DEVELOPMENT OF SUSTAINABLE PD-BASED CATALYSTS
FOR REMOVAL OF PERSISTENT CONTAMINANTS
FROM DRINKING WATER

BY

DANMENG SHUAI

DISSERTATION

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Doctoral Committee:

Professor Charles J. Werth, Chair
Professor John R. Shapley
Associate Professor Timothy J. Strathmann
Professor William F. Schneider, University of Notre Dame
ABSTRACT

Pd-based catalytic reduction has emerged as an advanced treatment technology for drinking water decontamination, and a suite of persistent contaminants including oxyanions, \( N \)-nitrosoamines, and halogenated compounds are amenable to catalytic reduction. The primary goal of this study is to develop novel Pd-based catalysts with enhanced performance (i.e., activity, selectivity, and sustainability) to remove contaminants from drinking water. The effects of water quality (i.e., co-contaminants in water matrix), catalyst support, and catalyst metal were explored, and they provide insights for preparing catalysts with faster kinetics, higher selectivity, and extended lifetime.

Azo dyes are wide-spread contaminants, and they are potentially co-exisiting with target contaminants amenable for catalytic removal. The probe azo dye methyl orange (MO) enhanced catalytic reduction kinetics of a suite of oxyanions (i.e., nitrate, nitrite, bromate, chlorate, and perchlorate) and diatrizoate significantly but not \( N \)-nitrosodimethylamine (NDMA) with a variety of Pd-based catalysts. Nitrate was selected as a probe contaminant, and several different azo dyes (i.e., methyl orange, methyl red, fast yellow AB, metanil yellow, acid orange 7, congo red, eriochrome black T, acid red 27, acid yellow 11, and acid yellow 17) were evaluated for their ability to enhance reduction. A hydrogen atom shuttling mechanism was proposed and a kinetic model was proposed based on Brønsted–Evans–Polanyi (BEP) theory, and they suggest sorbed azo dyes and reduced hydrazo dyes shuttle hydrogen atoms to oxyanions or diatrizoate to enhance their reduction kinetics.
Next, vapor-grown carbon nanofiber (CNF) supports were used to explore the effects of Pd nanoparticle size and interior versus exterior loading on nitrite reduction activity and selectivity (i.e., dinitrogen over ammonia production). In order to evaluate the amount of interior versus exterior loading of Pd nanoparticles, a fast and accurate geometric model was developed based on two-dimensional transmission electron microscopy (2D TEM). Results from this method agree adequately with 3D scanning transmission electron microscopy (3D TEM), which is recognized as a convincing method to evaluate interior versus exterior loading. By using Pd CNF catalysts for nitrite reduction, results show that both activity and selectivity are not significantly impacted by Pd interior versus exterior loading. Turnover frequencies (TOFs) among all CNF catalysts are consistent, suggesting faster kinetics are achieved on catalysts with smaller Pd nanoparticles, and suggesting nitrite reduction is neither sensitive to Pd location on CNFs nor Pd structure. However selectivity to dinitrogen is more favorable on larger Pd nanoparticles. Therefore, an optimum Pd nanoparticle size on CNFs balances high reduction kinetics and selectivity to dinitrogen. CNF Pd catalysts perform better than conventional activated or alumina supported Pd catalysts in term of kinetics and selectivity for nitrite reduction, and they maintain consistent activity during multiple reduction cycles.

Lastly, the structure-sensitