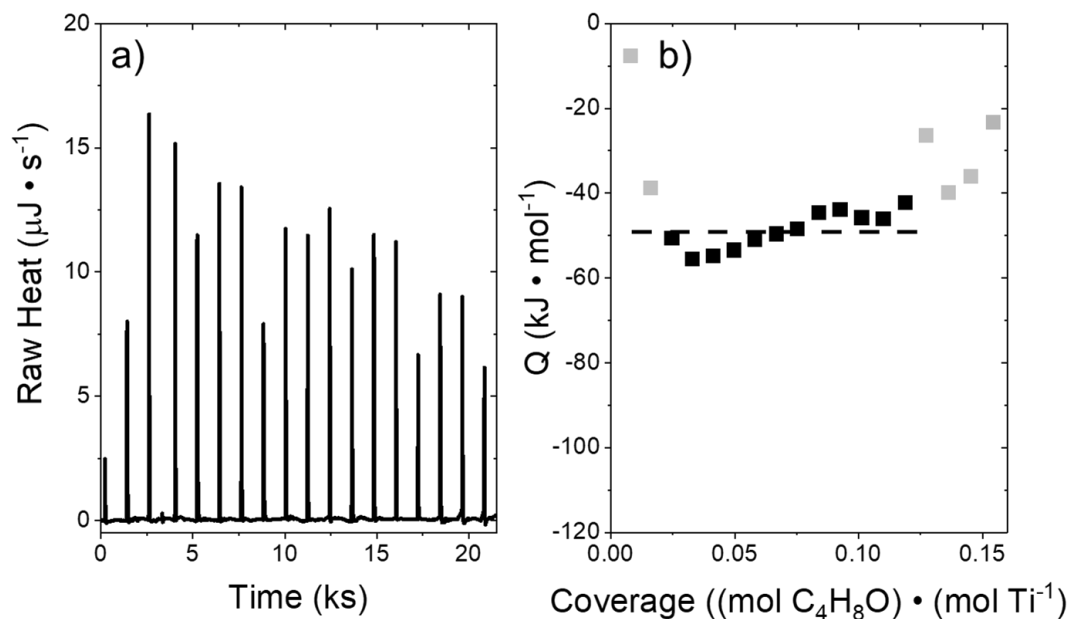


Figure C39. a) ITC thermogram from the titration of Ti-BEA with $\text{C}_4\text{H}_8\text{O}$ (0.005 M $\text{C}_4\text{H}_8\text{O}$ in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

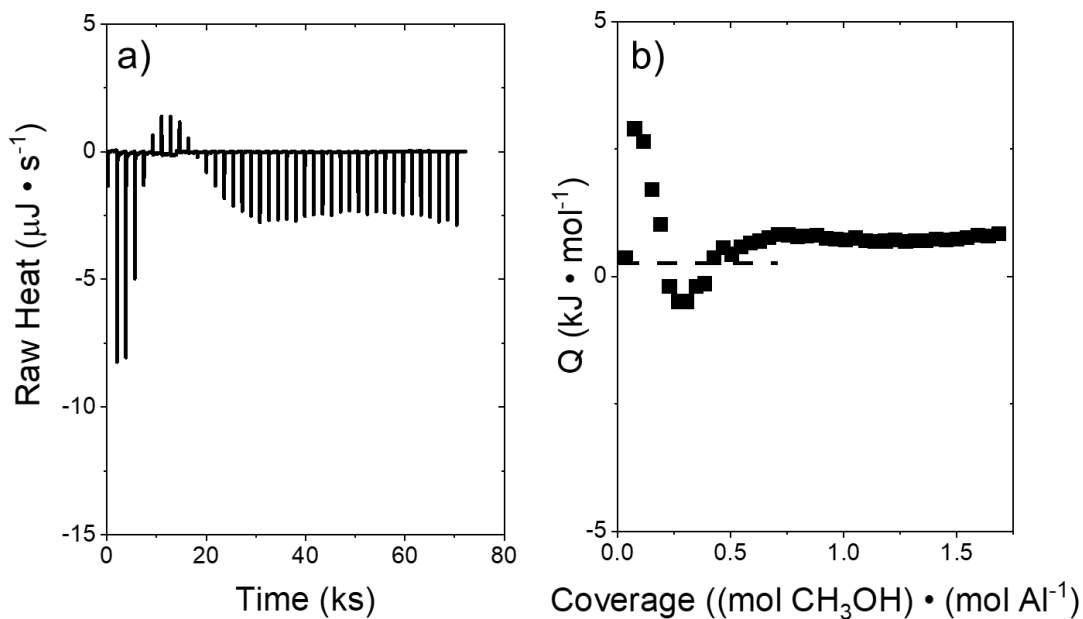


Figure C40. a) ITC thermogram from the titration of Al-BEA with CH_3OH (0.1 M CH_3OH in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

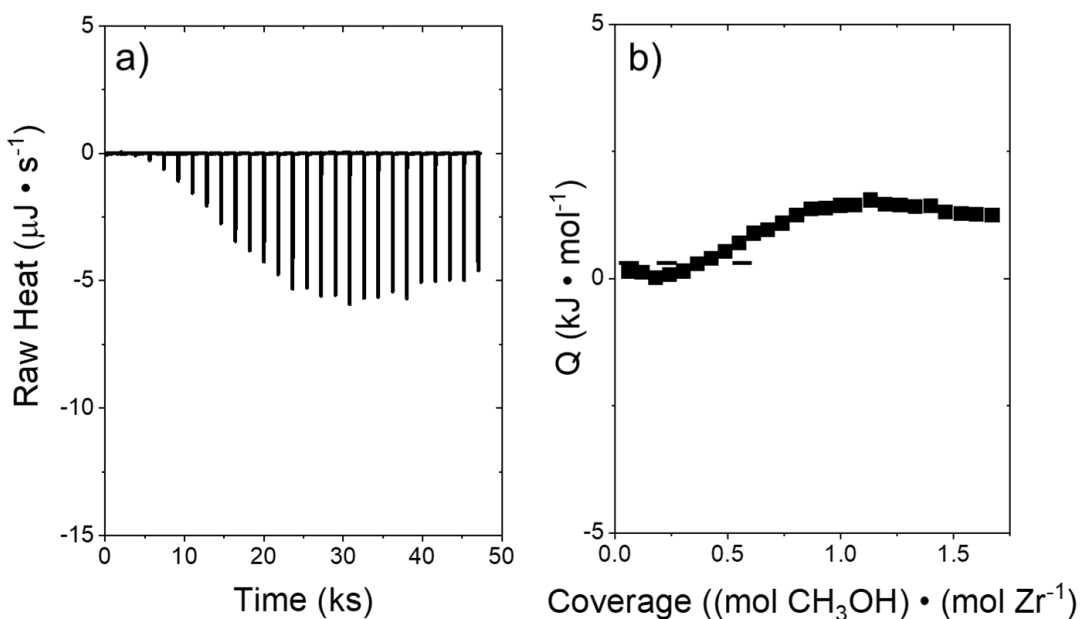


Figure C41. a) ITC thermogram from the titration of Zr-BEA with CH_3OH (0.1 M CH_3OH in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

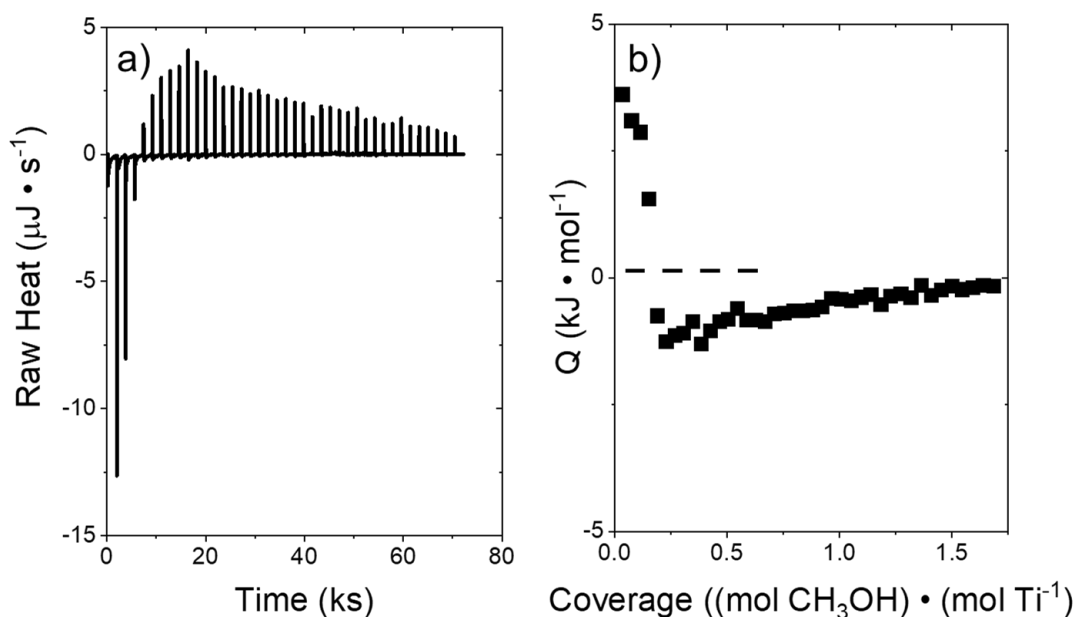


Figure C42. a) ITC thermogram from the titration of Ti-BEA with CH_3OH (0.1 M CH_3OH in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

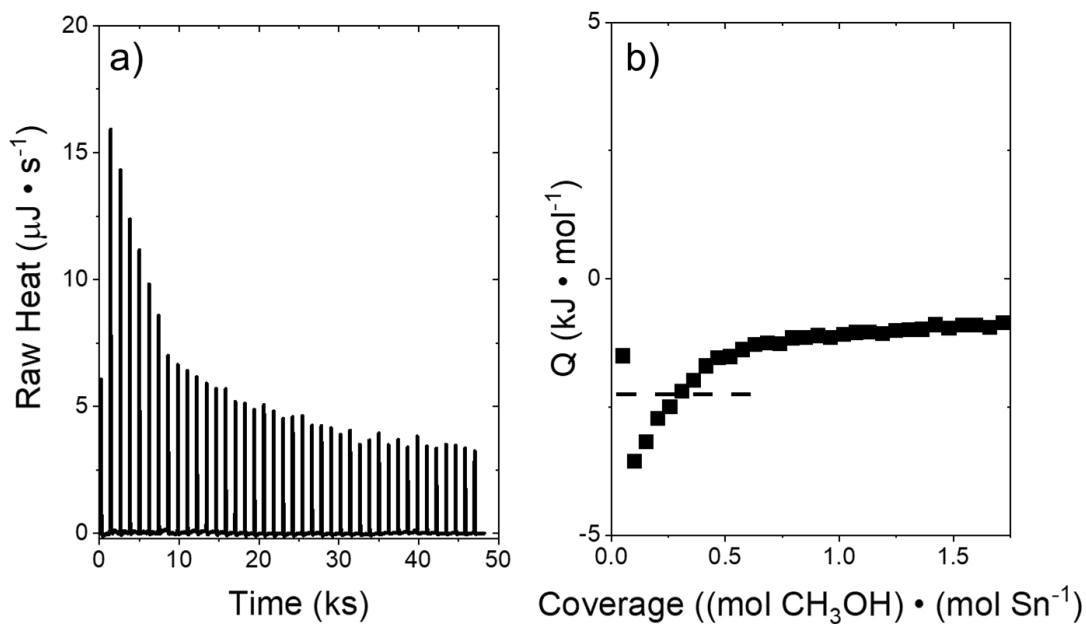


Figure C43. a) ITC thermogram from the titration of Sn-BEA with CH_3OH (0.1 M CH_3OH in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

C13. Reported Electronegativities of Metal Atoms

Active Atom	Mulliken Electronegativity (kJ mol ⁻¹) ^a	Pauling Electronegativity ^b	Sanderson Electronegativity ^c
Al	308	1.5	1.714
Sn	406	1.8	2.298
Ti	331	1.5	1.5
Zr	339	1.4	0.9
H ⁺	693	--	--

Table C8. ^aCalculated from average of electron affinity⁴²⁴⁻⁴²⁵ and first ionization energy⁴²⁵⁻⁴²⁶ of each atom. ^bTaken from reference 81.⁴²⁷ ^cValues for Al³⁺, Sn⁴⁺, Ti⁴⁺, and Zr⁴⁺ from reference 82.⁴²⁸

When comparing metals, none of the electronegativity scales shown in **Table C8** correlate directly to trends in rates or regioselectivities reported in **Chapter 4**. However, taking into consideration the Mulliken electronegativity of a proton (i.e., the active site in Al-BEA) demonstrates that active sites in M-BEA with a greater Mulliken electronegativity show a greater preference to form the terminal alcohol product, 2M1B (**Figure 4.7**).

APPENDIX D

SUPPLEMENTAL DATA AND ANALYSIS FOR CHAPTER 5

D1. Catalyst Characterization

D1.1 X-Ray Diffraction to Observe Crystallinity of M-BEA Catalysts

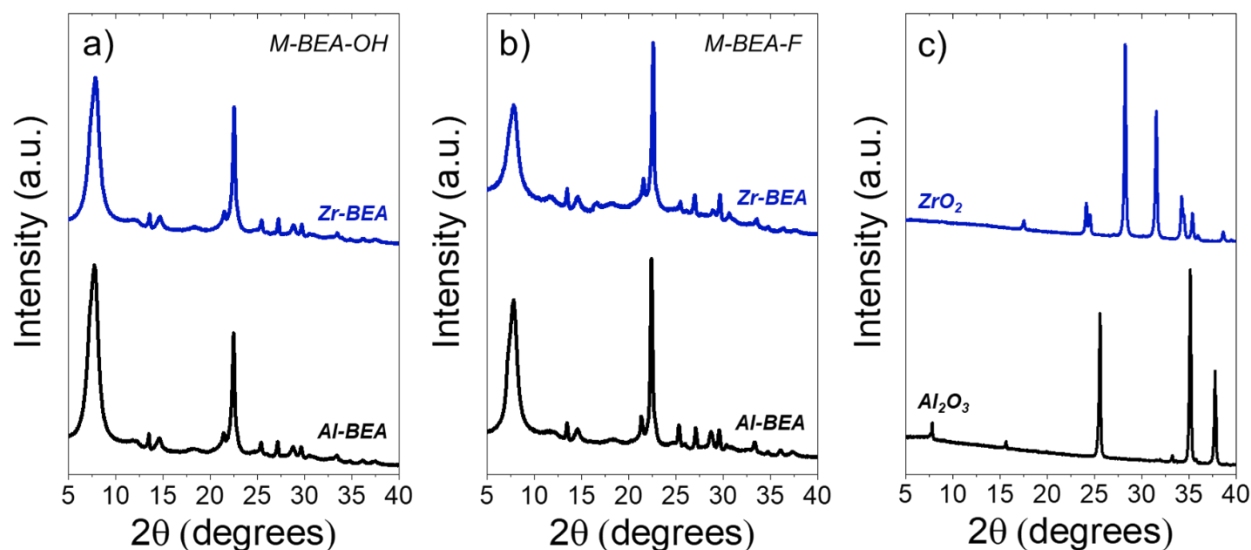


Figure D1. Powder X-ray diffractograms obtained with Cu K α radiation (0.15418 nm) under ambient conditions for a) M-BEA-OH, b) M-BEA-F (Al (black), Zr (blue)), and c) the corresponding bulk metal oxides (γ -Al₂O₃ (black), ZrO₂ (blue)). Spectra are vertically offset for clarity.

The crystallographic features for each M-BEA are representative of the *BEA framework.¹⁵¹ As displayed in **Figures D1a** and **D1b**, each M-BEA material shows weak features around 25.5, 27, 29, and 33 degrees. The sharper feature at ~22.5 degrees for the M-BEA-F materials in **Figure D1b** indicates a highly crystalline material, consistent with previous reports for zeolites synthesized in fluoride media.³³⁰ The broader feature for the M-BEA-OH in **Figure D1a** suggests a smaller crystallite size¹³⁸ and the presence of internal (SiOH)_x defects formed by dealumination of the parent Al-BEA material (Si:Al = 20).

Figure D1c reveals that each of these peak locations coincides with strong features in the diffractograms of at least one of the metal oxides. However, the presence of the weak features in all M-BEA suggests that the features are characteristic of the *BEA framework, rather than originating from the presence of metal oxide. Overall, the XRD patterns in **Figure D1** support that each M-BEA possesses the crystalline *BEA framework, with minimal to no detectable metal oxide crystallites present.

D1.2 Diffuse Reflectance UV-Vis Spectra to Infer Metal Atom Dispersy

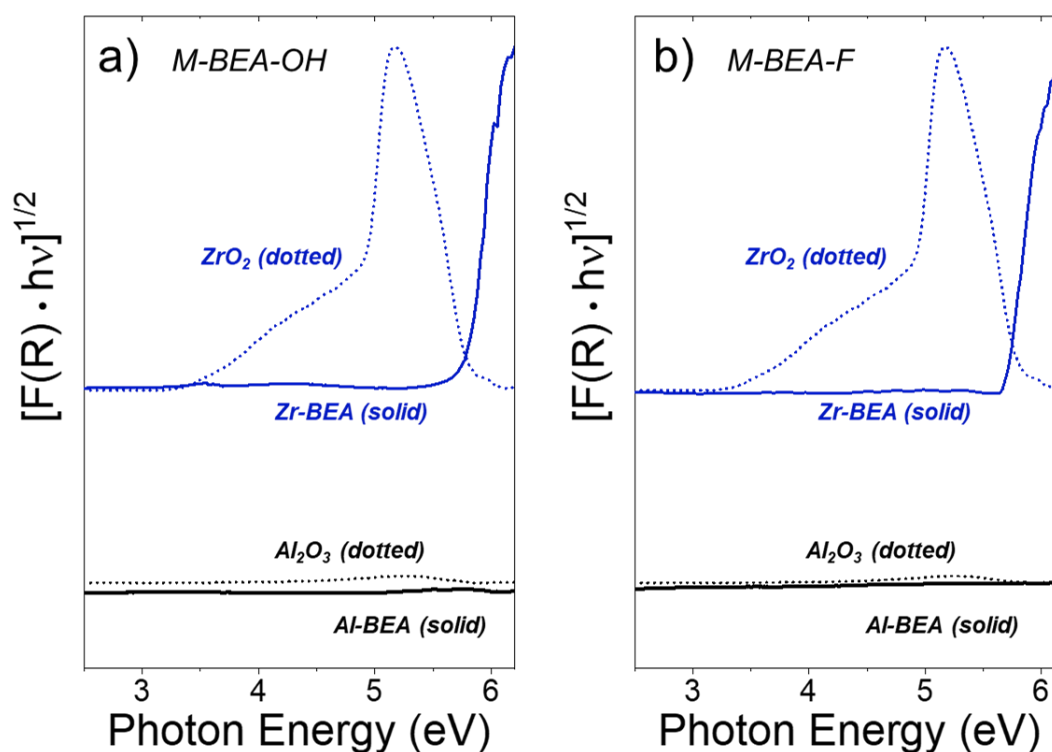


Figure D2. Tauc plots obtained with a UV-Vis spectrophotometer at ambient conditions for a) M-BEA-OH and b) M-BEA-F (solid lines; Al (—), Zr (—)) and the respective metal oxides (dotted lines; γ - Al_2O_3 (—), ZrO_2 (—)). UV-Vis spectra were obtained from 200 to 800 nm. The Tauc plots were normalized to the most intense features and are vertically offset for clarity.

The band gaps for each M-BEA and the respective metal oxides were obtained by extrapolating the linear absorbance region of the Tauc plot in **Figure D2** to the baseline. The

intersection of the baseline and linear region represents the band gap photon energy. Each Al-BEA and γ -Al₂O₃ show negligible features within the region of photon energies examined, consistent with reported band gaps greater than 7 eV for γ -Al₂O₃.³⁷⁵⁻³⁷⁶ **Table D1** reveals that the band gaps for each Al- and Zr-BEA are greater than the band gaps for the metal oxides, providing evidence that the metal atoms are well dispersed in the *BEA framework.

Catalyst	M-BEA Band Gap (eV)	Metal Oxide Band Gap (eV)
Al-BEA-F	--	--
Al-BEA-OH	--	--
Zr-BEA-F	5.7	4.9
Zr-BEA-OH	5.8	4.9

Table D1. Calculated band gaps for M-BEA and metal oxide materials. The band gaps for the Al materials likely exceeds the regime of wavelengths possible to measure on the DRUV-Vis spectrophotometer.

The photon energy E in electron volts (eV) was obtained from the wavelength as follows:

$$E = \frac{3 * 10^8 \frac{m}{s}}{Wavelength (nm) * \frac{1 m}{10^9 nm}} * h * \left(6.242 * 10^{18} \frac{eV}{J} \right)$$

where h equals the Planck constant. The ordinate from **Figure D2** was obtained from the ordinate of the raw spectra, the percent reflectance (% R). The Kubelka-Munk function ($F(R)$) was calculated from % R:

$$F(R) = \frac{\left(1 - \frac{\%R}{100} \right)^2}{2 * \left(\frac{\%R}{100} \right)}$$

$F(R)$ was then multiplied by the photon energy, and taking the square root of the resulting quantity yielded the ordinate for **Figure D2**.

D1.3 Ex situ Raman Spectra of M-BEA Materials to Confirm Metal Coordination

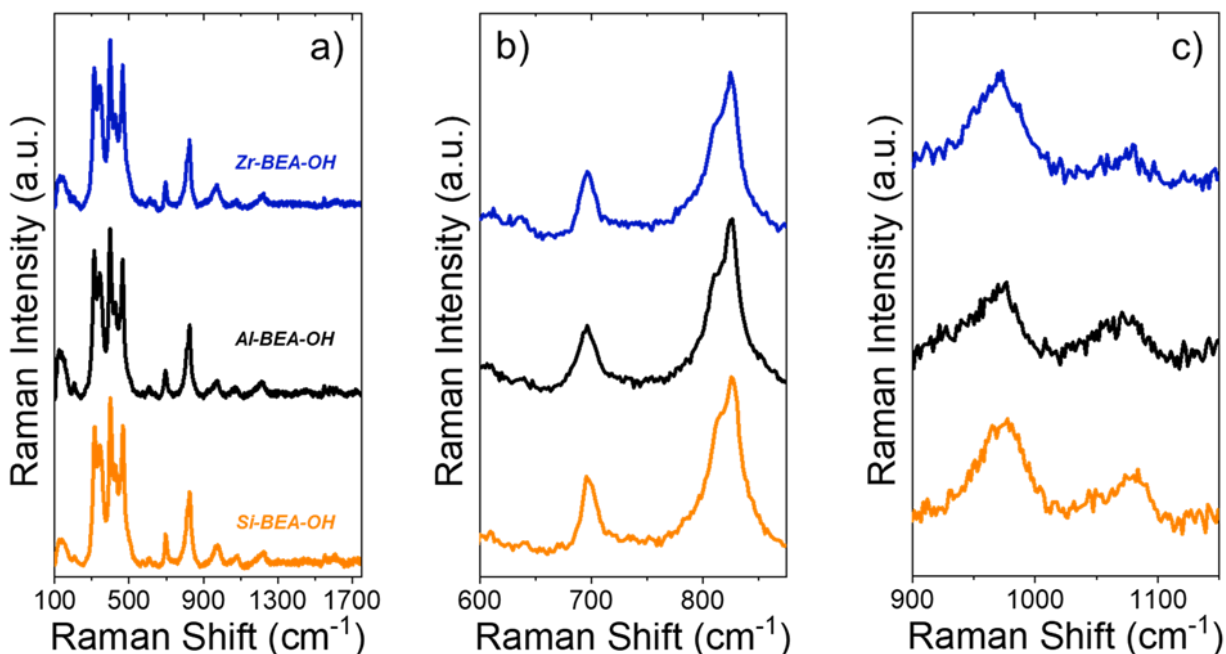


Figure D3. Ex situ Raman spectra of M-BEA-OH (Zr (blue), Al (black), Si (orange)) at (a) the full range of Raman shifts examined, (b) magnified view of the range of 600-875 cm^{-1} , and (c) magnified view of the 900-1150 cm^{-1} region. The spectra are an average of 10 scans with an exposure time of 20 s. Spectra are normalized by the maximum feature at $\sim 400 \text{ cm}^{-1}$ and are vertically offset for clarity. Spectra were taken at ambient conditions with a Raman spectrometer (Renishaw, InVia) equipped with a 532 nm laser that delivered a power density of $\sim 2 \text{ mW } \mu\text{m}^{-2}$.

Figures D3a and D4a reveal that each M-BEA and a dealuminated *BEA material (Si-BEA-OH) possess similar Raman spectra, with features characteristic of the *BEA framework. The intense peaks between 250 and 550 cm^{-1} represent features of the *BEA framework: the peaks at 315 and 345 cm^{-1} are assigned to six-membered rings, the peaks at 400 and 425 cm^{-1} are assigned to five-membered rings, and the peak at 465 cm^{-1} represents four-membered rings characteristic of the *BEA framework.³³³⁻³³⁴ The peak at $\sim 695 \text{ cm}^{-1}$ has previously been reported on Raman spectra of crystalline *BEA zeolites, suggesting the feature may be characteristic of the *BEA framework.³³⁵⁻³³⁶ The peak at $\sim 820 \text{ cm}^{-1}$ represents a symmetric skeletal mode of microporous silicates.³³⁷⁻³³⁸

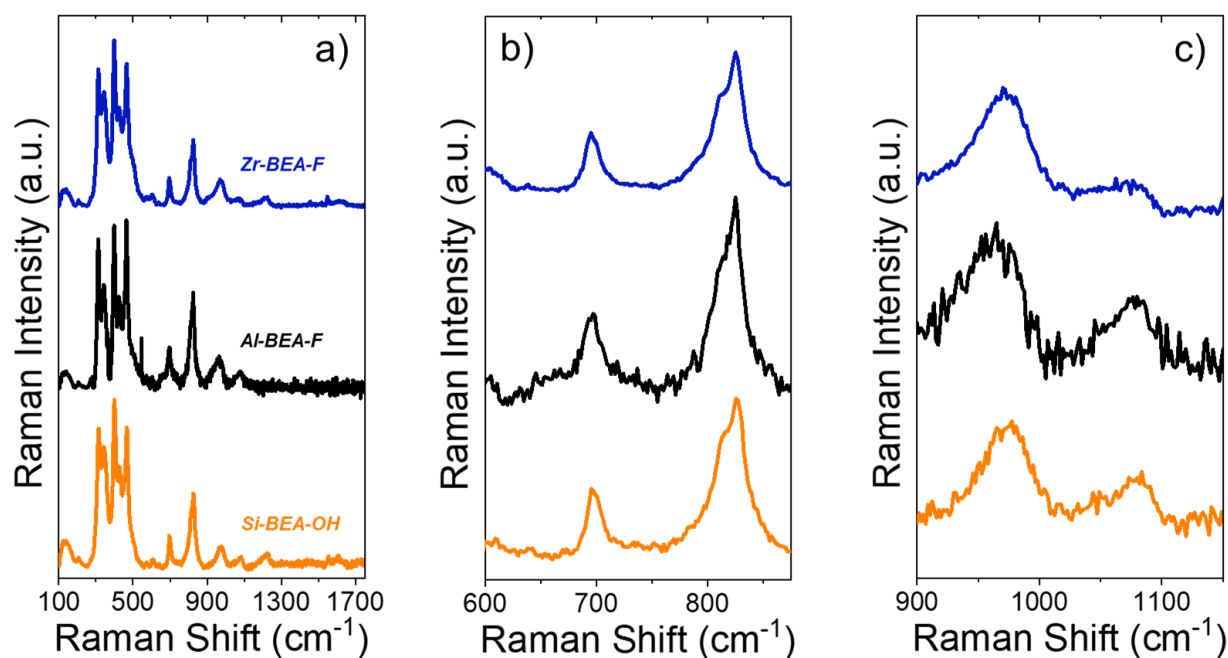


Figure D4. *Ex situ* Raman spectra of M-BEA-F (Zr (blue), Al (black)) with Si-BEA-OH for reference (orange).

All M-BEA materials show a feature at 144 cm^{-1} . The feature is also present in Si-BEA, which supports that the feature results from a mode inherent to the *BEA framework. Alternatively, the feature may simply be an artifact of the Raman filter used to suppress signal from Rayleigh scattering. **Figures D3b** and **D4b** zooms into a region in which Al_2O_3 ($640, 751\text{ cm}^{-1}$)³⁷⁸⁻³⁸⁰ and ZrO_2 ($610, 640\text{ cm}^{-1}$)³⁸⁴⁻³⁸⁶ have been reported to show Raman features. All M-BEA materials show nearly identical spectra in this region, with no notable features in the regions where the respective metal oxides contain features. These data support that all M-BEA materials do not contain oligomeric metal oxide structures.

Figure D3c and **D4c** show that each M-BEA possesses features at ~ 960 and $\sim 1080\text{ cm}^{-1}$. The feature at $\sim 960\text{ cm}^{-1}$ has been commonly attributed to silanol defects.^{150, 333, 339} The peak at $\sim 1080\text{ cm}^{-1}$ plausibly originates from the *BEA framework. Ti-O-Si features have been commonly reported in the literature at ~ 960 and $\sim 1125\text{ cm}^{-1}$, respectively.^{254, 342-344} However, similar features

have not been well reported for Al- or Zr-containing zeolites. Therefore, the presence of each metal in the framework cannot be confirmed with Raman spectra but is indirectly supported by the absence of metal oxide features.

The Raman spectra in **Figures D3** and **D4** suggest that the Al and Zr atoms within M-BEA predominately reside at tetrahedral framework positions within the *BEA zeolite framework.

D1.4 Infrared Spectra of M-BEA Materials to Measure Silanol Density

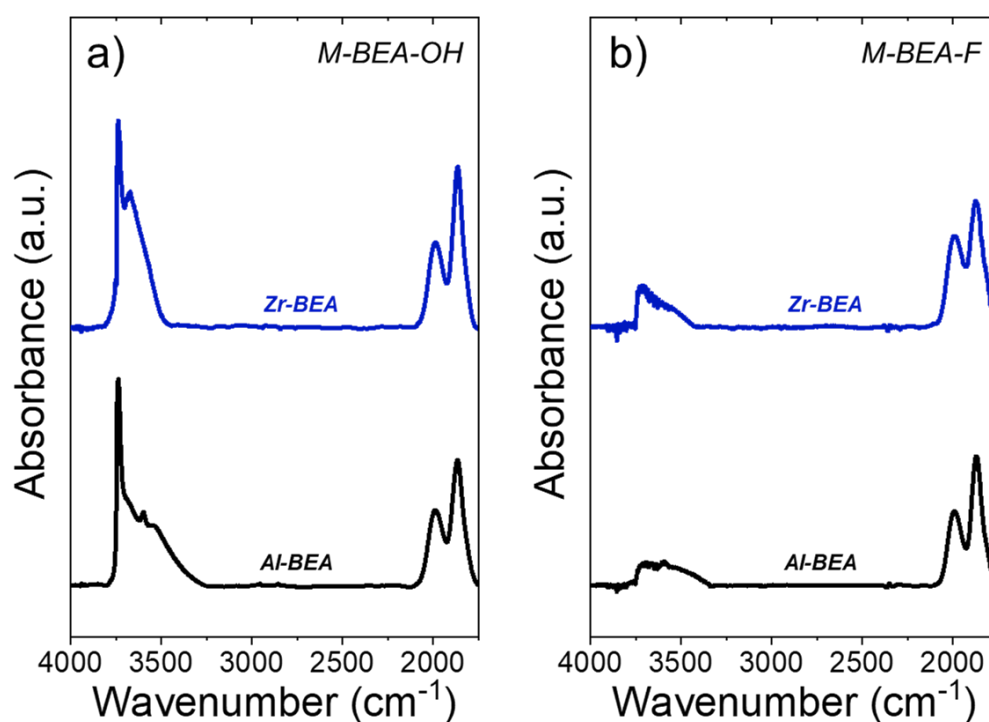


Figure D5. Infrared spectra of dehydrated samples of a) M-BEA-OH, b) M-BEA-F (Zr (blue), Al (black)). The samples were dehydrated under flowing He (101 kPa He, 50 cm³ min⁻¹) at 573 K prior to measurement. Spectra are vertically offset for clarity.

The greater $\nu(\text{O-H})$ areas (3300-3750 cm⁻¹) for each M-BEA-OH compared to M-BEA-F, with respect to the $\nu(\text{Si-O-Si})$ area (1800-2100 cm⁻¹), shows that the M-BEA-OH materials possess a greater density of (SiOH)_x groups than the M-BEA-F materials. The Φ_{IR} values in **Table 5.1**

were calculated by peak fitting on Origin 2021 (OriginLab Corporation). The peak areas for $\nu(\text{O-H})$ and $\nu(\text{Si-O-Si})$ were calculated with Gaussian fits (example shown in **Figure D6**).

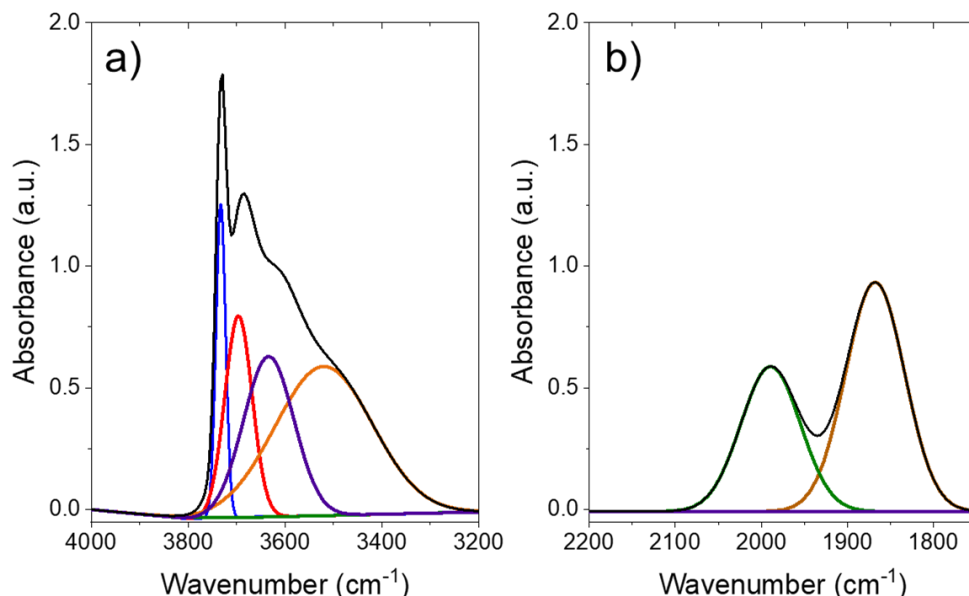


Figure D6. Fitted peaks for the (a) networked (red, purple, orange) and isolated (blue) Si-OH region and (b) Si-O-Si overtones at 1865 (brown) and 2000 cm^{-1} (green) for Zr-BEA-OH.

As shown in **Equation 5.1**, the equation to calculate Φ_{IR} is:

$$\Phi_{\text{IR}} = \frac{A_{\nu(\text{O-H})}}{A_{\nu(\text{Si-O-Si})}} \quad (\text{D1})$$

The red, purple, and orange peaks represent networked SiOH features which are summed to determine $A_{\nu(\text{O-H})}$. The green and brown peaks in the Si-O-Si region were summed together to get $A_{\nu(\text{Si-O-Si})}$. The blue peak in $\nu(\text{O-H})$ represent isolated SiOH features, so these peak areas were excluded from the Φ_{IR} calculations.

D1.5 Calculation of (SiOH)_x (unit cell)⁻¹ in M-BEA-OH

The density of (SiOH)_x per unit cell in M-BEA-OH was estimated based on the initial quantity of Al present in the commercial zeolite (Si:Al = 20). A *BEA unit cell contains 64 T atoms (i.e., Si, Al, or Zr), so the initial quantity of Al per unit cell equals 3.047:

$$Si + Al = 64$$

$$20Al + Al = 64$$

$$Al = 3.047 \text{ per unit cell}$$

Assuming all Al atoms are removed in the thorough dealumination treatment for the Lewis acids, the dealumination produces 3.047 (SiOH)_x (unit cell)⁻¹. The metal weight loading allows for the calculation of the Si:M ratio for each M-BEA:

$$Si + M = 64$$

$$(Si:M)M + M = 64$$

This can be used to calculate the number of metal atoms per unit cell incorporated into the formed (SiOH)_x. The final (SiOH)_x (unit cell)⁻¹ for Zr-BEA-OH is equal to the initial amount of Al (assumed that all Al is removed) subtracted by the added Zr. In contrast, the (SiOH)_x (unit cell)⁻¹ for the Brønsted acid equals the initial quantity of Al subtracted by the amount of Al removed:

$$(SiOH)_{x,Zr-BEA-OH} = 3.047 - \text{added Zr}$$

$$(SiOH)_{x,Zr-BEA-OH} = 3.047 - \text{removed Al}$$

Table D2 reports metal loadings per unit cell from ICP and calculated (SiOH)_x per unit cell. The calculated values predict a wider range of zeolite hydrophilicity than the Φ_{IR} calculations in **Section D1.4**. However, rate measurements as a function of metal loading (**Section D4**, *vide infra*) demonstrate a weak rate dependence on metal loading, and therefore (SiOH)_x (unit cell)⁻¹, within the range of loadings examined for the M-BEA-OH materials here.

Catalyst	M (unit cell) ⁻¹	(SiOH) _x (unit cell) ⁻¹
Al-BEA-OH	0.94	2.11
Zr-BEA-OH	0.45	2.59

Table D2. Metal loadings and (SiOH)_x per unit cell, determined from metal loadings from ICP and estimated Al removed by dealumination treatments.

D1.6 Infrared Spectra of C₅H₅N and CD₃CN Adsorption to Probe Active Site Character

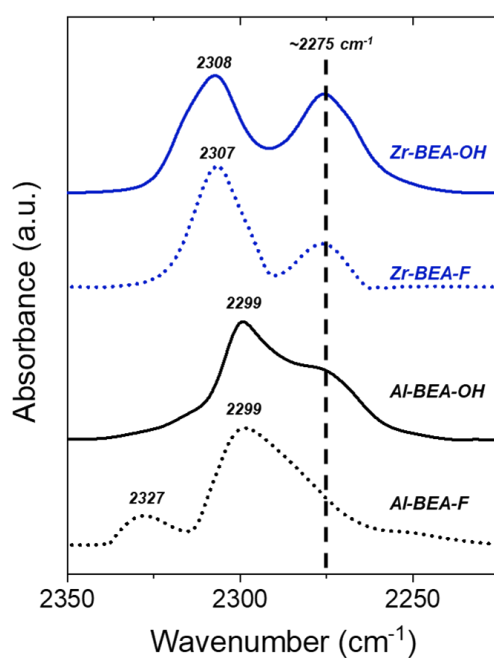


Figure D7. Infrared spectra of deuterated acetonitrile (CD₃CN) bound to hydrophilic (solid lines) and hydrophobic (dashed lines) Al-BEA (black) and Zr-BEA (blue) materials (0.03 kPa CD₃CN, 101 kPa Ar, 303 K). All spectra are normalized to the area of the Si-O-Si region of the zeolite from 1750-2100 cm⁻¹. Spectra are vertically offset for clarity.

Zr-BEA-OH and Zr-BEA-F possess single peaks at ~2308 cm⁻¹, in agreement with previous assignments of Lewis acid-bound CD₃CN within Zr-incorporated³⁹⁹⁻⁴⁰⁰ zeolites. Both Zr-BEA materials also show an absorbance feature at ~2275 cm⁻¹, which has been reported as CD₃CN coordinated to Si-OH groups within *BEA.³⁹⁵⁻³⁹⁶ Zr-BEA-F shows a less intense feature at ~2275 cm⁻¹, aligning with the lower density of (SiOH)_x groups within Zr-BEA-F compared to Zr-BEA-

OH. While each Zr-BEA only shows a single Lewis acid feature in **Figure D7**, each material likely contains both open and closed sites. Previous work demonstrated the presence of two Lewis acid features over Zr-incorporated zeolites from the infrared spectra of CO adsorption under cryogenic conditions, which the authors attributed to the presence of both open and closed Zr sites.³⁹⁹ We do not rule out that -OH functions at open Zr sites could also contribute to the feature at $\sim 2275\text{ cm}^{-1}$. Furthermore, several publications also argue that closed Lewis acid sites may open in the presence of protic molecules such as H_2O ^{392, 404-405} and alcohols,⁴⁰⁶⁻⁴⁰⁷ meaning that Lewis acid sites in M-BEA could open *in situ* in the presence of CH_3OH and convolute *ex situ* comparisons of site distributions.

The feature at $\sim 2299\text{ cm}^{-1}$ for Al-BEA-OH and Al-BEA-F is consistent with previous assignments for Brønsted acidic Al sites.³⁹⁶⁻³⁹⁷ Al-BEA-OH shows a shoulder at $\sim 2275\text{ cm}^{-1}$ that likely originates from $(\text{SiOH})_x$ nests in the hydrophilic material. The absence of a clear shoulder at $\sim 2275\text{ cm}^{-1}$ in Al-BEA-F agrees with the lower $(\text{SiOH})_x$ density of the material relative to Al-BEA-OH. Notably, Al-BEA-F also shows a feature at $\sim 2327\text{ cm}^{-1}$ that is not present in Al-BEA-OH. Extraframework Lewis acidic Al species have been reported to show a feature in this range,³⁹⁶⁻³⁹⁷ suggesting that not all Al exists as framework Brønsted acid sites within Al-BEA-F. Nevertheless, active site titration experiments and ^{27}Al NMR spectra (**Figures D10** and **Figure D16**, *vide infra*) suggest that $\sim 90\%$ of Al sites are active in Al-BEA-F, and the Raman spectra for Al-BEA-F does not show noticeable extraframework Al features. Al-BEA-F likely contains a minor fraction of extraframework Lewis acid Al sites, but the Al atoms predominantly exist as Brønsted acid sites. Collectively, the spectra of adsorbed CD_3CN in **Figure D7** demonstrate the presence of Lewis and Brønsted acid sites within the M-BEA materials.

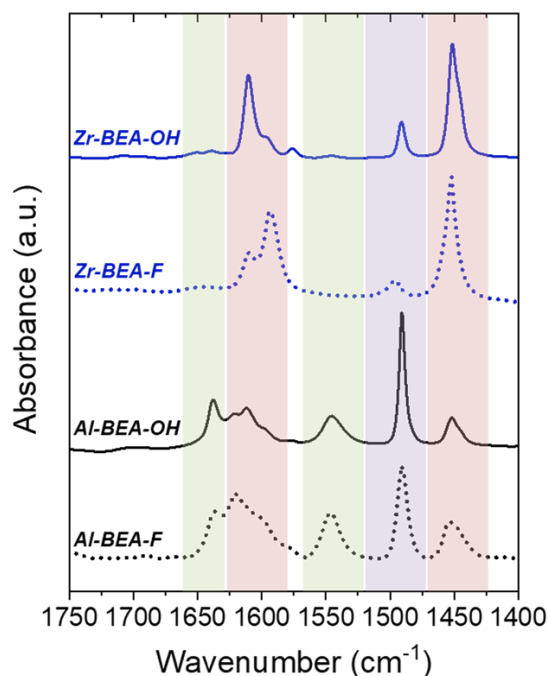


Figure D8. Infrared spectra of pyridine (C_5H_5N) bound to Lewis and Brønsted acid sites over hydrophilic (solid lines) and hydrophobic (dashed lines) Al-BEA (black) and Zr-BEA (blue) materials (1.4 kPa C_5H_5N , 101 kPa Ar, 393 K). All spectra are normalized to the area of the Si-O-Si region of the zeolite from 1750-2100 cm^{-1} . The highlighted regions on the plot represent regions for C_5H_5N absorbance features coordinated to only Brønsted acid sites (green), only Lewis acid sites (red), and either Lewis or Brønsted acid sites (purple). Spectra are vertically offset for clarity.

Each material possesses a feature at $\sim 1450\text{ cm}^{-1}$ that has been attributed to C_5H_5N bound to only Lewis acid sites.^{408, 410-412} All M-BEA materials also show features at $\sim 1490\text{ cm}^{-1}$, corresponding to C_5H_5N bound to Lewis or Brønsted acid sites.⁴⁰⁸⁻⁴⁰⁹ Each material also shows peaks in the region of $1580\text{-}1625\text{ cm}^{-1}$, commonly attributed to Lewis acid-bound C_5H_5N .⁴¹³⁻⁴¹⁵ The presence of these features in the Al-BEA zeolites may signal the presence of some fraction of extraframework Lewis acidic Al species. This aligns with the presence of the Lewis acid Al feature on the CD_3CN spectra of Al-BEA-F, but contrasts with the absence of any Lewis acid feature for CD_3CN adsorption over Al-BEA-OH. Both Al-BEA-OH and Al-BEA-F also show features at ~ 1550 and $\sim 1640\text{ cm}^{-1}$, which solely originate from protonated C_5H_5N at Brønsted acid sites.⁴⁰⁸⁻⁴¹² Zr-BEA-OH and Zr-BEA-F do not contain features in this region, suggesting that all Zr sites in

these materials are Lewis acidic. Each material also shows a feature at $\sim 1575\text{ cm}^{-1}$ of varying intensity, which has been attributed to physisorbed $\text{C}_5\text{H}_5\text{N}$.^{408, 412, 416}

Notably, the Zr-BEA materials show distinct features at ~ 1595 and $\sim 1610\text{ cm}^{-1}$. The peak at $\sim 1610\text{ cm}^{-1}$ has previously been assigned to $\text{C}_5\text{H}_5\text{N}$ coordinated to Lewis acidic Zr sites.^{65, 429} However, the peak at $\sim 1595\text{ cm}^{-1}$ resides in a position previously assigned to $\text{C}_5\text{H}_5\text{N}$ hydrogen-bonded to -OH groups.^{409, 411-412, 414} This peak may arise from $\text{C}_5\text{H}_5\text{N}$ coordinated to the -OH group from Zr-OH or the adjacent Si-OH in open sites within Zr-BEA. However, a feature at $\sim 1595\text{ cm}^{-1}$ has also been attributed to gas-phase $\text{C}_5\text{H}_5\text{N}$, which convolutes the assignment of that feature the Zr-BEA materials. Overall, the spectra of adsorbed $\text{C}_5\text{H}_5\text{N}$ in **Figure D8** provide insight into the distribution of active sites within each M-BEA.

D1.7 Identifying Al Structure within Al-BEA Materials Using ^{27}Al NMR Spectra

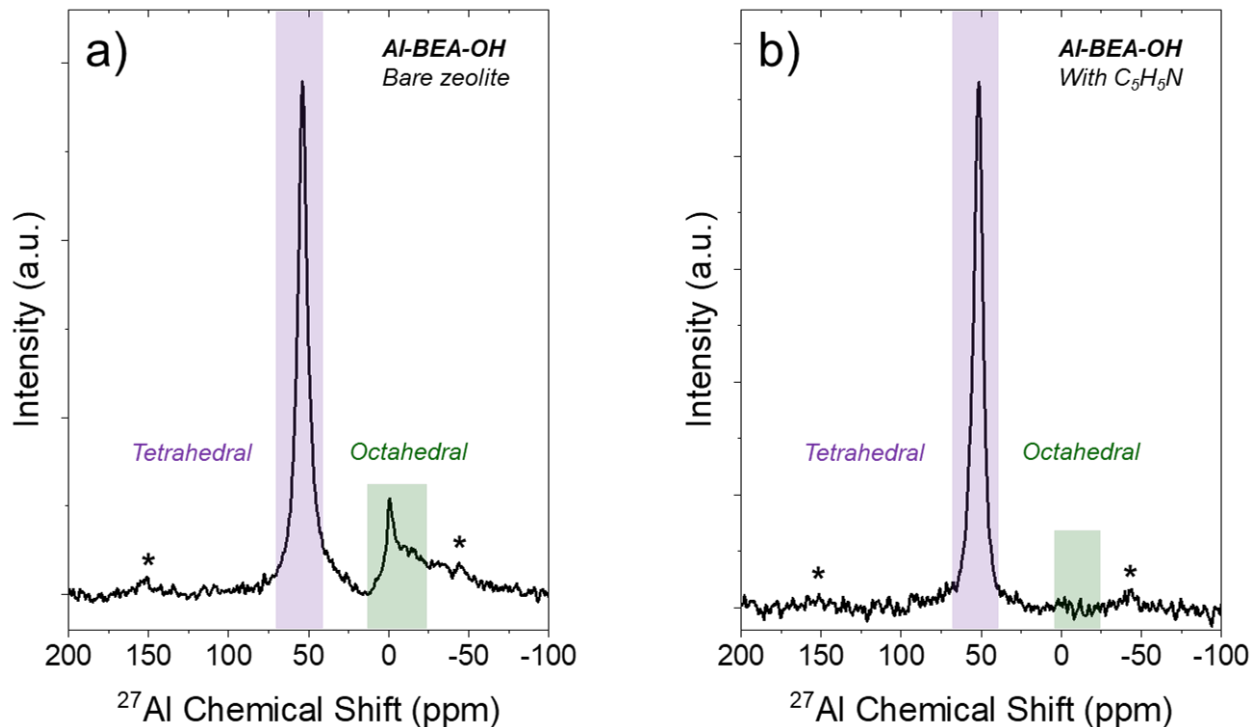


Figure D9. ^{27}Al NMR spectra for a) bare Al-BEA-OH and b) Al-BEA-OH impregnated with $\text{C}_5\text{H}_5\text{N}$ (298 K). The peaks representing tetrahedral and octahedral Al species are highlighted in purple and green, respectively. Asterisks represent spinning side-band features.

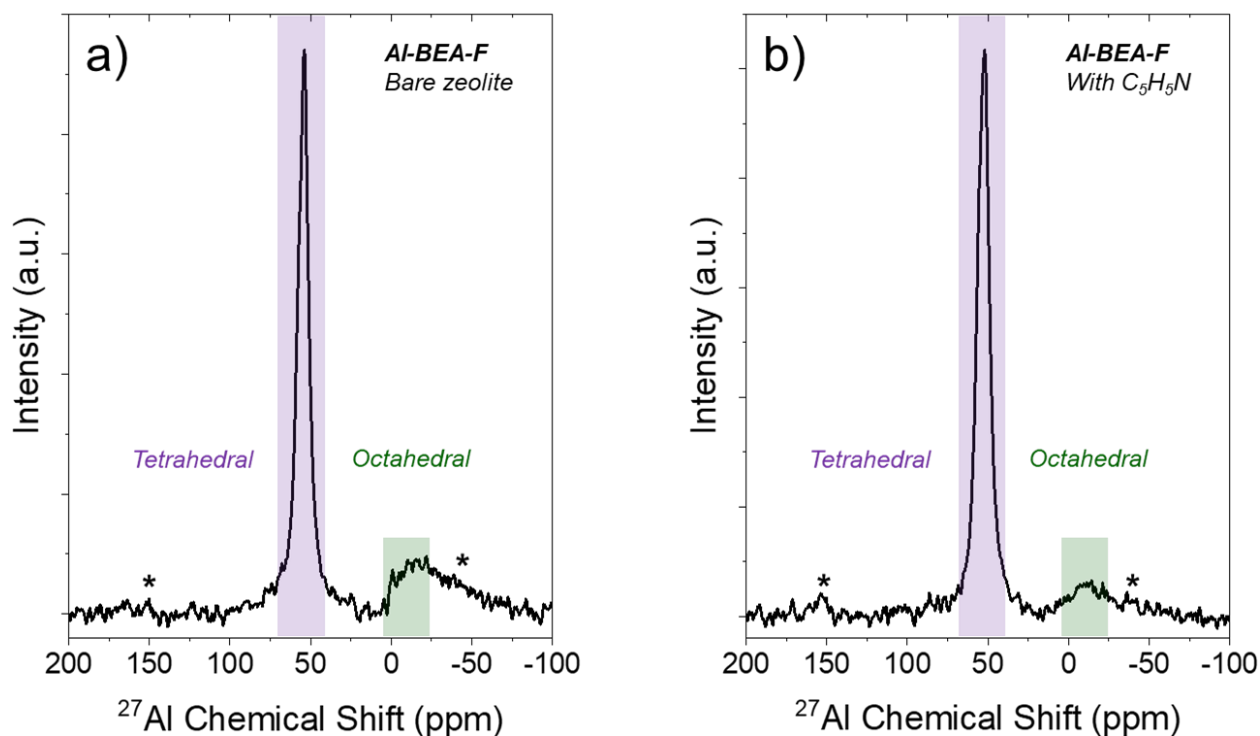


Figure D10. ^{27}Al NMR spectra for a) bare Al-BEA-F and b) Al-BEA-F impregnated with $\text{C}_5\text{H}_5\text{N}$ (298 K). The peaks representing tetrahedral and octahedral Al species are highlighted in purple and green, respectively. Asterisks represent spinning side-band features.

Figures D9 and **D10** present the ^{27}Al NMR spectra for the Al-BEA materials in the presence and absence of $\text{C}_5\text{H}_5\text{N}$. The percentage of octahedral Al was calculated from the ratio of the tetrahedral to octahedral peak area features (**Table D3**). Notably, the bare zeolites show greater percentages of octahedral Al than the materials impregnated with $\text{C}_5\text{H}_5\text{N}$. In the presence of H_2O , tetrahedral Al atoms may bind with H_2O molecules convert to an octahedral coordination.⁴³⁰⁻⁴³² We argue that adventitious H_2O adsorbed from the atmosphere contributes to the larger quantities of octahedral Al observed in the bare zeolite materials in **Figures D9** and **D10**. Previous works demonstrate that loading hydrated Brønsted acid zeolites with ammonia converts octahedral Al species back to tetrahedral Al sites, thus providing a reliable strategy to report octahedral Al content without interference from H_2O .⁴³²⁻⁴³⁴

Motivated by the role of ammonia shown in previous studies, we impregnated the Al-BEA materials with $\text{C}_5\text{H}_5\text{N}$ to revert hydrated Al species back to tetrahedral Al atoms. **Table D3** shows that the $\text{C}_5\text{H}_5\text{N}$ -incorporated materials show lower quantities of octahedral Al than the bare materials, but Al-BEA-OH (4%) and Al-BEA-F (10%) still contain nonzero quantities of octahedral Al. The percentages of octahedral Al obtained from this measurement align closely with the values from active site titrations (**Section D4**, *vide infra*), which yield octahedral Al percentages of 3% and 8% for Al-BEA-OH and Al-BEA-F, respectively. Overall, the spectra in **Figures D9** and **D10** support that Al-BEA-OH and Al-BEA-F contain minor quantities of octahedral Al that do not convolute the kinetics reported in **Chapter 5**.

Catalyst	% octahedral Al (bare zeolite)	% octahedral Al (with $\text{C}_5\text{H}_5\text{N}$)
Al-BEA-OH	12	4
Al-BEA-F	22	10

Table D3. Percentage of octahedral Al measured from ^{27}Al NMR spectra.

D1.8 Scanning Electron Micrographs of M-BEA Catalysts

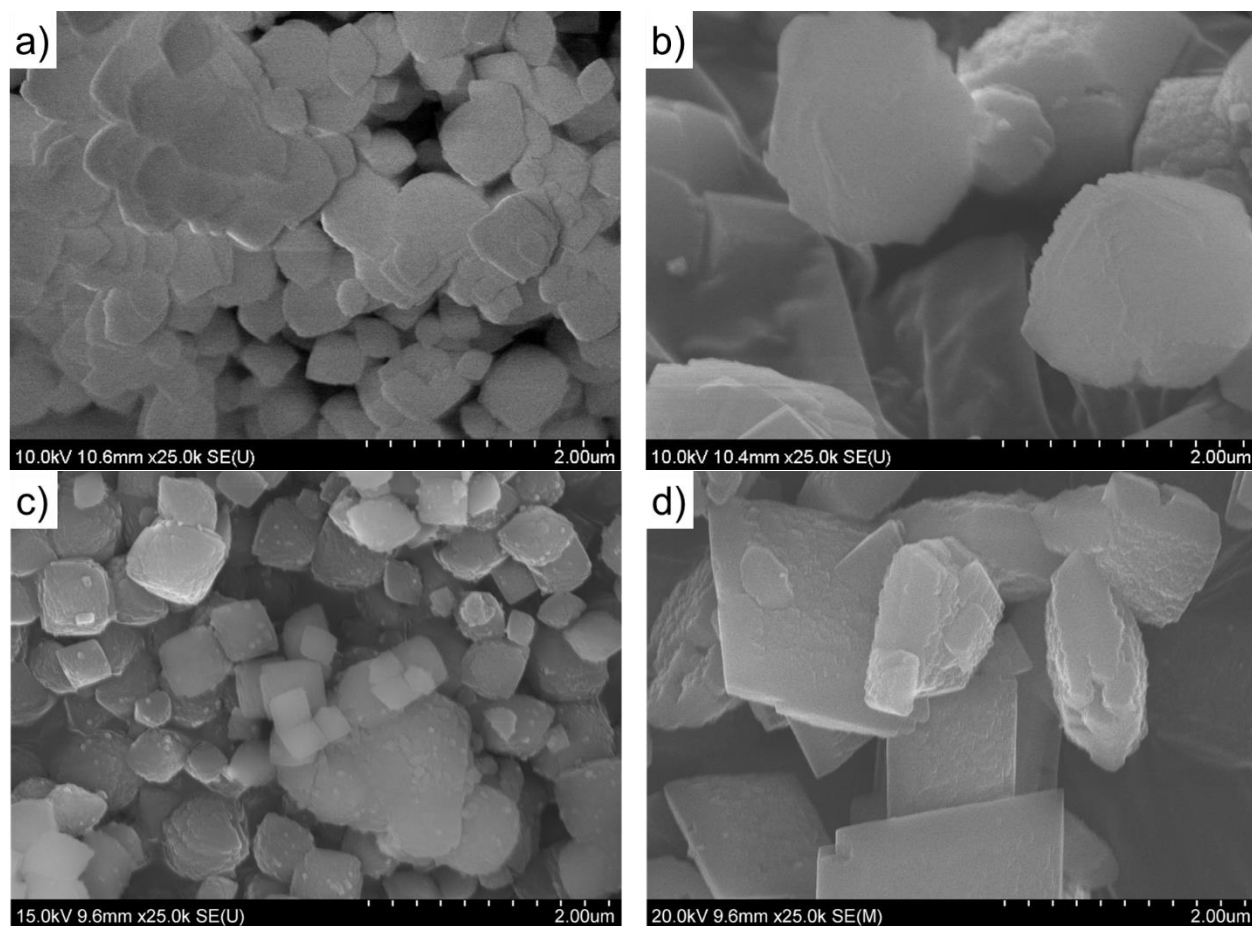


Figure D11. Representative high resolution scanning electron micrograph images of a) Al-BEA-OH, b) Al-BEA-F, c) Zr-BEA-OH, d) Zr-BEA-F.

The particle diameters of the M-BEA materials were estimated from scanning electron microscopy (SEM), with representative SEM images shown in **Figure D11**. Al-BEA-OH and Zr-BEA-OH both possess particles with mean diameters of $0.5 \pm 0.2 \mu\text{m}$, while Al-BEA-F and Zr-BEA-F show mean diameters of $2.0 \pm 0.5 \mu\text{m}$. The larger particle size of materials prepared in fluoride media compared to hydroxide media is consistent with previous reports over Ti-MFI^{134, 264} and Al-BEA⁴³⁵⁻⁴³⁸ materials.

The differences in particle size can lead to internal mass transfer artifacts. However, we exclude this possibility because site titration experiments with 1,2-diphenyl-1,2-ethylenediamine show that all M-BEA materials possess approximately 100% active metal atoms (**Figure D16**, *vide infra*). Therefore, differences in C_4H_8O ring-opening rates between M-BEA-OH and M-BEA-F materials do not stem from differences in the particle diameter.

D2. Calculation of Epoxide and Product Sensitivity Factors

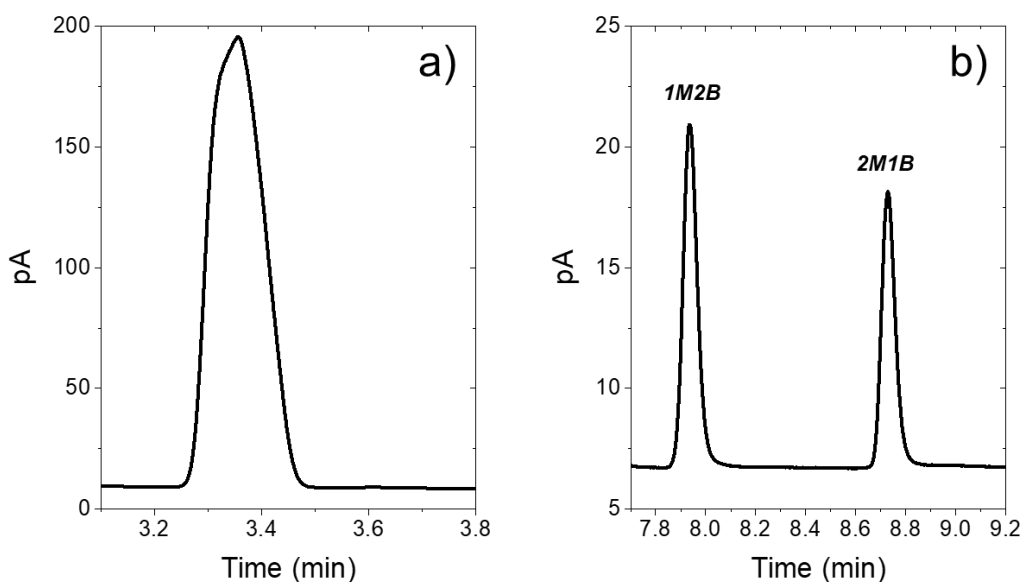


Figure D12. Raw GC chromatograms zoomed in to show peaks corresponding to (a) C_4H_8O , and (b) 1-methoxy-2-butanol and 2-methoxy-1-butanol formed by reaction of C_4H_8O with CH_3OH over Zr-BEA-OH for 1 h (0.005 M C_4H_8O , 6 M CH_3OH , CH_3CN , 308 K).

Figure D12 demonstrates the high signal-to-noise ratio of the epoxide and product peaks from the GC chromatograms, as well as the peak separation between the ring-opening products. GC chromatograms were collected as a function of concentrations (**Figure D13**) to determine the sensitivity factors of the epoxide and products using the as-purchased chemicals (see **Sections**

5.2.3 and 5.2.4 for sources and purities). **Table D4** reports the sensitivity factors, which equal the slope of the calibration curve fit lines in **Figure D13**.

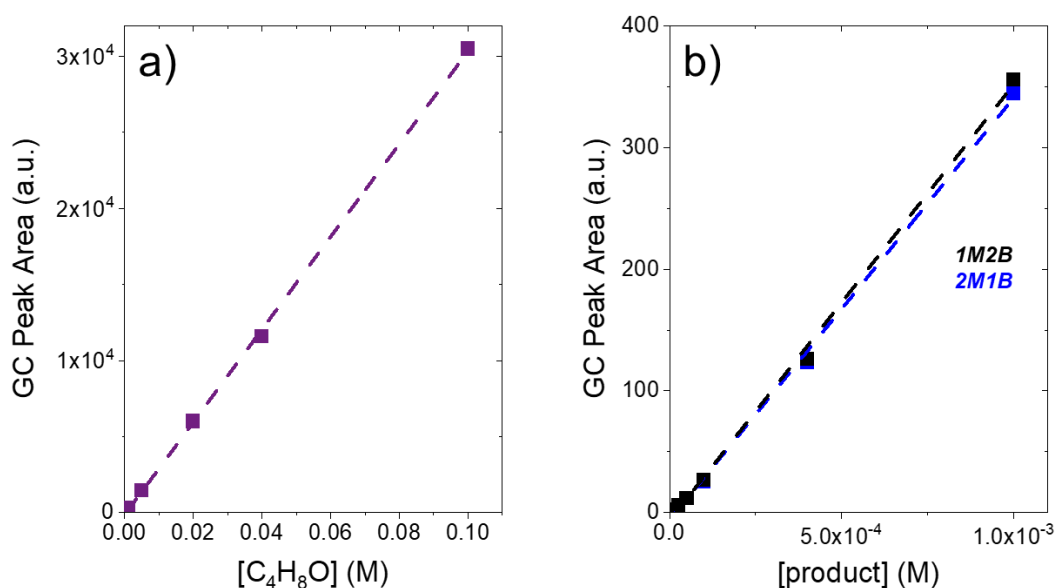


Figure D13. Integrated GC peak areas as a function of concentration for (a) C₄H₈O, and (b) 1-methoxy-2-butanol (black) and 2-methoxy-1-butanol (blue) in CH₃CN.

Compound	Sensitivity Factor (peak area M ⁻¹)
C ₄ H ₈ O	302810
1M2B	349380
2M1B	338550

Table D4. Sensitivity factors determined from calibration curves in **Figure D13**.

During reactions, the concentration of the products was calculated with the integrated peak areas and measured sensitivity factors:

$$[product] = \frac{GC\ Peak\ Area}{Sensitivity\ Factor} \quad (D2)$$

D3. Hot Filtrations and Madon-Boudart Criterion Tests to Identify Active Centers for Ring-Opening

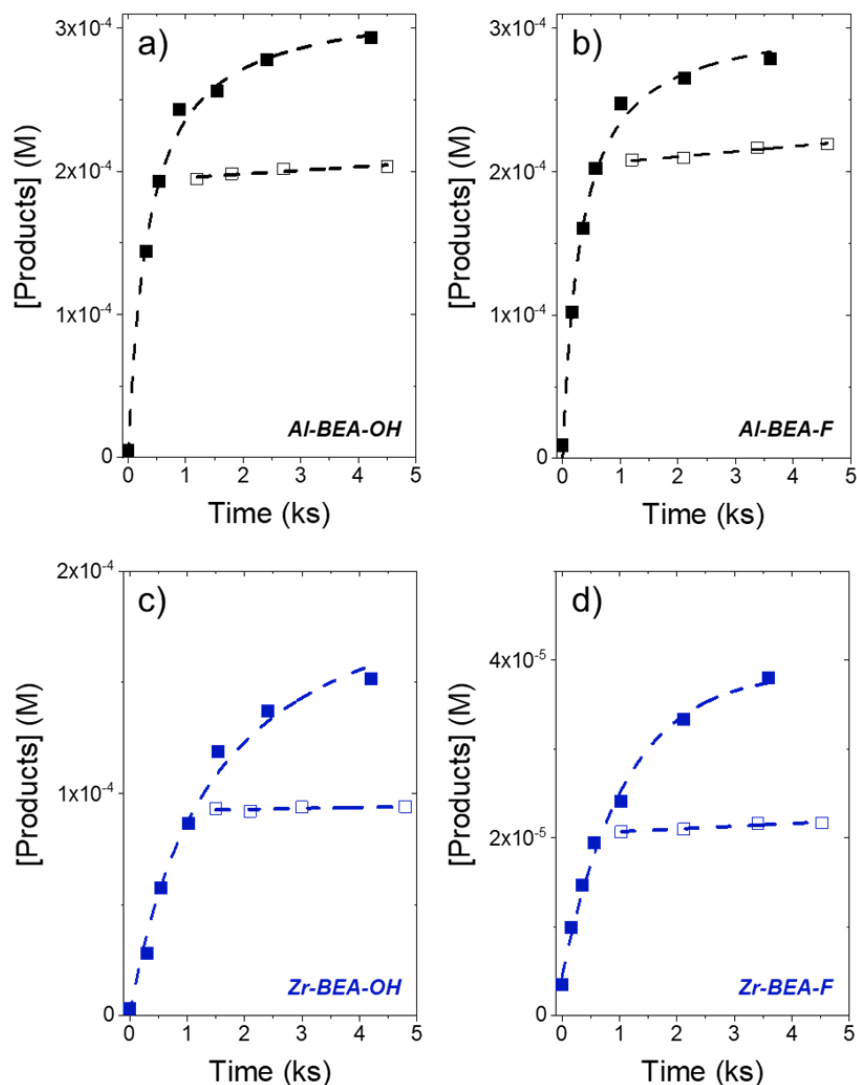


Figure D14. Measured total product concentrations (sum of [1M2B] and [2M1B]) as functions of time during hot filtration tests (0.005 M C_4H_8O , 6 M CH_3OH , CH_3CN solvent, 308 K) over (a) Al-BEA-OH, (b) Al-BEA-F, (c) Zr-BEA-OH, and (d) Zr-BEA-F. The hollow points represent epoxide concentrations from aliquots that were separated from the catalyst after ~10-15 min, while solid points indicate concentrations from aliquots that were kept in contact with the catalyst over the course of the reaction.

Figure D14 displays the results of the hot filtration tests for all M-BEA. For all M-BEA, product formation ceases after separating the solution from the catalyst (hollow points). This result

provides evidence that metal atoms do not leach from the *BEA framework, and the active sites remain within the framework during catalysis.

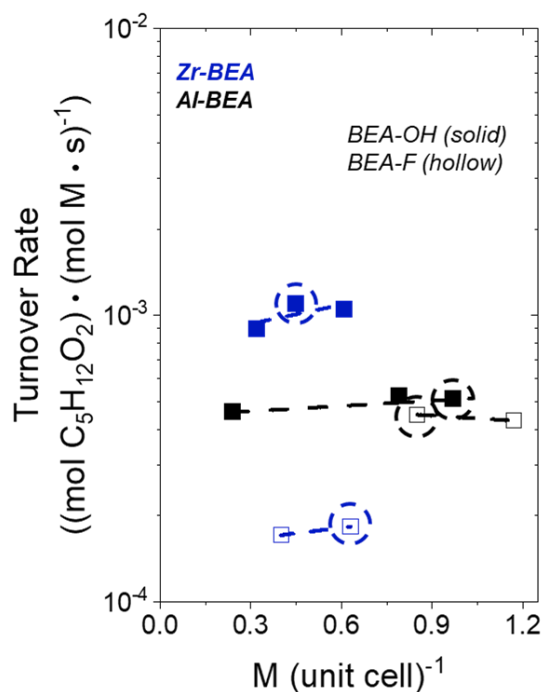


Figure D15. Total product formation rates from C₄H₈O ring-opening with CH₃OH (0.02 M C₄H₈O, 0.4 M CH₃OH, CH₃CN solvent, 308 K) as a function of active metal loading over hydrophilic (solid points) and hydrophobic (hollow) Zr- (blue) and Al-BEA (black) materials. The circled points signify the catalyst used for this study.

Figure D15 presents turnover rates as a function of metal loading for each M-BEA. Rates depend negligibly on metal loading within the range of loadings examined for all materials, ruling out contributions from intrapore mass transfer to turnover rate measurements.

Table D5 compares product formation rates per gram of catalyst for the catalysts used in this study and a dealuminated *BEA zeolite (Si-BEA-OH). The Si-BEA-OH materials shows formation rates 13 times less than the least active catalyst in this study (Zr-BEA-F), providing evidence that (SiOH)_x and Si-O-Si functions do not contribute significantly to the calculated

turnover rates for C₄H₈O ring-opening over M-BEA materials. Instead, C₄H₈O ring-opening occurs primarily at the active Al or Zr sites within M-BEA.

Catalyst	Product Formation Rate (mol C ₅ H ₁₂ O ₂) · (g _{cat} · s) ⁻¹
Al-BEA-OH	1.35 x 10 ⁻⁷
Al-BEA-F	1.17 x 10 ⁻⁷
Zr-BEA-OH	2.38 x 10 ⁻⁷
Zr-BEA-F	3.89 x 10 ⁻⁸
Si-BEA-OH	2.88 x 10 ⁻⁹

Table D5. Product formation rates per gram of catalyst for the M-BEA catalysts used in this study compared to Si-BEA-OH (0.02 M C₄H₈O, 0.4 M CH₃OH, CH₃CN solvent, 308 K). Rates for Si-BEA-OH were normalized by the number of (SiOH)_x groups in the material (3.047, see **Section D1.5**)

D4. Counting Active Sites with 1,2-Diphenyl-1,2-Ethylenediamine Titrations

Recently, phosphonic acids^{30, 32, 419-420} have been employed as titrants during liquid phase reactions to count or distinguish acid sites in Lewis acid materials. Amines have been used to probe both Lewis acid^{214, 421} and Brønsted acid sites⁴²²⁻⁴²³ for similar purposes. Therefore, we selected 1,2-diphenyl-1,2-ethylenediamine (DPED) as a titrant that could poison active sites in both Lewis and Brønsted acidic M-BEA. A line was fit to the linear portion of the plots in **Figure D16** and extrapolated to the x-axis to estimate the number of active sites present in the M-BEA materials. All materials show greater than 90% active metal atoms, providing evidence that differences in the quantity of active metal do not contribute to rate differences between M-BEA.

The change in concentration of DPED during the reactions in **Figure D16** was quantified by GC-FID. A GC calibration curve was developed for DPED, from which the moles of DPED in the liquid phase before and at the completion of the reaction was determined with GC peak areas. A separate DPED adsorption measurement was carried out in a dealuminated *BEA catalyst (Si-

BEA) to estimate contributions from DPED bound to $(\text{SiOH})_x$ and pore walls (i.e., Si-O-Si). The DPED volume for the Si-BEA control was chosen to match the largest volume used in an experiment in **Figure D16**. Noticeably, the liquid phase DPED concentration decreases by more than 97% in all experiments in **Figure D16** and the Si-BEA control after 1 h. This result suggests that any DPED that does not coordinate to Lewis or Brønsted acid sites can bind to $(\text{SiOH})_x$ or Si-O-Si linkages. Nevertheless, the suppression of rates and extrapolated linear fits in **Figure D16** provide strong evidence that DPED preferentially binds to Lewis and Brønsted acid sites, suppressing $\text{C}_4\text{H}_8\text{O}$ ring-opening over M-BEA.

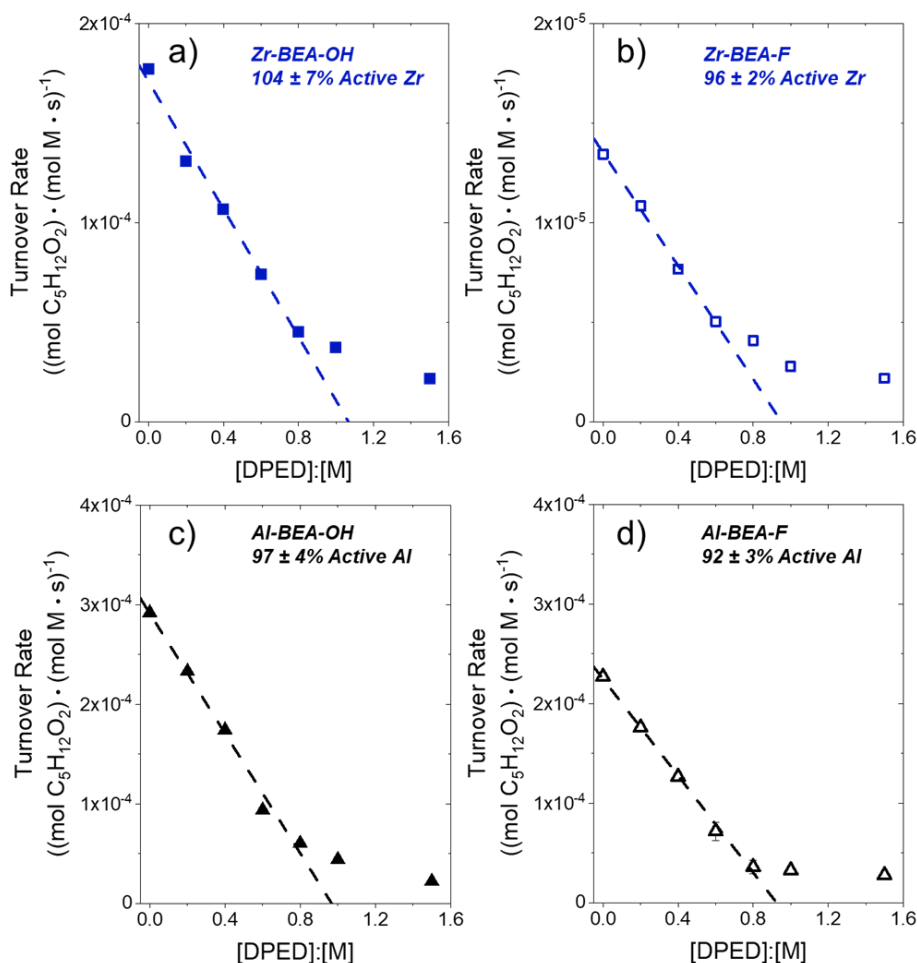


Figure D16. Total product formation rates from $\text{C}_4\text{H}_8\text{O}$ ring-opening with CH_3OH (0.005 M $\text{C}_4\text{H}_8\text{O}$, 0.4 M CH_3OH , CH_3CN solvent, 308 K) as a function of 1,2-diphenyl-1,2-ethylenediamine (DPED) to active metal ratio over hydrophilic (solid points) and hydrophobic (hollow) Zr- (blue) and Al-BEA (black) materials.

D5. Formation Rates of Individual Products of C₄H₈O Ring-Opening with CH₃OH

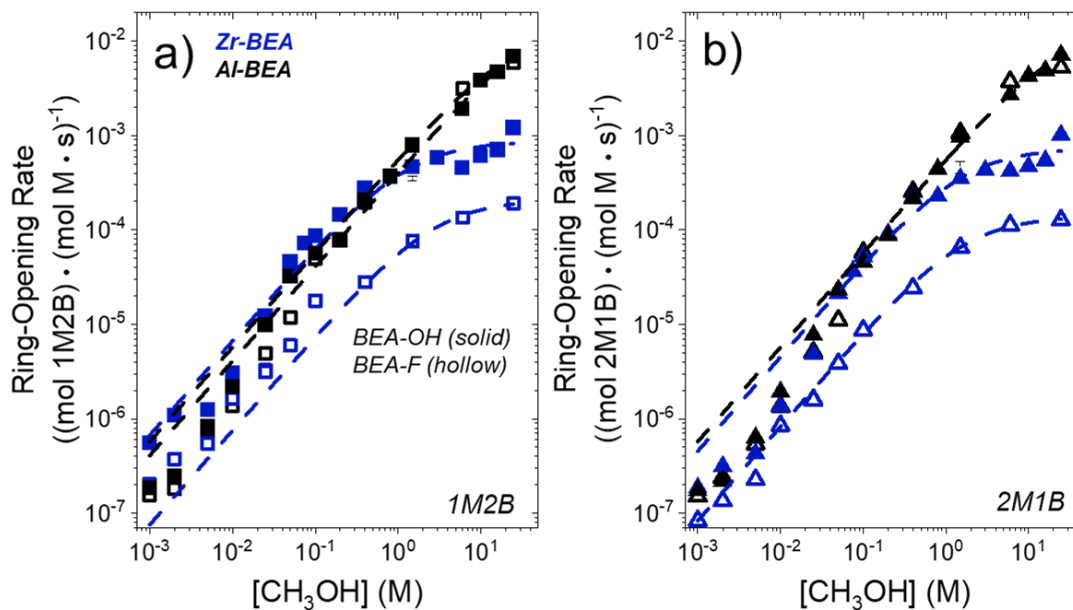


Figure D17. Formation rates of a) 1-methoxy-2-butanol (1M2B) and b) 2-methoxy-1-butanol (2M1B) products from C₄H₈O ring-opening with CH₃OH as functions of CH₃OH concentration over hydrophilic (solid points) and hydrophobic (hollow) Zr- (blue) and Al-BEA (black) materials (0.005 M C₄H₈O, CH₃CN solvent, 308 K).

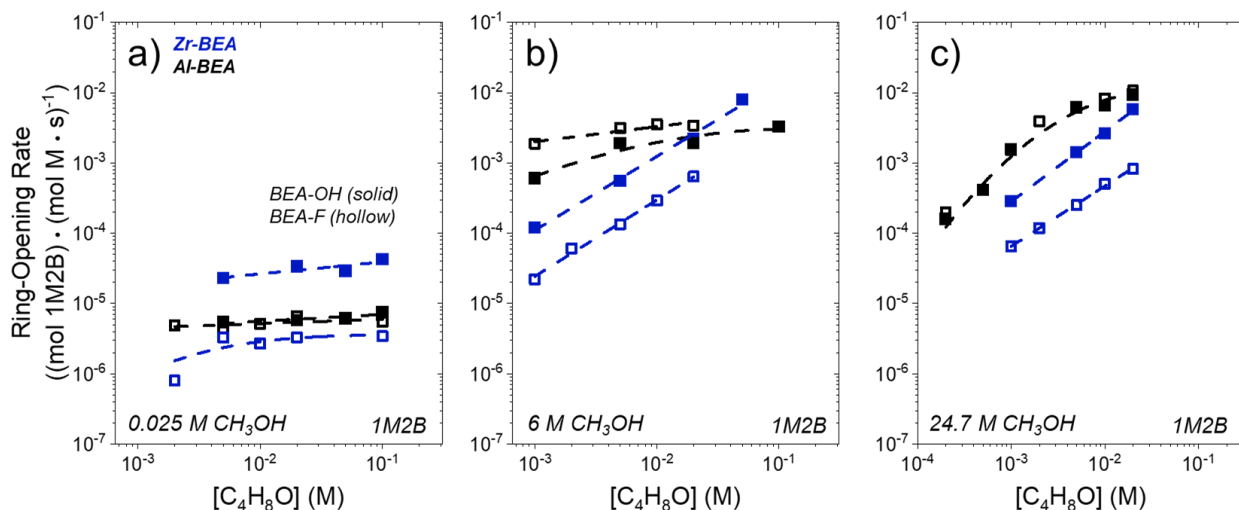


Figure D18. Formation rates of 1-methoxy-2-butanol (1M2B) from C₄H₈O ring-opening with CH₃OH as a function of C₄H₈O concentration at a) 0.025 M CH₃OH, b) 6 M CH₃OH, or c) neat (24.7 M) CH₃OH (CH₃CN solvent, 308 K) over hydrophilic (solid points) and hydrophobic (hollow) Zr- (blue) and Al-BEA (black) materials.

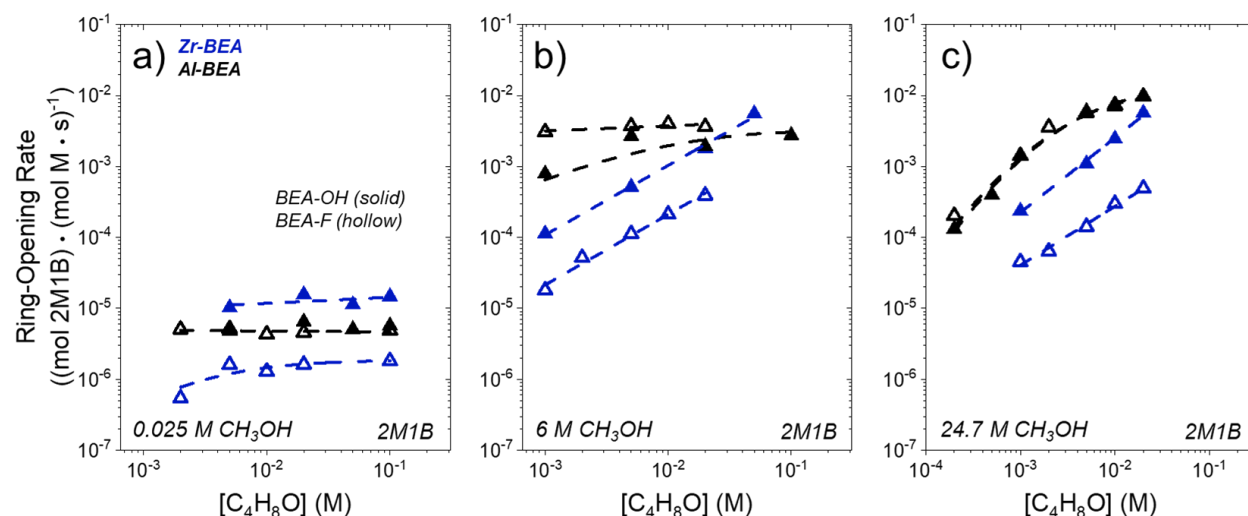
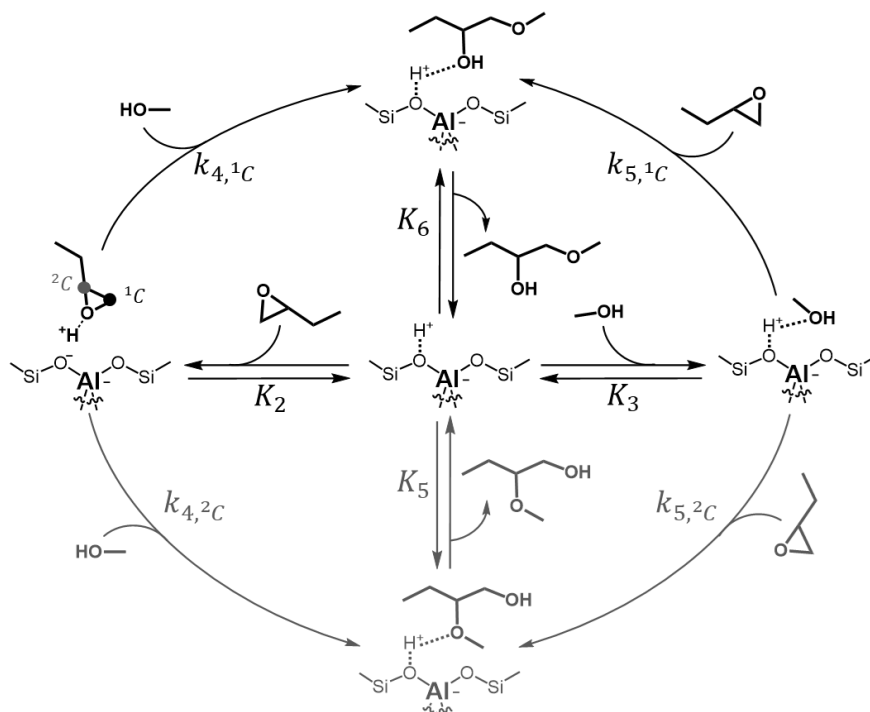


Figure D19. Formation rates of 2-methoxy-1-butanol (2M1B) from C_4H_8O ring-opening with CH_3OH as a function of C_4H_8O concentration at a) 0.025 M CH_3OH , b) 6 M CH_3OH , or c) neat (24.7 M) CH_3OH (CH_3CN solvent, 308 K) over hydrophilic (solid points) and hydrophobic (hollow) Zr- (blue) and Al-BEA (black) materials.

Figures D17 to D19 present the formation rates of the individual products from C_4H_8O ring-opening over M-BEA (total ring-opening rates shown in **Figures 5.1** and **5.2**). In all M-BEA and solvent composition combinations, both products show nearly identical formation rate dependences on $[C_4H_8O]$ and $[CH_3OH]$. The similar rate dependences provide compelling evidence that each product forms from identical reaction pathways and reactive intermediates, and differences in the stability of transition states between the products drive changes in regioselectivities.

D6. Derivation of Rate Expression for C₄H₈O Ring-Opening with CH₃OH over M-BEA



Scheme D1. Proposed catalytic cycle for C₄H₈O ring-opening with CH₃OH in CH₃CN solvent over Al-BEA zeolites. All adsorption steps are currently assumed as reversible. Steps to form 1M2B and 2M1B are denoted as ¹C or ²C, to signify nucleophilic attack on the primary and secondary carbons in the epoxide ring, respectively. For brevity, we do not show the reversible adsorption of CH₃CN molecules (step 1) in this cycle.

Scheme 5.2 and **Scheme D1** above present proposed catalytic cycles for the ring-opening of C₄H₈O with CH₃OH over Lewis and Brønsted acidic M-BEA materials, respectively. Each mechanism begins with the adsorption of CH₃CN (step 1), C₄H₈O (step 2), or CH₃OH (step 3). The 1M2B or 2M1B products may then form through one of two plausible kinetically relevant steps (4 and 5), where a liquid-phase CH₃OH or C₄H₈O molecule may then react with adsorbed C₄H₈O or CH₃OH, respectively. The products then desorb in a reversible step to complete the cycle, with steps 6 and 7 accounting for the individual products that can form.

The reaction likely does not proceed as a bimolecular Langmuir-Hinshelwood reaction between surface-bound CH₃OH and C₄H₈O because this would lead to squared dependences on

the CH₃OH and C₄H₈O terms in the denominator at sufficiently high coverages of either species. Rates would eventually decrease with increasing concentrations of CH₃OH and C₄H₈O in a bimolecular surface reaction. Rates show linear or zero order dependences over all conditions studied here, providing support that the reaction proceeds through an Eley-Rideal mechanism as illustrated in **Scheme 5.2** and **Scheme D1**.

Epoxide ring-opening rates for the two possible reaction paths can be modeled with **Equation 5.2**:

$$r_{RO} = r_4 + r_5 = k_4[C_4H_8O^*][CH_3OH] + k_5[C_4H_8O][CH_3OH^*] \quad (D3)$$

where k_4 and k_5 are the sum of the rate constants to form each product in steps 4 ($k_{4,1C}$, $k_{4,2C}$) and 5 ($k_{5,1C}$, $k_{5,2C}$) in **Scheme D1**, and $[C_4H_8O^*]$ and $[CH_3OH^*]$ represent the number of bound intermediates from each reactant. We apply the pseudo-state hypothesis to the respective bound intermediates, which gives:

$$r_{RO,C_4H_8O^*} = \frac{k_2k_4[C_4H_8O][CH_3OH][*]}{k_{-2}+k_4[CH_3OH]} + \frac{k_3k_5[C_4H_8O][CH_3OH][*]}{k_{-3}+k_5[C_4H_8O]} \quad (D4)$$

The total number of active sites in each M-BEA ([L]) can be written as:

$$[L] = [*] + [CH_3CN^*] + [CH_3OH^*] + [C_4H_8O^*] + [1M2B^*] + [2M1B^*] \quad (D5)$$

Where $[*]$ is the number of unoccupied active sites and the other terms represent the number of adsorbed solvent, reactant, and product molecules. Substituting in terms for the solvent, product, and reactant concentrations, rate constants, and equilibrium constants yields:

$$[L] = [*] \left(1 + K_1[CH_3CN] + \frac{k_2[C_4H_8O]}{k_{-2}+k_4[CH_3OH]} + \frac{k_3[CH_3OH]}{k_{-3}+k_5[C_4H_8O]} + \frac{k_4[CH_3OH]+k_5[C_4H_8O]+k_{-6}[1M2B]}{k_6} + \frac{k_4[CH_3OH]+k_5[C_4H_8O]+k_{-7}[2M1B]}{k_7} \right) \quad (D6)$$

Using **Equation D6** to substitute an expression for $[*]$ in **Equation D4** yields a full rate expression (**Equation 5.3**):

$$\frac{r_{RO}}{[L]} = \frac{\frac{k_2 k_4 [C_4H_8O][CH_3OH]}{k_{-2} + k_4 [CH_3OH]} + \frac{k_3 k_5 [C_4H_8O][CH_3OH]}{k_{-3} + k_5 [C_4H_8O]}}{1 + K_1 [CH_3CN] + \frac{k_2 [C_4H_8O]}{k_{-2} + k_4 [CH_3OH]} + \frac{k_3 [CH_3OH]}{k_{-3} + k_5 [C_4H_8O]} + \frac{k_4 [CH_3OH] + k_5 [C_4H_8O] + k_{-6} [1M2B]}{k_6} + \frac{k_4 [CH_3OH] + k_5 [C_4H_8O] + k_{-7} [2M1B]}{k_7}} \quad (D7)$$

Rates depend linearly on $[CH_3OH]$ and weakly on $[C_4H_8O]$ at ratios of $[CH_3OH]$ to $[C_4H_8O]$ less than 40 over each M-BEA, implicating active sites saturated with a C_4H_8O -derived species. In this case, the $[C_4H_8O^*]$ term dominates in the denominator of **Equation D7**, allowing all other terms to be canceled out:

$$\frac{r_{RO}}{[L]} = \frac{k_2 k_4 [CH_3OH](k_{-3} + k_5 [C_4H_8O]) + k_3 k_5 [CH_3OH](k_{-2} + k_4 [CH_3OH])}{k_2 (k_{-3} + k_5 [C_4H_8O])} \quad (D8)$$

This equation predicts a superlinear dependence of rates on $[CH_3OH]$ and a weak dependence on $[C_4H_8O]$ at low ratios of $[CH_3OH]$ to $[C_4H_8O]$. However, the form of this equation matches the trends observed in **Figures 5.1** and **5.2** at ratios of $[CH_3OH]$ to $[C_4H_8O]$ up to ~40 in Zr-BEA and ~1000 over Al-BEA only when the first term in the numerator dominates, which leads to the following:

$$\frac{r_{RO}}{[L]} = k_4 [CH_3OH] \quad (D9)$$

Neglecting the second term implies that the value of $k_2 k_4$ far exceeds $k_3 k_5$. C_4H_8O shows much larger adsorption enthalpies (~ -50 to -100 kJ mol⁻¹) than CH_3OH (~ 0 to -5 kJ mol⁻¹) over M-BEA, measured by ITC (*vide infra*, **Section D12**). These comparisons suggest that values for the equilibrium constants for binding C_4H_8O (K_2) exceed those for CH_3OH (K_3), which implies that C_4H_8O adsorbs more readily than CH_3OH (i.e., $k_2 \gg k_3$). The much greater values of k_2 relative to k_3 may lead to the first term in the numerator of **Equation D8** dominating up to $[CH_3OH]$ to $[C_4H_8O]$ ratios of ~40 in Lewis acids and ~1000 over Al-BEA, even if k_4 and k_5 have similar values. Consequently, these comparisons indicate that the difference in adsorption strength between C_4H_8O and CH_3OH leads to rate trends that agree with the form of **Equation 5.4** at sufficiently low ratios of $[CH_3OH]$ to $[C_4H_8O]$. These assumptions and adsorption enthalpy

measurements justify the simplification of **Equation D8** to **Equation D9** and the conclusion that C₄H₈O-derived species dominate active sites at these conditions.

At sufficiently high ratios of [CH₃OH] to [C₄H₈O] (> 500 for Lewis acids and > 5000 for Al-BEA), ring-opening rates shift to a weak dependence on [CH₃OH] and linear dependence on [C₄H₈O]. The [CH₃OH*] term now dominates in the denominator of **Equation D7**:

$$\frac{r_{RO}}{[L]} = \frac{k_2 k_4 [C_4H_8O] (k_{-3} + k_2 k_4 k_5 [C_4H_8O]) + k_3 k_5 [C_4H_8O] (k_{-2} + k_4 [CH_3OH])}{k_3 (k_{-2} + k_4 [CH_3OH])} \quad (D10)$$

Here, the numerator simplifies to a form that matches the linear rate dependence on [C₄H₈O] and weak dependence on [CH₃OH] under greater ratios of [CH₃OH]:[C₄H₈O] when the second term of the numerator dominates, which gives:

$$\frac{r_{RO}}{[L]} = k_5 [C_4H_8O] \quad (D11)$$

At sufficiently high ratios of [CH₃OH] to [C₄H₈O] (>500 in Lewis acids and ~5000 over Al-BEA), [CH₃OH] likely dominates over all terms in **Equation D10**, leading to a negligible value for the first term in the numerator. These assumptions lead to the form of **Equation D11** in solutions with a large stoichiometric excess of CH₃OH, even if k_4 and k_5 possess values of a similar magnitude. The rate expressions in **Equations D9** and **D11** account for all kinetic regimes observed as functions of reactant concentrations in **Figures 5.1** and **5.2**.

D7. Excess Energies to Probe Liquid-Phase C₄H₈O and CH₃OH Stability

	C ₄ H ₈ O			CH ₃ OH		
Solvent	γ	H^E (kJ mol ⁻¹)	G^E (kJ mol ⁻¹)	γ	H^E (kJ mol ⁻¹)	G^E (kJ mol ⁻¹)
CH ₃ CN	2.23	1.01	2.08	2.64	2.39	2.53
6 M CH ₃ OH (in CH ₃ CN)	2.91	3.52	2.78	1.77	2.43	1.48
12 M CH ₃ OH (in CH ₃ CN)	2.85	3.20	2.72	1.29	0.9	0.66
CH ₃ OH	3.62	1.70	3.35	1	0	0

Table D6. Activity coefficients (γ), excess enthalpies (H^E), and excess free energies (G^E) calculated at 308 K in mixtures of CH₃CN and CH₃OH. Activity coefficients were obtained with the UNIFAC method on ChemCAD.

Table D6 presents the excess energies and activity coefficients for C₄H₈O and CH₃OH in mixtures of CH₃OH and CH₃CN at 308 K. The equations used to compute the excess energies from the activity coefficients are as follows:

$$G_j^E = RT * \ln(\gamma_j) \quad (D12)$$

$$H_j^E = -RT^2 * \frac{d \ln(\gamma_j)}{dT} \quad (D13)$$

where j represents C₄H₈O or CH₃OH here, R equals the ideal gas constant, and T represents temperature. The differential term $\left(\frac{d \ln(\gamma_j)}{dT}\right)$ was obtained by calculating activity coefficients between 303-323 K by increments of 5 K. The natural log of the activity coefficients was plotted against the temperature, and the slope of this line equaled the differential term.

Notably, γ values vary by factors of less than 2 and 3 for C₄H₈O and CH₃OH, respectively, across the range of solvent compositions examined for ring-opening and C₄H₈O adsorption. Furthermore, both H^E and G^E values span a range of less than 3 kJ mol⁻¹ across solvent compositions. The weak dependences of these values on the mixing ratios of CH₃OH and CH₃CN

support that the stability of reactive species and adsorbates in the liquid phase does not drive changes in ring-opening rates, activation enthalpies for ring-opening, and enthalpies of adsorption for C₄H₈O.

D8. Activation Enthalpy and Entropy Calculations and Supplemental Data

$\Delta H^\ddagger$ and $\Delta S^\ddagger$ values to form each ring-opening product were calculated using van't Hoff analysis. Applying transition state theory and substituting an expression for the apparent free energy to **Equations D14** and **D15** yields alternate rate expressions for ring-opening through either the bound C₄H₈O path (C₄H₈O MARI) or bound CH₃OH route (CH₃OH MARI):

$$\frac{r_x}{[L]} = \frac{k_B T}{h} \cdot \exp\left(-\frac{\Delta G_x^\ddagger}{RT}\right) \cdot [CH_3OH] \quad (D14)$$

$$\frac{r_x}{[L]} = \frac{k_B T}{h} \cdot \exp\left(-\frac{\Delta G_x^\ddagger}{RT}\right) \cdot [C_4H_8O] \quad (D15)$$

Where x represents the two possible products, 1M2B and 2M1B. Rearranging and substituting in the apparent activation enthalpy and entropy:

$$\ln\left(\frac{r_x}{[L]} \frac{h}{k_B T [CH_3OH]}\right) = \frac{1}{T} \left(\frac{-\Delta H_x^\ddagger}{R}\right) + \frac{\Delta S_x^\ddagger}{R} \quad (D16)$$

$$\ln\left(\frac{r_x}{[L]} \frac{h}{k_B T [C_4H_8O]}\right) = \frac{1}{T} \left(\frac{-\Delta H_x^\ddagger}{R}\right) + \frac{\Delta S_x^\ddagger}{R} \quad (D17)$$

The natural log term on the left side of **Equations D16** and **D17** was plotted against the inverse temperature for each product. A line was fit to this data (**Figure D20**), where the slope of this line equaled the negative of the apparent activation enthalpy divided by the ideal gas constant, and the y-intercept equaled the apparent activation entropy divided by the ideal gas constant (**Table D6**).

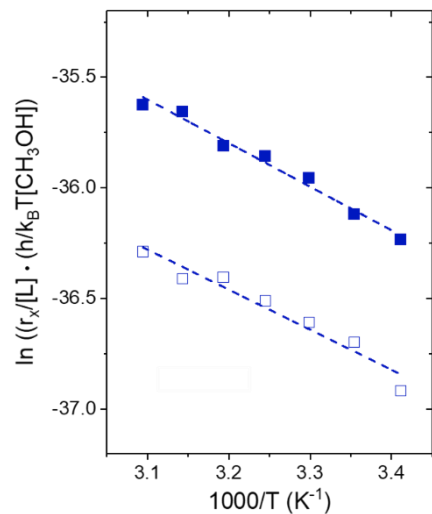


Figure D20. Representative Eyring plot for C₄H₈O ring-opening (0.005 M C₄H₈O, 0.025 M CH₃OH, CH₃CN solvent, 293-323 K) over Zr-BEA-OH to form 1-methoxy-2-butanol (solid points) and 2-methoxy-1-butanol (hollow points).

$\frac{-\Delta H_{1M2B}^{\ddagger}}{R}$	$\frac{\Delta S_{1M2B}^{\ddagger}}{R}$	$\frac{-\Delta H_{2M1B}^{\ddagger}}{R}$	$\frac{\Delta S_{2M1B}^{\ddagger}}{R}$
-2.0 ± 0.1	-29.5 ± 1.0	-1.8 ± 0.2	-30.7 ± 0.6

Table D7. Activation enthalpy and entropy to form each product in C₄H₈O ring-opening divided by the ideal gas constant, obtained from the slope and intercept, respectively, of **Figure D20**.

D9. Kinetic Measurements Under C₄H₈O-Covered Active Sites at High [C₄H₈O]

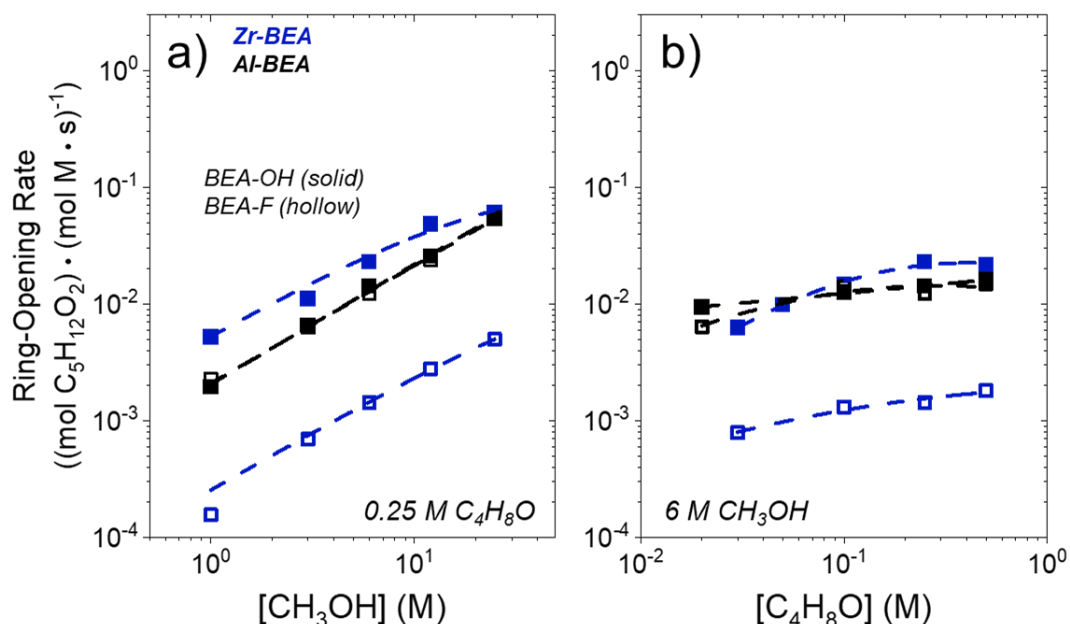


Figure D21. Turnover rates for C₄H₈O ring-opening with CH₃OH as functions of a) CH₃OH concentration at 0.25 M C₄H₈O (CH₃CN solvent, 308 K) and b) C₄H₈O concentration at 6 M CH₃OH (CH₃CN solvent, 308 K) over hydrophilic (solid points) and hydrophobic (hollow) Zr- (blue) and Al-BEA (black) materials.

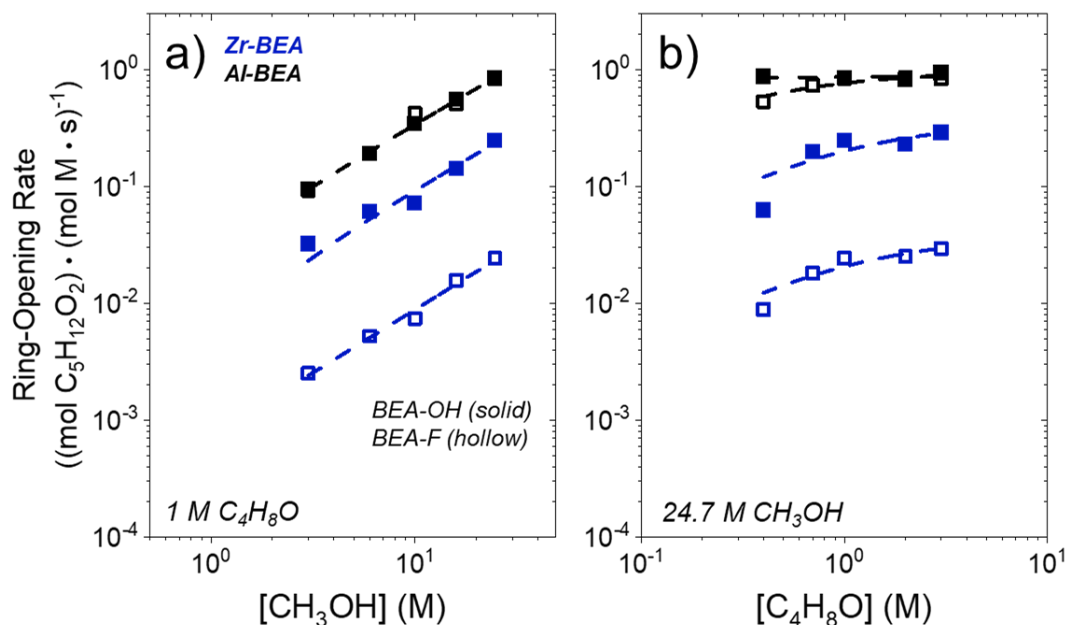


Figure D22. Turnover rates for C₄H₈O ring-opening with CH₃OH as functions of a) CH₃OH concentration at 1 M C₄H₈O (CH₃CN solvent, 308 K) and b) C₄H₈O concentration at 24.7 M CH₃OH (308 K) over hydrophilic (solid points) and hydrophobic (hollow) Zr- (blue) and Al-BEA (black) materials.

Figure D21 and **Figure D22** present turnover rates for C_4H_8O ring-opening as a function of $[CH_3OH]$ and $[C_4H_8O]$ at high concentrations of $[C_4H_8O]$. All materials show a regime of first-order rate dependence on $[CH_3OH]$, under which rates were then measured at varying $[C_4H_8O]$. Under this regime, materials show a corresponding zero-order rate dependence on $[C_4H_8O]$, suggesting that C_4H_8O saturates active sites even at these high concentrations of $[C_4H_8O]$. The activation barriers reported in **Figure 5.3** were made under these conditions to ensure C_4H_8O -covered active sites at each $[CH_3OH]$.

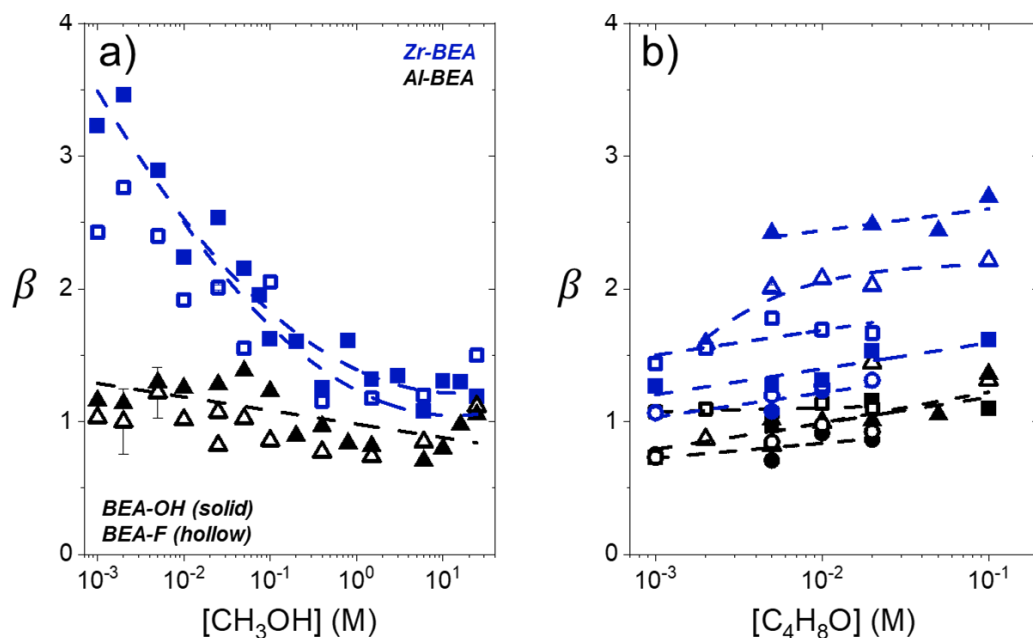


Figure D23. Values of β for C_4H_8O ring-opening with CH_3OH as a function of a) CH_3OH concentration (0.005 M C_4H_8O , CH_3CN solvent, 308 K), and b) C_4H_8O concentration at 0.01 M (triangles), 6 M (circles), or 24.7 M CH_3OH (squares) (CH_3CN , 308 K) over hydrophilic (solid) and hydrophilic (hollow) Al- (black) and Zr-BEA (blue).

Figure D23a shows β values for C_4H_8O ring-opening at a constant $[C_4H_8O]$ (0.005 M), with regimes under which C_4H_8O or CH_3OH covers active sites. **Figure D23b** reveals the β values under several $[CH_3OH]$, also under a regime where either C_4H_8O or CH_3OH covers active sites. Notably, **Figure D23** shows very similar trends to **Figure 5.7**, where greater $[CH_3OH]$ leads to

lower β values and greater $[C_4H_8O]$ provides higher β values. The similarity among the trends demonstrates that the shift from C_4H_8O to CH_3OH -saturated active sites at high $[CH_3OH]$ in **Figure D23** does not strongly affect trends in β , supporting that the differences in β in **Figure 5.7** stem from changes in the intrapore solvent environment rather than any influence of the dominant surface intermediate.

D10. Measurements of Intrapore Solvent Composition

The liquid-phase concentrations of mixtures of CH_3OH and CH_3CN were quantified by GC before and after contact with M-BEA to determine the intrapore solvent composition. The ratio of the GC peak areas for each component was calculated for each sample before ($A_{CH_3OH:CH_3CN,initial}$) and after ($A_{CH_3OH:CH_3CN,final}$) adding the catalyst to the mixture. Then, the known initial mole fraction of CH_3OH ($x_{CH_3OH,bulk,initial}$) was used to calculate the final bulk solvent fractions:

$$x_{CH_3OH,bulk,final} = x_{CH_3OH,bulk,initial} * \frac{A_{CH_3OH:CH_3CN,final}}{A_{CH_3OH:CH_3CN,initial}} \quad (D18)$$

$$x_{CH_3CN,bulk,final} = 1 - x_{CH_3OH,bulk,final} \quad (D19)$$

The fraction of the initial solvent volume remaining in the bulk solvent after adsorption ($x_{bulk,final}$) was then calculated by estimating the fraction of solvent adsorbed from the bulk solvent ($V_{solvent,ads}$):

$$V_{solvent,ads} = m_{zeolite} * V_{pore,*BEA} \quad (D20)$$

$$x_{bulk,final} = 1 - \left(\frac{V_{solvent,ads}}{V_{solvent,total}} \right) \quad (D21)$$

where $m_{zeolite}$ is the mass of M-BEA added to the solvent and $V_{pore,*BEA}$ is the pore volume of *BEA, measured for a Ti-BEA material in a previous study by Ar physisorption²¹¹ and assumed to be identical for all M-BEA here.

From there, the intrapore molar ratio ($\frac{n_{CH_3OH,pore}}{n_{CH_3CN,pore}}$) and CH_3OH fraction ($x_{CH_3OH,pore}$) can be calculated:

$$\frac{n_{CH_3OH,pore}}{n_{CH_3CN,pore}} = \frac{x_{CH_3OH,bulk,initial} - (x_{bulk,final} * x_{CH_3OH,bulk,final})}{x_{CH_3CN,bulk,initial} - (x_{bulk,final} * x_{CH_3CN,bulk,final})} \quad (D22)$$

$$x_{CH_3OH,pore} = \frac{\frac{n_{CH_3OH,pore}}{n_{CH_3CN,pore}}}{1 - \frac{n_{CH_3OH,pore}}{n_{CH_3CN,pore}}} \quad (D23)$$

Figure 5.4a reports $x_{CH_3OH,bulk}$ values as a function of the ratio of $x_{CH_3OH,pore}$ to $x_{CH_3OH,bulk}$, defined as χ in **Equation 5.11**:

$$\chi = \frac{x_{CH_3OH,pore}}{x_{CH_3OH,bulk}} \quad (D24)$$

A full analysis of these solvent uptake measurements are included in **Section 5.3.3**. Generally, **Figure 5.4a** demonstrates that β values decrease at greater $x_{CH_3OH,pore}$ for all M-BEA, providing evidence that the solvent structure surrounding active sites may strongly influence regioselectivities for C_4H_8O ring-opening through changes in $G_{2M1B}^{\ddagger,\varepsilon}$ and $G_{1M2B}^{\ddagger,\varepsilon}$. Of note, this result demonstrates that the choice of active metal not only influences G^0 values of reactive species through covalent interactions, but also can indirectly affect G^ε values by influencing the surrounding solvent structure. The choice of active metal leads to a span of β values even at nearly identical $x_{CH_3OH,pore}$, showing that differences in G^0 stemming from the properties of the active site contribute to differences in β .

D11. Isothermal Titration Calorimetry Thermograms and Heats per Injection

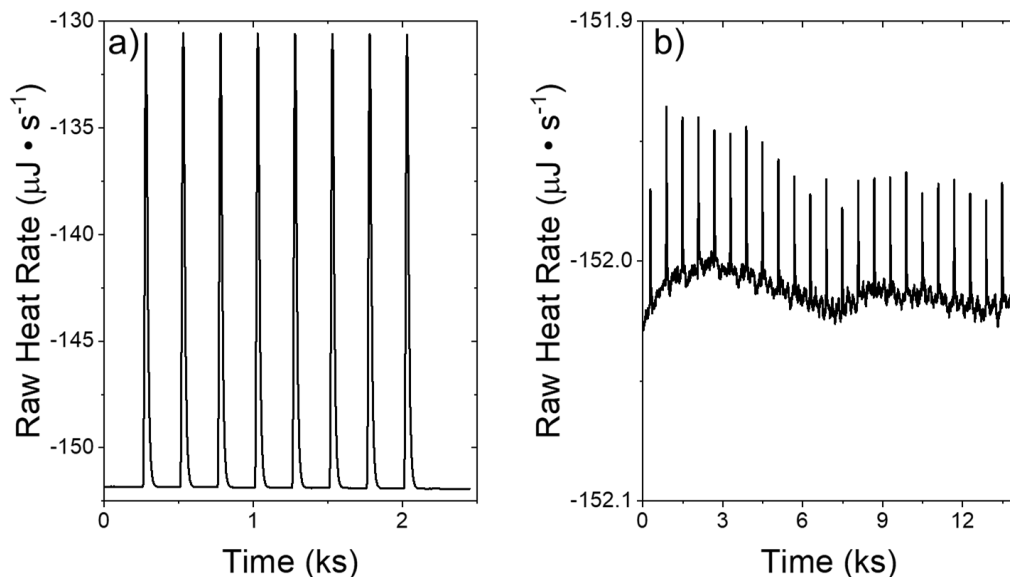


Figure D24. a) ITC thermogram from the electrical calibration of the NanoITC. b) ITC thermogram from the water-water adsorption to check the cleanliness of the ITC cell.

The plots in **Figure D24** were obtained during the cleaning and calibration procedures for isothermal titration calorimetry (ITC), as discussed in **Section 5.2.4**. **Figure D24a** shows the heat released from the sequential pulses during the electrical calibration. The instrument gave a calibration factor after the calibration was completed, for which values greater than 0.98 were assumed to be satisfactory. **Figure D24b** shows the heat released during the water-water injection, during which each 1 μL injection led to a peak with an area between -3 and +3 μJ .

Figure D25 shows an acid-base titration of NaHCO_3 into HNO_3 , which was used as a standard to verify the results obtained from the NanoITC. The adsorption enthalpy calculated from **Figure D25b** was $-8.1 \pm 1.2 \text{ kJ mol}^{-1}$, which agrees well with the reported enthalpy of -9.1 kJ mol^{-1} .^{1, 353-354} ΔH_{ads} values for all ITC experiments shown here and **Figure 5.5** were calculated by averaging the non-opaques points in the heat vs. coverage plot, from a regime in which the integrated heat remains approximately constant. The ΔH_{ads} values are illustrated by the dashed

line intersecting these points. The uncertainties were calculated from a single standard deviation among the points used to calculate ΔH_{ads} .

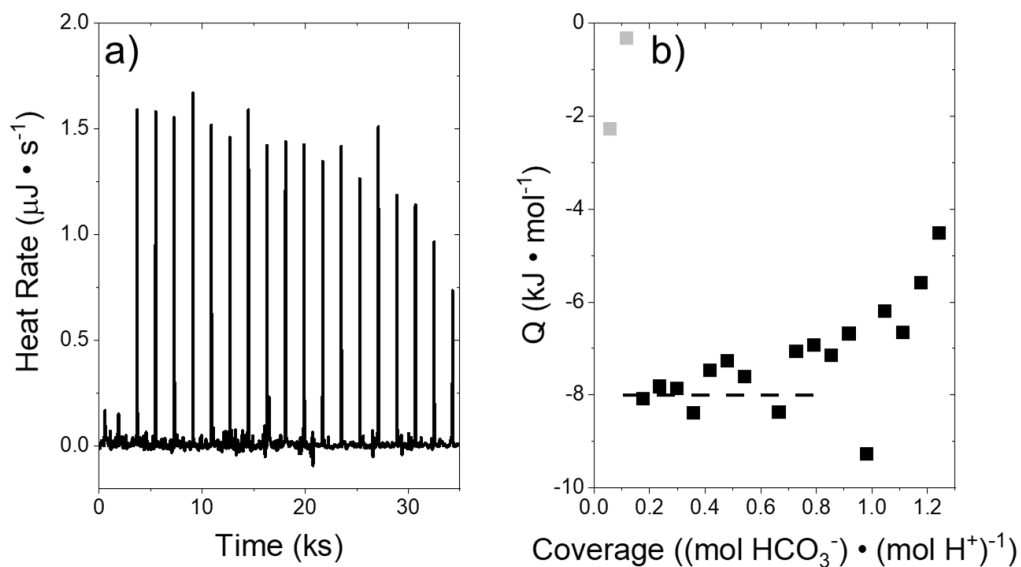


Figure D25. a) ITC thermogram from the acid-base titration of HNO_3 (0.0005 M in 0.1 M NaCl) with NaHCO_3 (0.0052 M in 0.1 M NaCl), b) the corresponding heats released as a function of bicarbonate ion coverage.

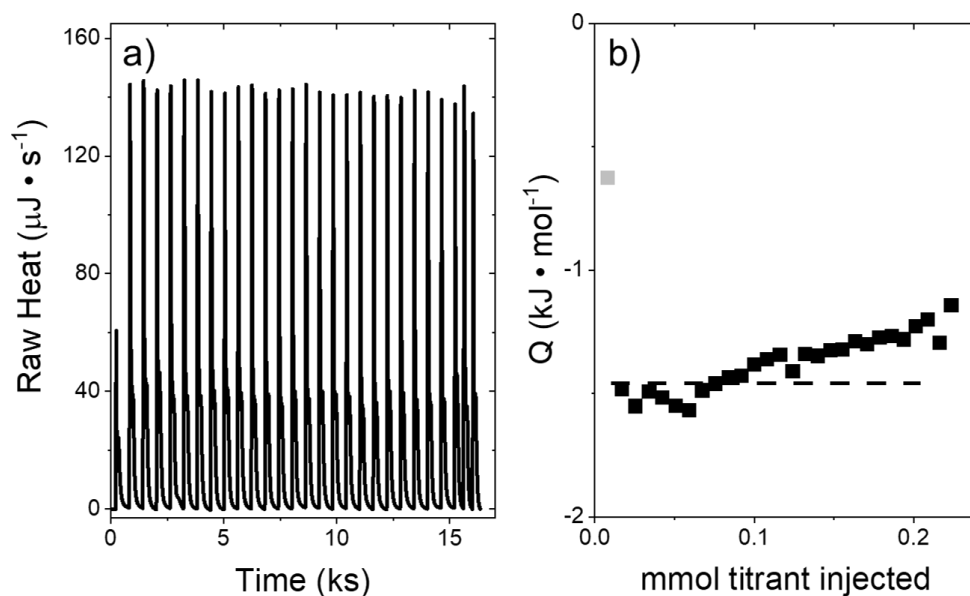


Figure D26. a) ITC thermogram from the titration of CH_3OH with neat 1M2B (8.7 M 1M2B, 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

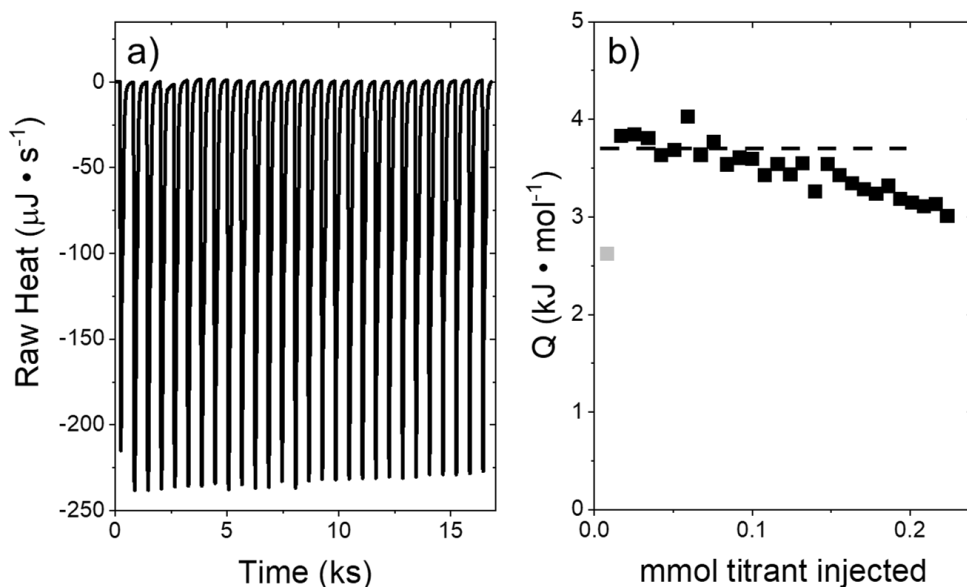


Figure D27. a) ITC thermogram from the titration of CH_3CN with neat 1M2B (8.7 M 1M2B, 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

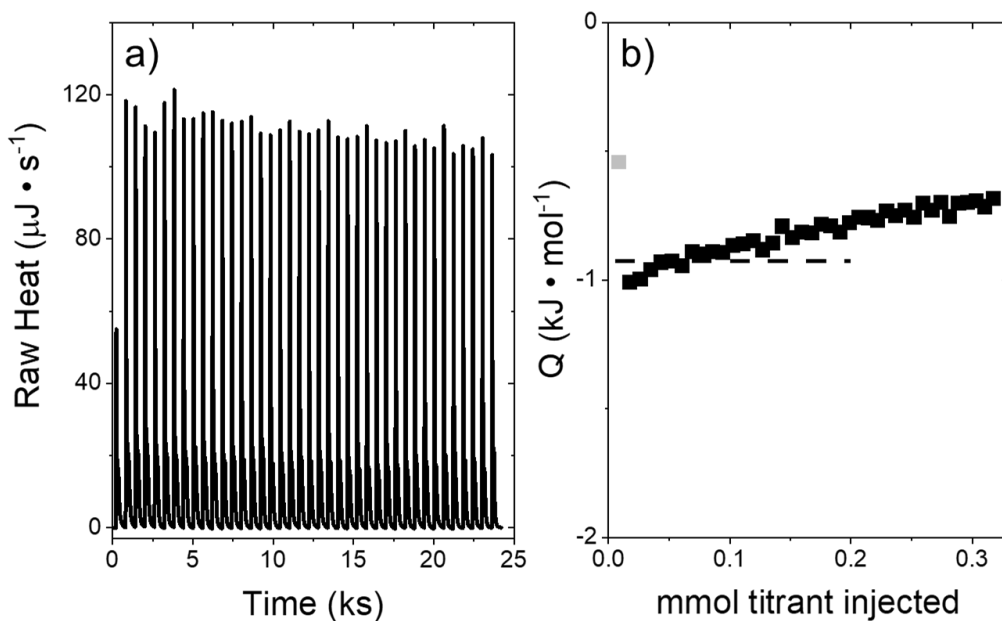


Figure D28. a) ITC thermogram from the titration of CH_3OH with neat 2M1B (8.9 M 2M1B, 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

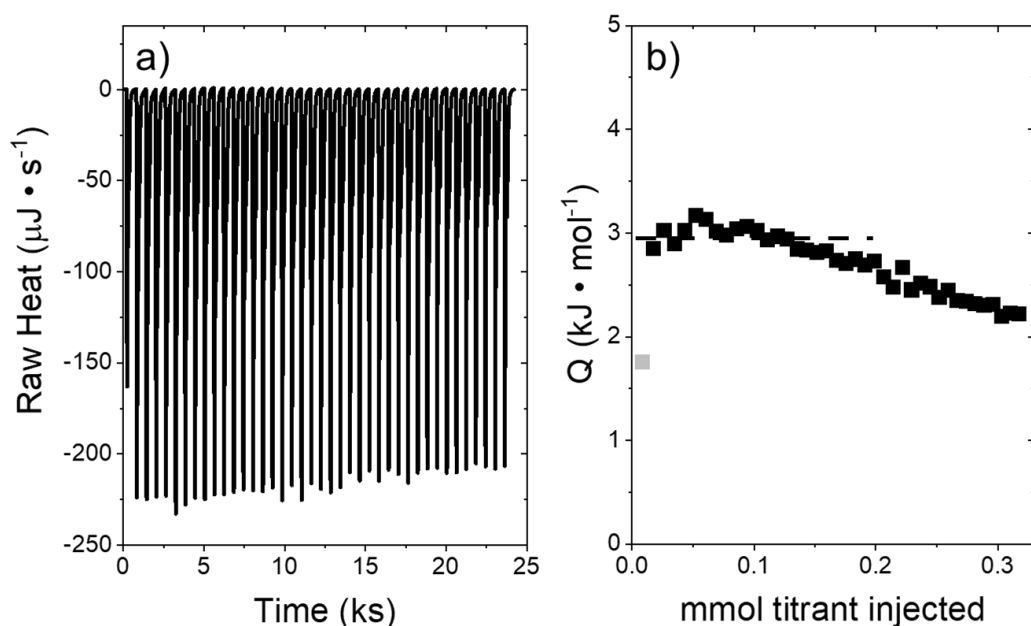


Figure D29. a) ITC thermogram from the titration of CH_3CN with neat 2M1B (8.9 M 2M1B, 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

Figures D26 to D29 report the heat changes from the injection of the neat ring-opening products into CH_3OH or CH_3CN . Each product adsorbs exothermically into CH_3OH and endothermically into CH_3CN . 1M2B shows a more exothermic enthalpy of mixing into CH_3OH than 2M1B, but 2M1B shows a less endothermic enthalpy of mixing into CH_3CN than 1M2B. While these measurements provide insight into the stability of the products in CH_3OH and CH_3CN -rich solvents, they do not correlate with the trends of β values or $\Delta H_{\text{ads,prod.}}$ values into each solvent, indicating that the active metal and solvating environment within the pores of M-BEA govern these differences.

Figure D30 presents an ITC thermogram and heat release plot from the adsorption of $\text{C}_4\text{H}_8\text{O}$ into Al-BEA at high coverages, to test if lateral interactions between nearby active sites play a role in the adsorption enthalpy of $\text{C}_4\text{H}_8\text{O}$. The integrated heat begins to decrease sharply near an epoxide coverage of 1, which supports that the Brønsted acid sites bind 1 epoxide molecule on average. Furthermore, the integrated heats change negligibly as the epoxide coverage

approaches 1, which suggests that lateral interactions do not play a strong role between proximal active sites. The absence of these effects in the material with Al-BEA, which shows the highest density of active sites (Si:M ~70), also indicates that lateral interactions will not play a role in Ti-, Sn-, or Zr-BEA (Si:M > 90).

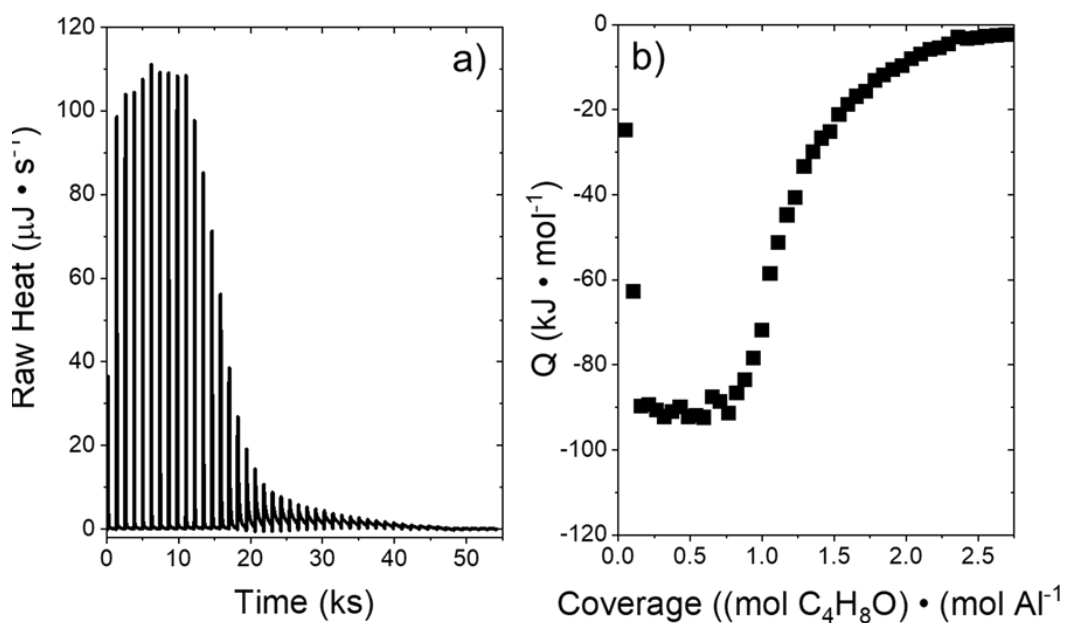


Figure D30. a) ITC thermogram from the titration of Al-BEA-OH with $\text{C}_4\text{H}_8\text{O}$ (0.05 M $\text{C}_4\text{H}_8\text{O}$ in CH_3OH , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

The ITC thermogram and heat release plots for all ITC experiments used to calculate the adsorption enthalpies of $\text{C}_4\text{H}_8\text{O}$ into M-BEA, which were run at low coverages as compared to **Figure D30**, are shown below. ITC measurements for CH_3OH adsorption into M-BEA are also shown below, although these were performed at higher titrant concentrations (and thus higher coverages) because CH_3OH adsorbs weakly and higher concentrations are needed to observe sufficiently large peaks in the thermogram.

As discussed in **Section 5.3.3**, early injections often show lower heat released than expected due to the evaporation of liquid from the syringe needle. Although less common, some

of the experiments below show outlier points at later injections, which may result from an inconsistent volume or epoxide concentration in those injections.

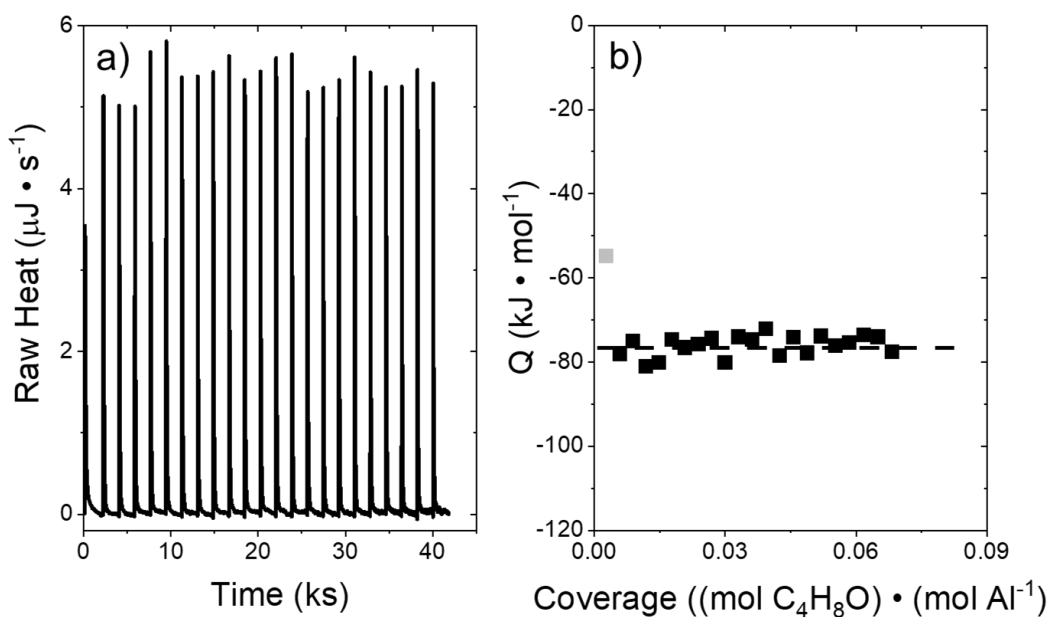


Figure D31. a) ITC thermogram from the titration of Al-BEA-OH with $\text{C}_4\text{H}_8\text{O}$ (0.005 M $\text{C}_4\text{H}_8\text{O}$ in CH_3OH , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

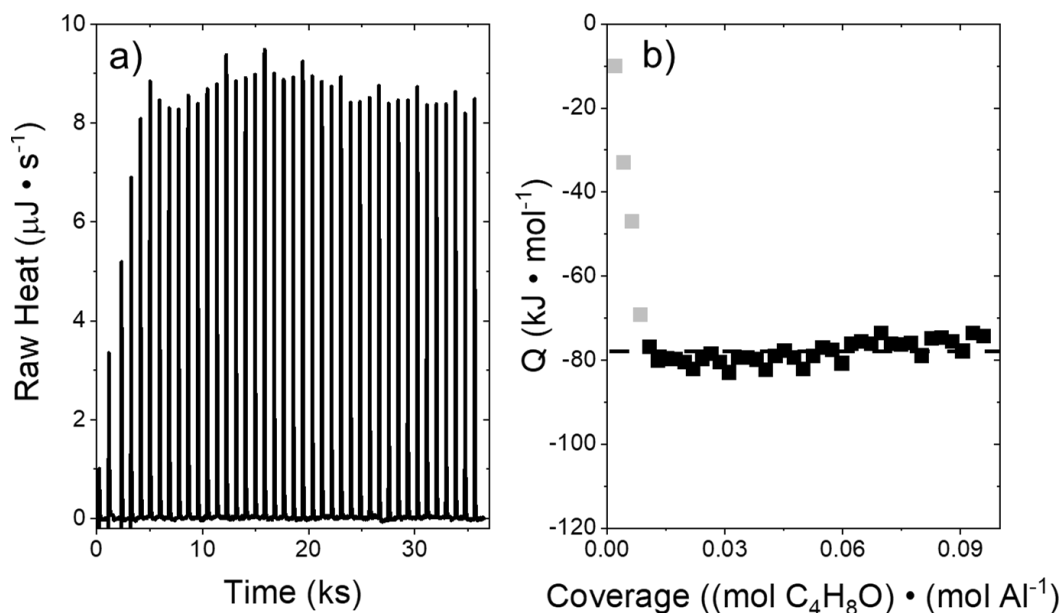


Figure D32. a) ITC thermogram from the titration of Al-BEA-OH with $\text{C}_4\text{H}_8\text{O}$ (0.005 M $\text{C}_4\text{H}_8\text{O}$ in CH_3OH , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected. This point was repeated to ensure accuracy and reproducibility of measurements.

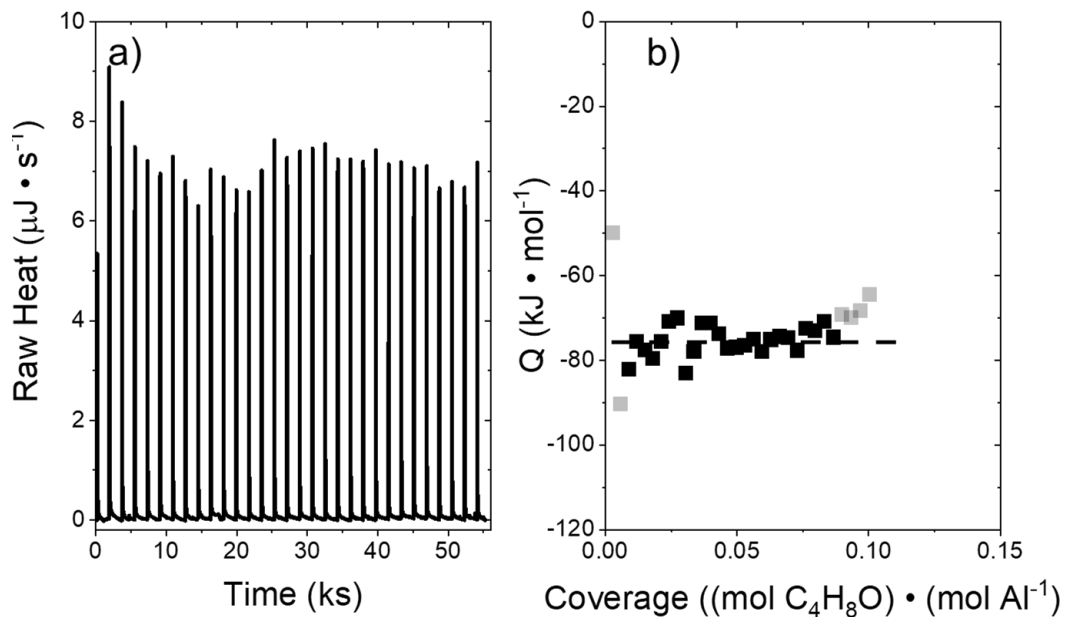


Figure D33. a) ITC thermogram from the titration of Al-BEA-F with $\text{C}_4\text{H}_8\text{O}$ (0.005 M $\text{C}_4\text{H}_8\text{O}$ in CH_3OH , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

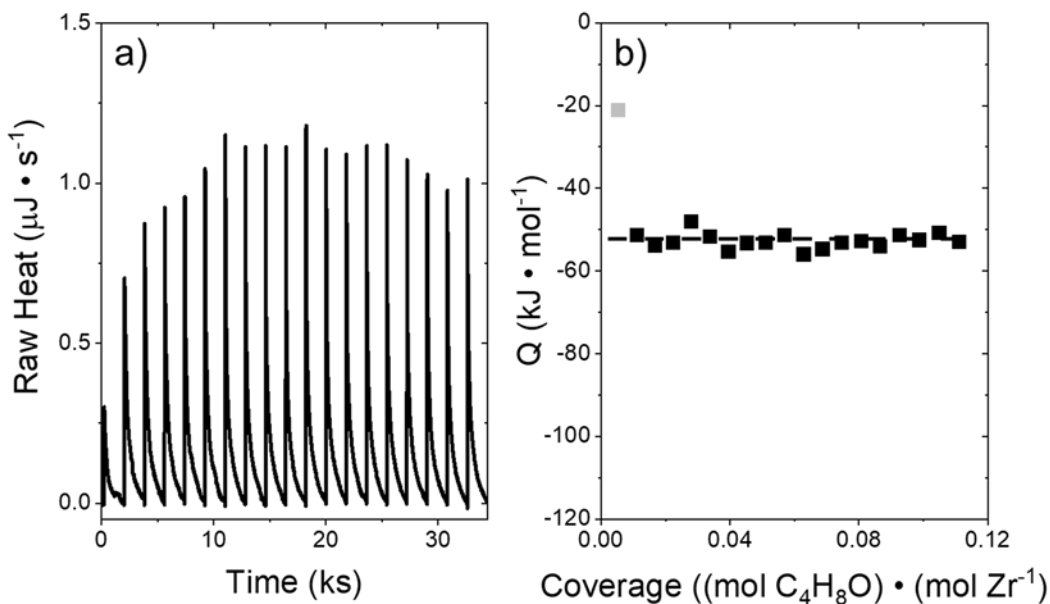


Figure D34. a) ITC thermogram from the titration of Zr-BEA-OH with $\text{C}_4\text{H}_8\text{O}$ (0.005 M $\text{C}_4\text{H}_8\text{O}$ in CH_3OH , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

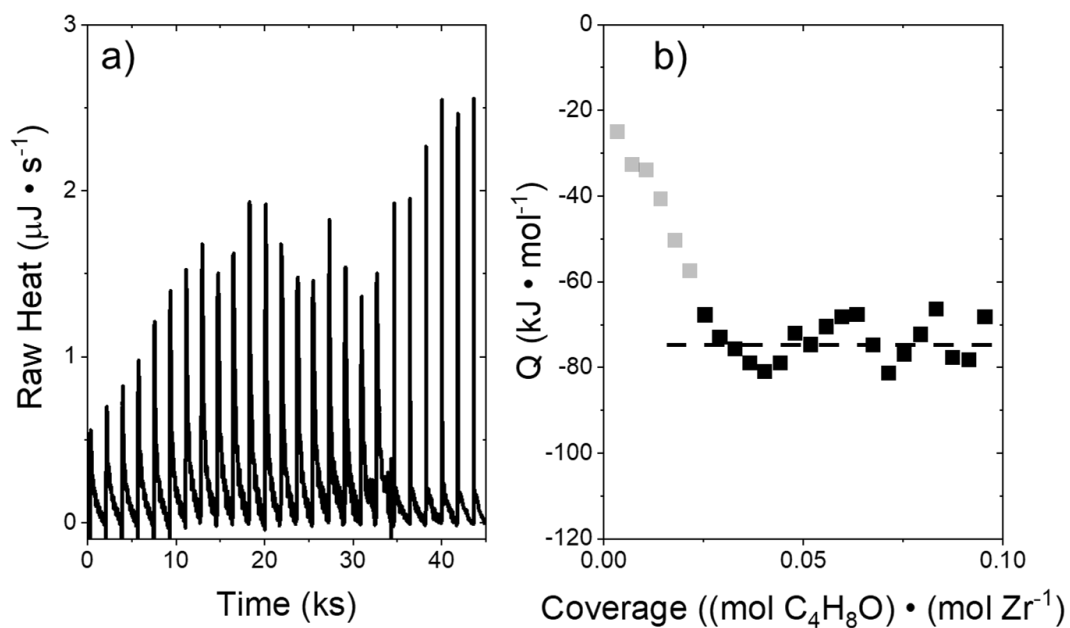


Figure D35. a) ITC thermogram from the titration of Zr-BEA-F with $\text{C}_4\text{H}_8\text{O}$ (0.005 M $\text{C}_4\text{H}_8\text{O}$ in CH_3OH , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

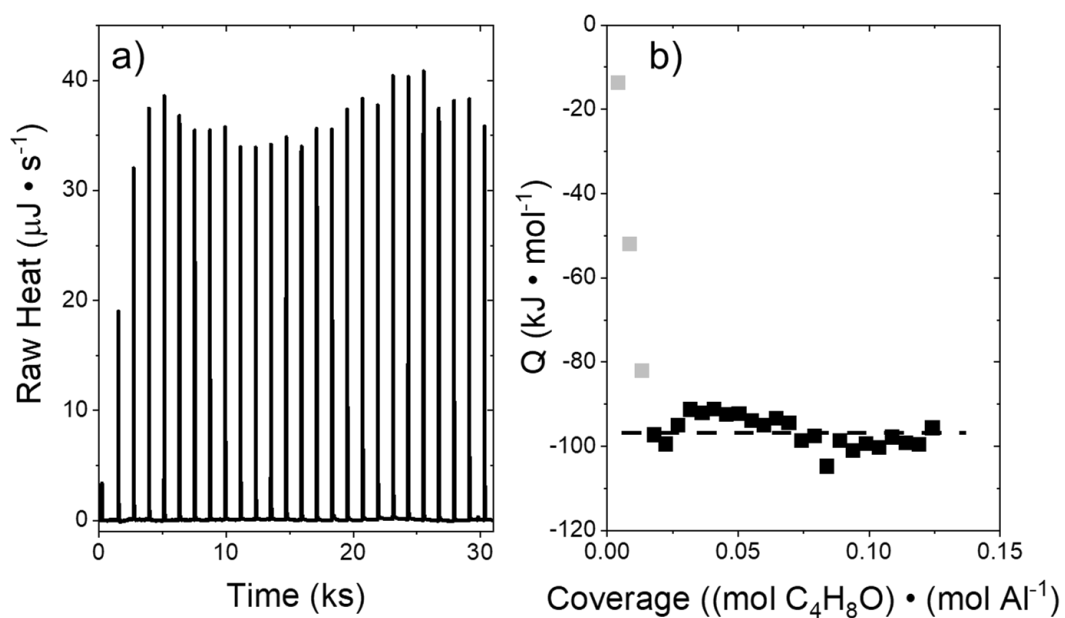


Figure D36. a) ITC thermogram from the titration of Al-BEA-OH with $\text{C}_4\text{H}_8\text{O}$ (0.005 M $\text{C}_4\text{H}_8\text{O}$ in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

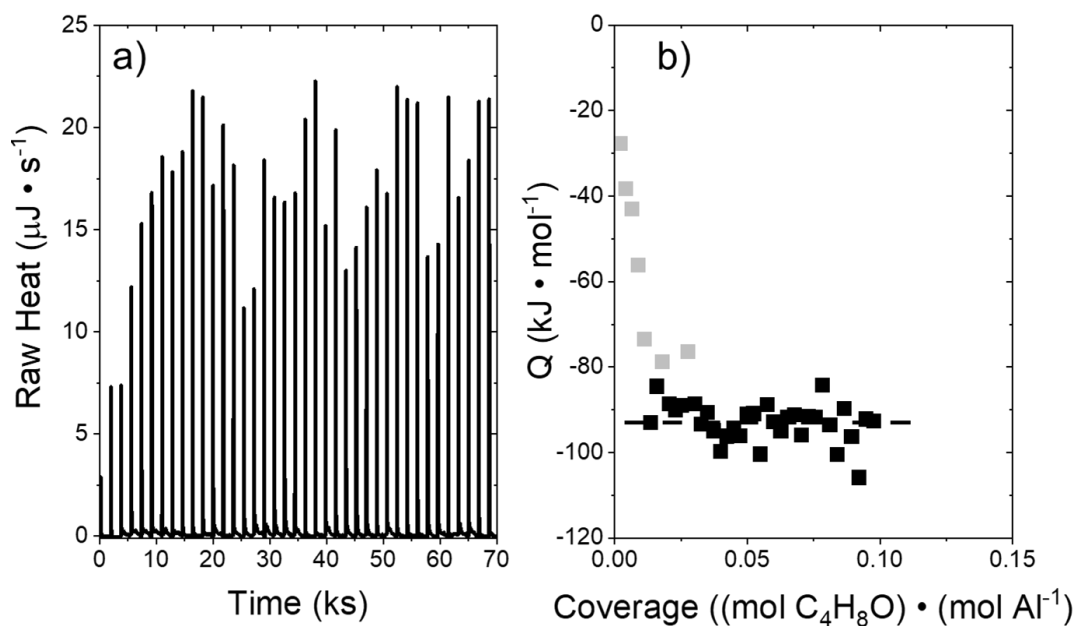


Figure D37. a) ITC thermogram from the titration of Al-BEA-F with $\text{C}_4\text{H}_8\text{O}$ (0.005 M $\text{C}_4\text{H}_8\text{O}$ in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

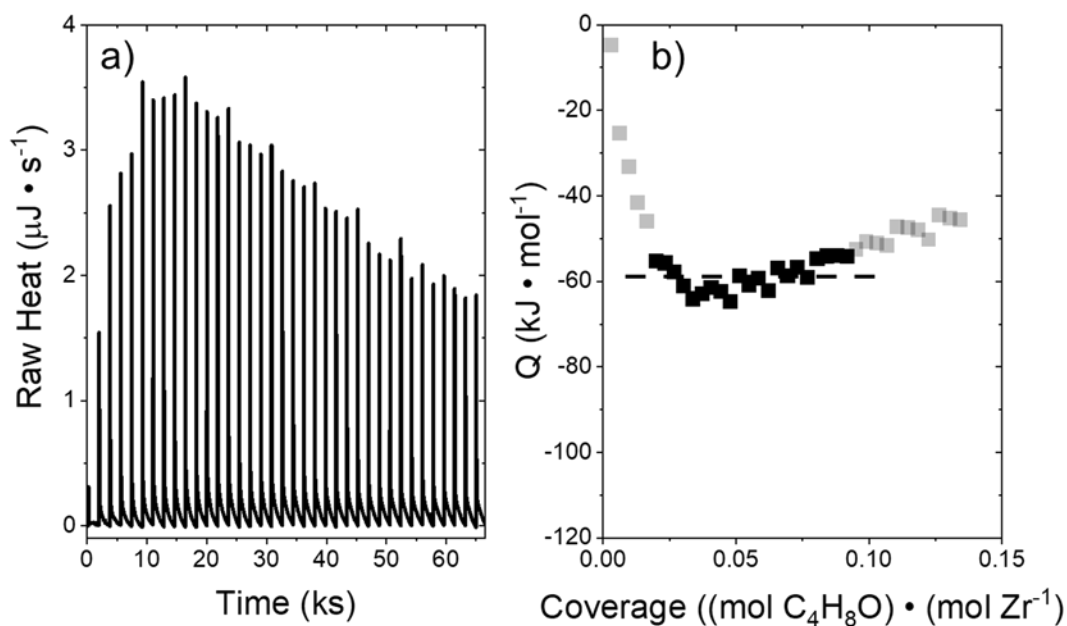


Figure D38. a) ITC thermogram from the titration of Zr-BEA-OH with $\text{C}_4\text{H}_8\text{O}$ (0.005 M $\text{C}_4\text{H}_8\text{O}$ in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

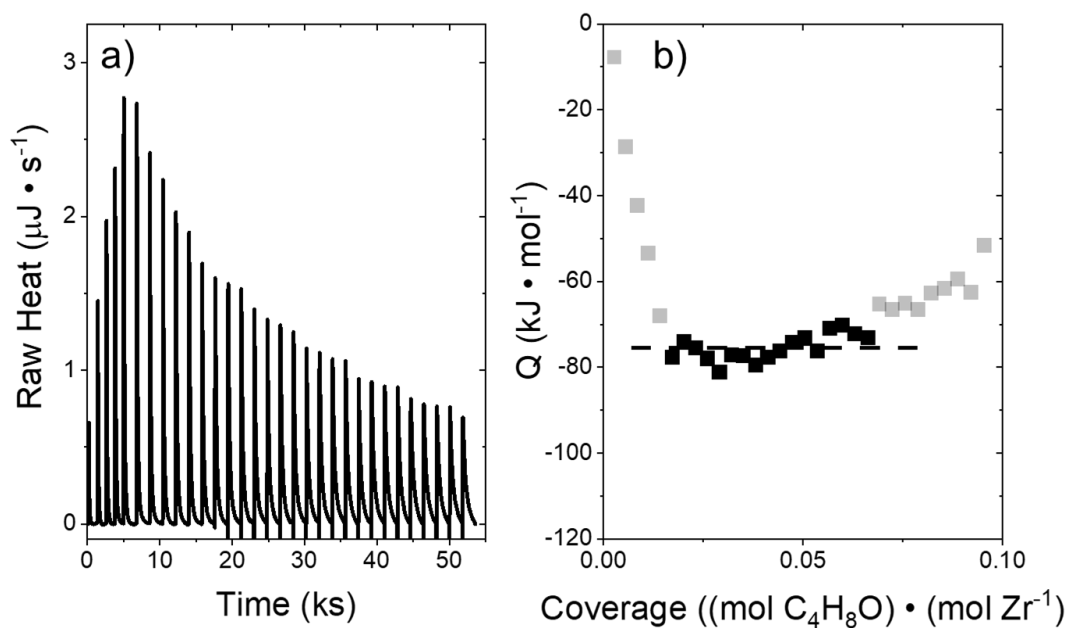


Figure D39. a) ITC thermogram from the titration of Zr-BEA-F with $\text{C}_4\text{H}_8\text{O}$ (0.005 M $\text{C}_4\text{H}_8\text{O}$ in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

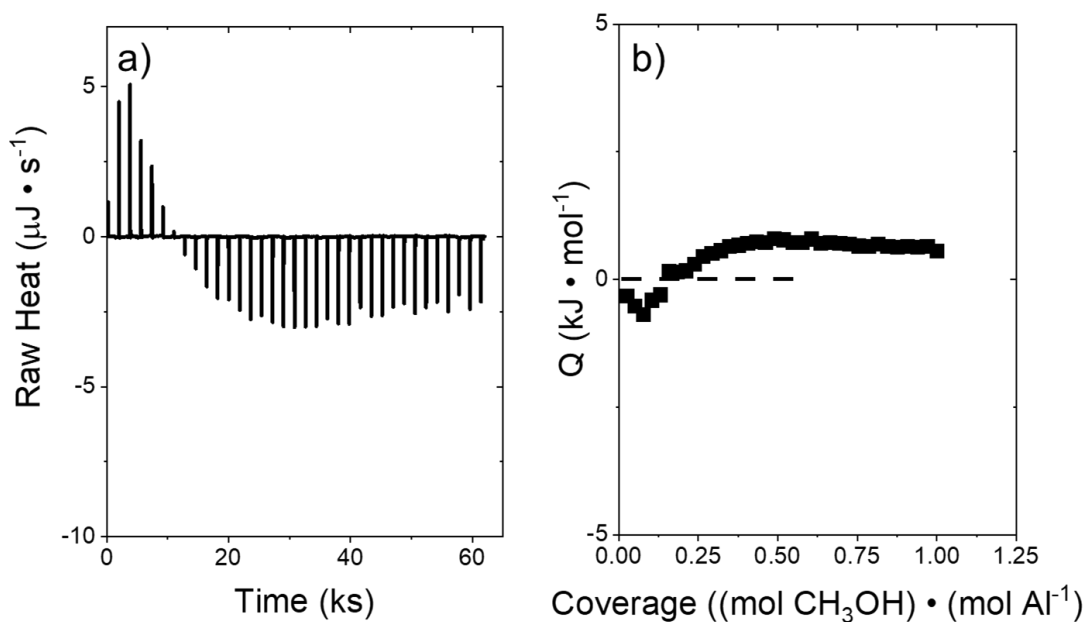


Figure D40. a) ITC thermogram from the titration of Al-BEA-OH with CH_3OH (0.1 M CH_3OH in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

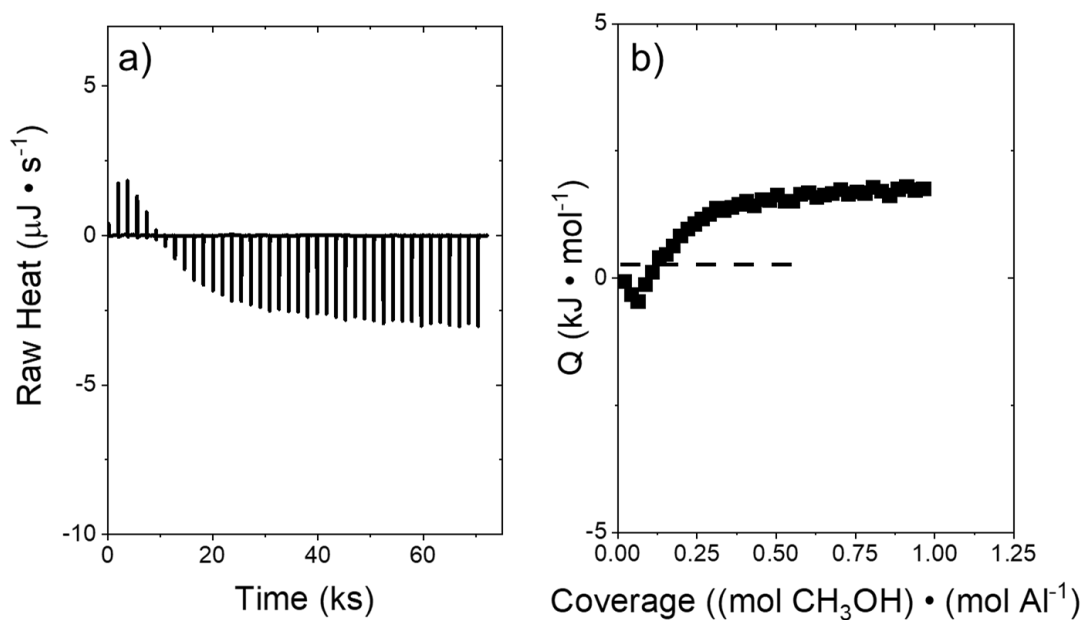


Figure D41. a) ITC thermogram from the titration of Al-BEA-F with CH_3OH (0.1 M CH_3OH in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

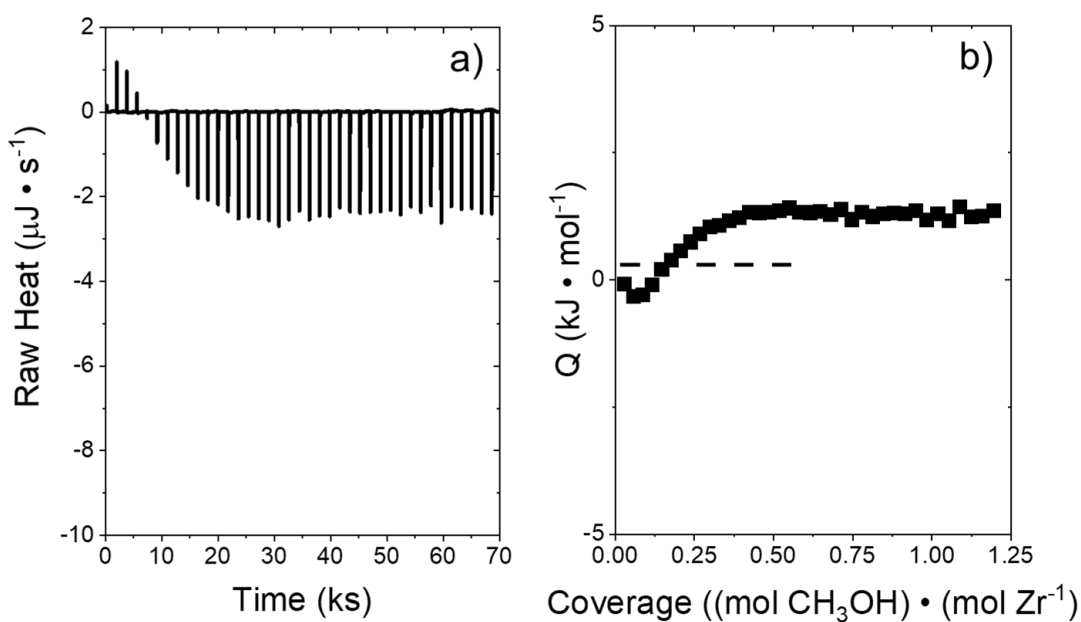


Figure D42. a) ITC thermogram from the titration of Zr-BEA-OH with CH_3OH (0.1 M CH_3OH in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

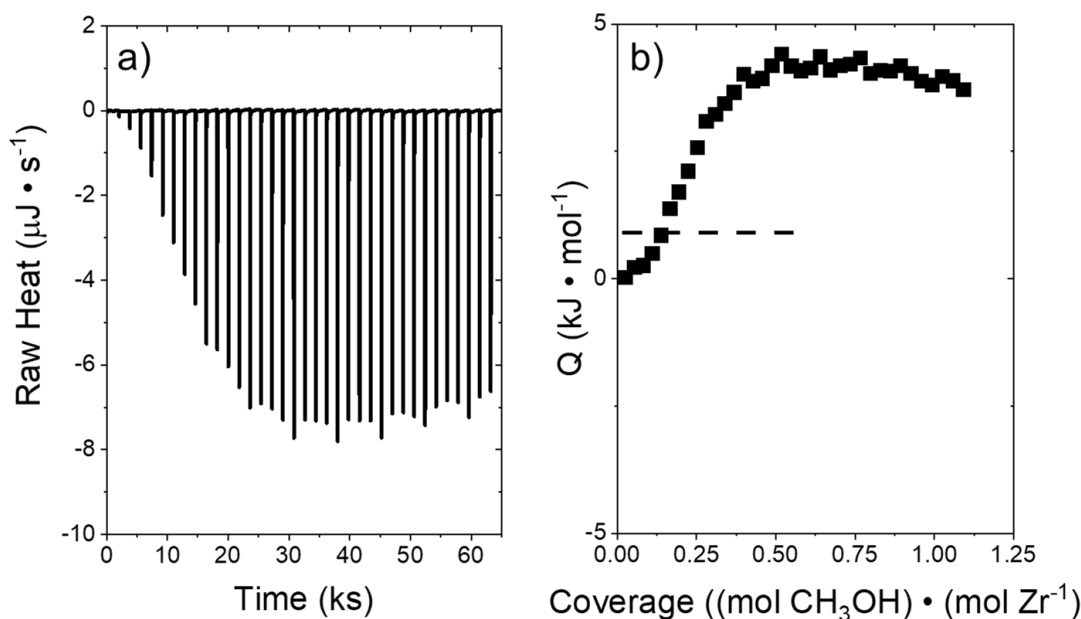


Figure D43. a) ITC thermogram from the titration of Zr-BEA-F with CH_3OH (0.1 M CH_3OH in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

D12. Accounting for Reaction Enthalpy Contribution in $\Delta H^\ddagger$ - $\Delta H_{\text{ads},\text{C}_4\text{H}_8\text{O}}$ Correlation

The enthalpy of reaction was estimated from the gas-phase formation enthalpies for the products and reactants:

$$\Delta H_{\text{rxn}} = \Delta H_{f,\text{C}_5\text{H}_{12}\text{O}_2} - \Delta H_{f,\text{C}_4\text{H}_8\text{O}} - \Delta H_{f,\text{CH}_3\text{OH}} \quad (\text{D25})$$

The formation enthalpies of $\text{C}_4\text{H}_8\text{O}$ (-185.1 kJ mol^{-1}) and CH_3OH (-201.3 kJ mol^{-1}) are tabulated¹⁹⁴ but the values for the products are not ($\text{C}_5\text{H}_{12}\text{O}_2$ – 1M2B and 2M1B). These values were estimated using the Joback group-contribution method,⁴³⁹ which yielded equal values for both products (-436.3 kJ mol^{-1}). These values give an estimated ΔH_{rxn} value of -49.9 kJ mol^{-1} .

The corrected adsorption enthalpy in **Figure D44** assumes that all epoxide that adsorbs at 24.7 M CH_3OH reacts over the course of the injection period (1800 – 2400 s), and subtracts out a contribution equivalent to the estimated ΔH_{rxn} value:

$$\Delta H_{\text{ads},\text{C}_4\text{H}_8\text{O}(\text{corr})} = \Delta H_{\text{ads},\text{C}_4\text{H}_8\text{O}} - \Delta H_{\text{rxn}} \quad (\text{D26})$$

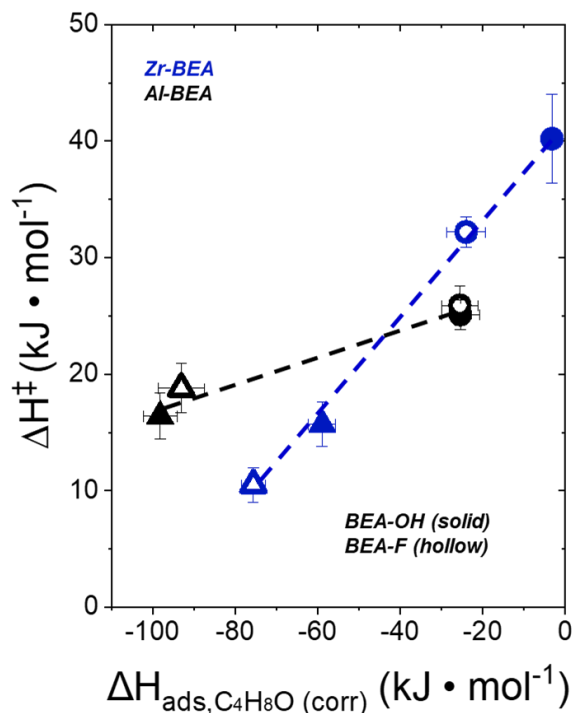


Figure D44. $\Delta H^\ddagger$ values for C_4H_8O ring-opening (from **Figure 5.3**, 0.025 M CH_3OH in CH_3CN (triangles) or 24.7 M CH_3OH (circles)) as a function of the reaction-corrected adsorption enthalpy of C_4H_8O ($\Delta H_{ads,C_4H_8O}(corr)$) over hydrophilic (solid) and hydrophilic (hollow) Al- (black) and Zr-BEA (blue) materials. Assumed contribution from enthalpy of reaction between C_4H_8O and CH_3OH are subtracted from $\Delta H_{ads,C_4H_8O}$ (reported in **Figure 5.7**) to get $\Delta H_{ads,C_4H_8O}(corr)$.

The correction shifts all adsorption enthalpies to more endothermic values. All points for Zr-BEA fall on a line after this correction, in contrast to the discontinuity in **Figure 5.7**. The points for Al-BEA still scale linearly as in **Figure 5.7**, but with a much shallower slope. The reaction-corrected adsorption enthalpy can be expressed as follows:

$$\Delta H_{ads,C_4H_8O}(corr) = H_{C_4H_8O}^* - H_{C_4H_8O} - H_* \quad (D27)$$

where H_* represents the enthalpy of the Lewis and Brønsted acid sites within Zr- and Al-BEA, respectively. The solvation of the proton by CH_3OH may decrease H_* values, leading to less exothermic H_* values and the shallower slope for the Al-BEA correlation compared to Zr-BEA.

While the reaction-corrected adsorption enthalpies do show linear correlations, they rely on the assumption that all epoxide molecules react within the span of each injection into the ITC

cell. The rate and extent of reaction cannot be monitored over time in the ITC, making it impossible to test the validity of the assumption. However, the conclusions discussed in **Section 5.3.4** irrespective of the extent of reaction during C_4H_8O adsorption into CH_3OH . The correlations between $\Delta H^\ddagger$ and $\Delta H_{ads,C_4H_8O}$ at a given solvent composition demonstrate that the adsorption of C_4H_8O and the formation of the C_4H_8O ring-opening transition state reorganize the surrounding solvent structure in similar ways, which leads to differences in both the kinetics and thermodynamics of epoxide ring-opening.

D13. Adsorption Enthalpies of C_4H_8O and CH_3OH to M-BEA in CH_3CN

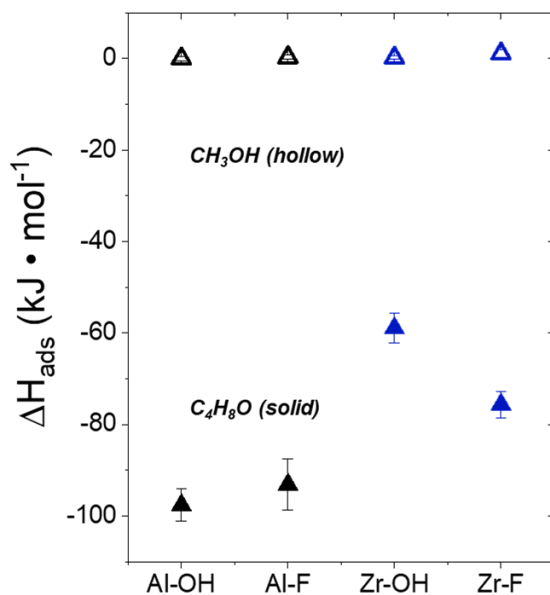


Figure D45. Adsorption enthalpies of C_4H_8O (solid points, 0.005 M C_4H_8O , 308 K) and CH_3OH (hollow points, 0.1 M CH_3OH , 308 K) as a function of active metal in CH_3CN over Zr- (blue) and Al-BEA (black) materials.

The adsorption enthalpies of C_4H_8O and CH_3OH in **Figure D45** were obtained with isothermal titration calorimetry (see **Section D11** for thermograms). For all M-BEA, C_4H_8O shows an adsorption enthalpy at least 50 kJ mol^{-1} more exothermic than CH_3OH . These values suggest

that C_4H_8O adsorbs more readily to the active sites in M-BEA and likely explains why CH_3OH only saturates active sites under when $[CH_3OH]:[C_4H_8O]$ exceeds 500 (see **Section 5.3.1**).

Figure D46 displays the heat released from CH_3OH adsorption over M-BEA as a function of CH_3OH coverage. Notably, Zr-BEA-OH and each Al-BEA material show similar trends with CH_3OH coverage. CH_3OH adsorbs exothermically at a CH_3OH coverage below 0.25, after which the adsorption heat gradually increases to reach a nearly constant and endothermic value. In contrast, Zr-BEA-F shows an endothermic heat at all CH_3OH coverages, with the most endothermic heats of all M-BEA at high coverages. These trends suggest that CH_3OH adsorbs more favorably over Zr-BEA-OH and each Al-BEA than Zr-BEA-F, aligning with the trends of CH_3OH uptake from binary mixtures with CH_3CN (**Figure 5.4a**). Furthermore, the curves of Al-BEA-OH and Al-BEA-F show more similar trends than Zr-BEA-OH and Zr-BEA-F, providing further support that the intrapore environment within Brønsted acid zeolite materials depends less strongly on $(SiOH)_x$ density than Lewis acid zeolites.

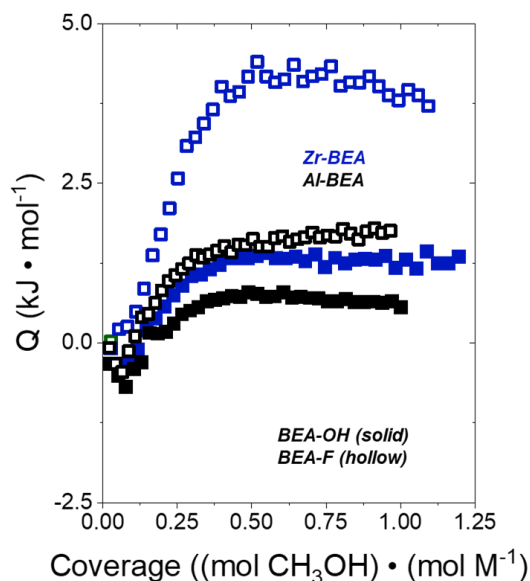


Figure D46. Adsorption enthalpies of C_4H_8O (solid points, 0.005 M C_4H_8O , 308 K) and CH_3OH (hollow points, 0.1 M CH_3OH , 308 K) as a function of active metal in CH_3CN over Zr- (blue) and Al-BEA (black) materials.

APPENDIX E

SUPPLEMENTAL DATA AND ANALYSIS FOR CHAPTER 6

E1. Single-Pulse ^{13}C -NMR Spectra from $\text{C}_3\text{H}_5\text{ClO}$ Ring-Opening with CH_3OH

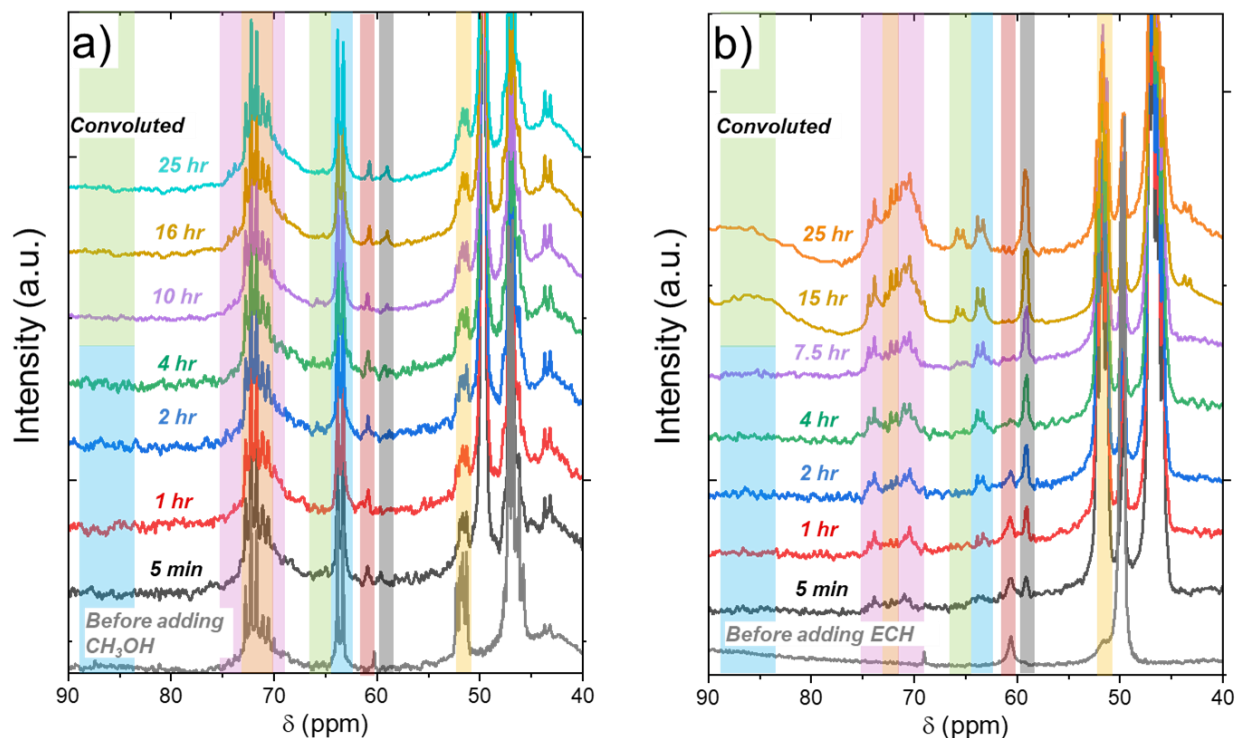
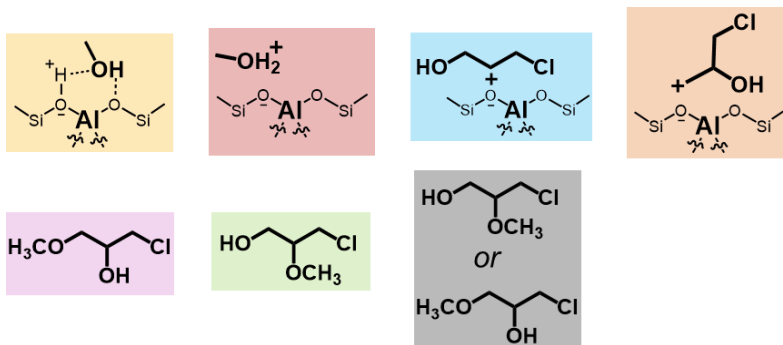


Figure E1. ^{13}C NMR single-pulse spectra during ring-opening of $\text{C}_3\text{H}_5\text{ClO}$ with CH_3OH (0.2 M ^{13}C - $\text{C}_3\text{H}_5\text{ClO}$, 0.2 M ^{13}C - CH_3OH , CH_3CN , Al-BEA-OH , 298 K), where reaction was initiated by adding a) ^{13}C - $\text{C}_3\text{H}_5\text{ClO}$ or b) ^{13}C - CH_3OH to the NMR rotor after pre-mixing all other components. Concentration-time profiles in **Figure 6.4** were derived from these plots.



Scheme E1. Assignments for highlighted peaks in **Figure E1**.

Figure E1 presents ^{13}C NMR single-pulse spectra for the ring-opening of $^{13}\text{C}_3\text{H}_5\text{ClO}$ with CH_3OH over Al-BEA-OH at low $[\text{CH}_3\text{OH}]$ (0.2 M CH_3OH), where the reaction was initiated by either adding ^{13}C - $\text{C}_3\text{H}_5\text{ClO}$ (**Figure E1a**) or ^{13}C - CH_3OH (**Figure E1b**). The grey spectra show the adsorbate structure before initiating the reaction. **Scheme E1** shows the assignments for the highlighted peaks in the spectra, which represent intermediates and ring-opening product species.

Overlap among reactant, product, and intermediate peak features present a challenge in monitoring changes in species concentration over time. The peak originating from CH_3OH chemisorbed at Brønsted acid sites (gold highlight) cannot be detected in the presence of $\text{C}_3\text{H}_5\text{ClO}$, making it impossible to track changes in concentration of that species during the reaction. The products and ring-opened carbocations contain features in the range of 40-47 ppm, but these features overlap with features from $\text{C}_3\text{H}_5\text{ClO}$ and are therefore difficult to track over time. The methoxy groups ($-\text{OCH}_3$) from the products contain features around 59 ppm, but overlap and cannot easily be distinguished between the products.

The broad nature of the terminal alcohol and secondary ring-opened carbocation features around 85 ppm prevent the deconvolution of those peaks. Nevertheless, these species contain unique features at 63 ppm (secondary carbocation) and 65 ppm (terminal alcohol) that enable the monitoring of their concentrations over time. The primary ring-opened carbocation shows features from 70-73 ppm, which partially overlap with the terminal ether feature from 69-71 ppm. However, the terminal ether also shows a feature from 73-74 ppm, allowing for independent tracking of both the terminal ether and primary carbocation. To summarize, the intermediates, reactants, and products contain sufficient numbers of unique peak shifts to track species concentrations and make mechanistic conclusions, as described in **Section 6.2.1**.

E2. Cross-Polarization ^{13}C -NMR Spectra from $\text{C}_3\text{H}_5\text{ClO}$ Ring-Opening with CH_3OH

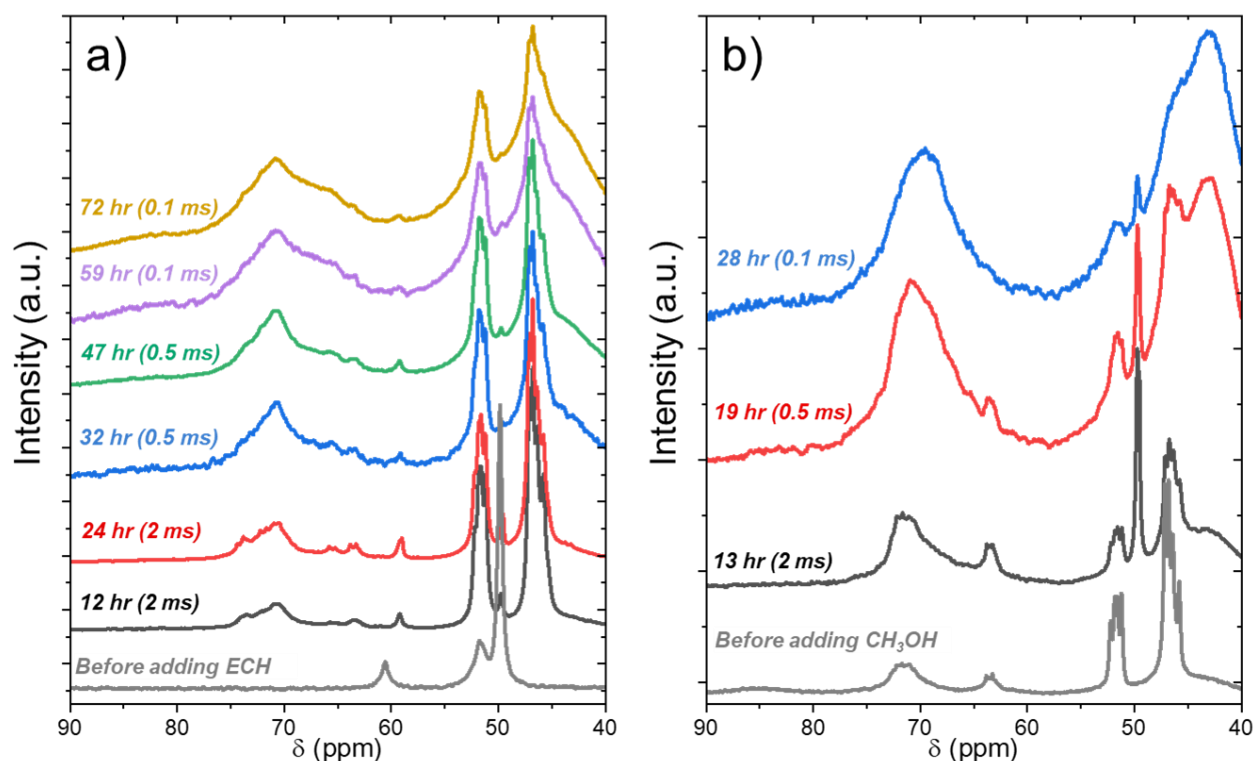


Figure E2. ^{13}C NMR cross-polarization spectra during ring-opening of $\text{C}_3\text{H}_5\text{ClO}$ with CH_3OH (0.2 M ^{13}C - $\text{C}_3\text{H}_5\text{ClO}$, 0.2 M ^{13}C - CH_3OH , CH_3CN , Al-BEA-OH, 298 K), where reaction was initiated by adding a) ^{13}C - $\text{C}_3\text{H}_5\text{ClO}$ or b) ^{13}C - CH_3OH to the NMR rotor. Numbers in parentheses represent the contact times for each measurement.

Figure E2 presents the cross-polarization spectra for the same experiment as the single-pulse spectra shown in **Figure E1**. **Figure E1b** shows features representing adsorbed primary and secondary ring-opened carbocations before initiating the reaction. These species also appear in **Figure E1a** upon initiating the reaction by adding $\text{C}_3\text{H}_5\text{ClO}$, along with features corresponding to the terminal ether and terminal alcohol products. Notably, measurements with shorter contact times show greater intensities of $\text{C}_3\text{H}_5\text{ClO}$, ring-opened carbocation, and product-derived species as compared to CH_3OH -derived species (~ 49 ppm). Decreasing the contact time causes strongly bound species to appear more intensely, suggesting that the CH_3OH -derived species bind more weakly than species originating from $\text{C}_3\text{H}_5\text{ClO}$. Overall, these spectra align with interpretation of

the peak growth patterns from the single-pulse spectra and provide insight into the strength of adsorbates on the surface.

E3. Isothermal Titration Calorimetry Thermograms and Heats per Injection

The isothermal titration calorimetry thermograms and heat release plots for $\text{C}_3\text{H}_5\text{ClO}$ (**Figure E3**) and CH_3OH (**Figure E4**) are presented below. Notably, $\text{C}_3\text{H}_5\text{ClO}$ shows a much more exothermic adsorption enthalpy (-150 kJ mol^{-1}) than CH_3OH (0 kJ mol^{-1}). These data suggest that $\text{C}_3\text{H}_5\text{ClO}$ preferentially coordinates to Brønsted acid sites over CH_3OH . Unless CH_3OH adsorbs irreversibly to the Brønsted acid sites, $\text{C}_3\text{H}_5\text{ClO}$ can likely easily displace CH_3OH during catalysis. Taking these measurements together with the kinetic and spectroscopic data in **Section 6.2.1** provides insight into what species may saturate the surface and what species serve as dominant reactive intermediates during $\text{C}_3\text{H}_5\text{ClO}$ ring-opening with CH_3OH .

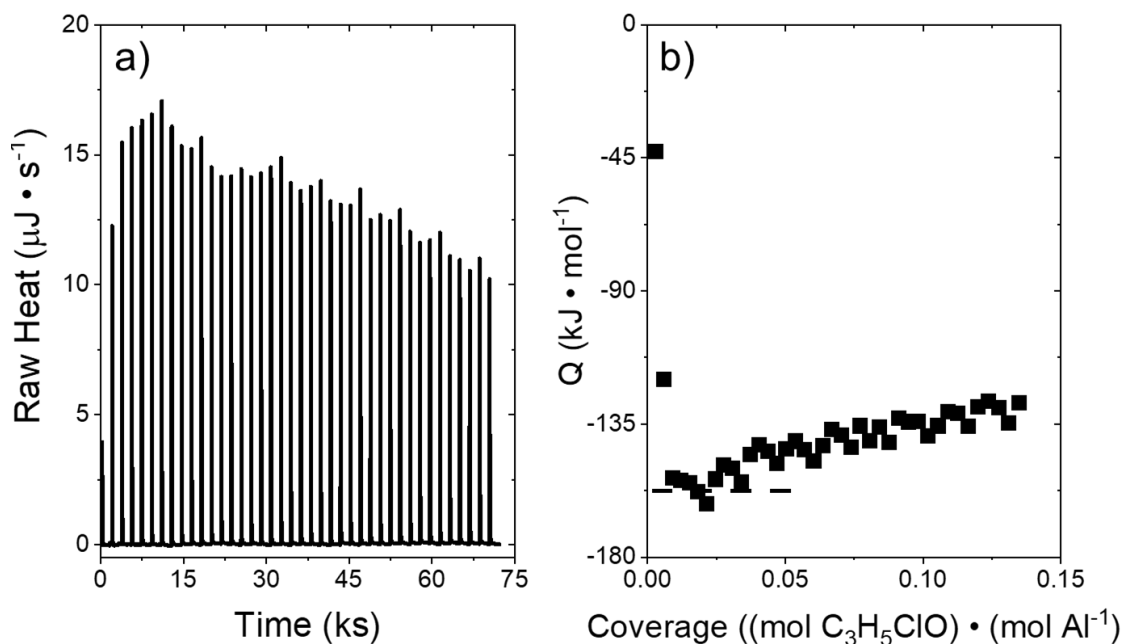


Figure E3. a) ITC thermogram from the titration of Al-BEA-OH with $\text{C}_3\text{H}_5\text{ClO}$ (0.005 M CH_3OH in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.

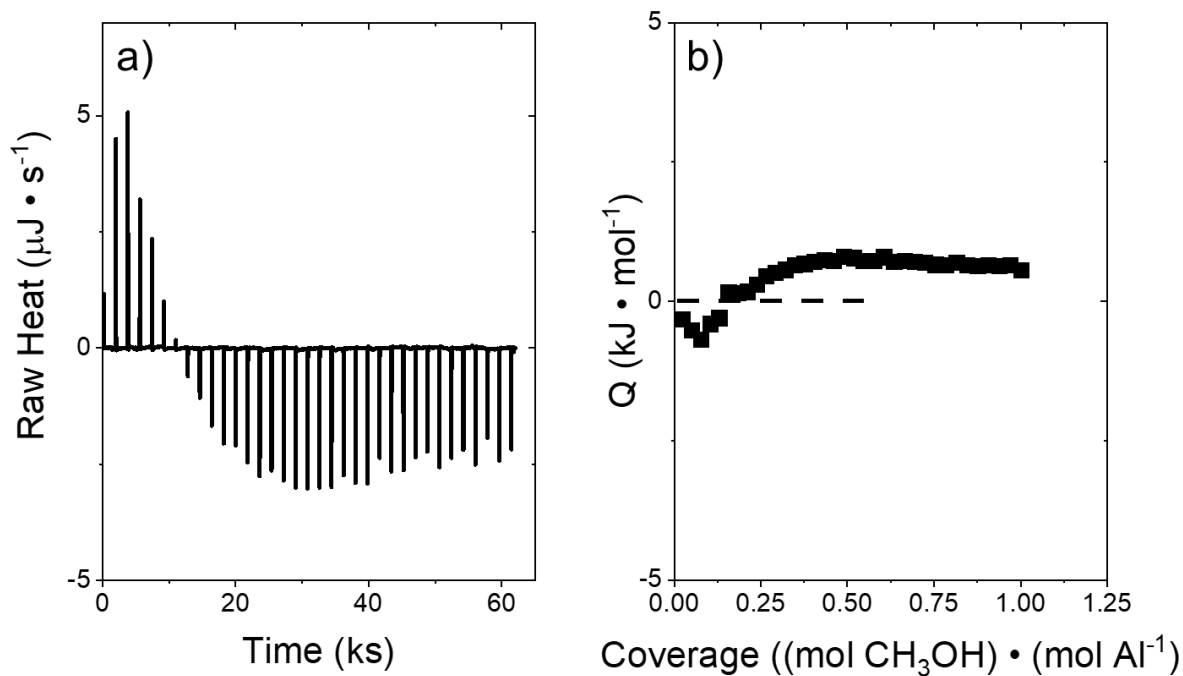


Figure E4. a) ITC thermogram from the titration of Al-BEA-OH with CH_3OH (0.1 M CH_3OH in CH_3CN , 308 K, 1 μL per injection), b) the corresponding heats released as a function of titrant injected.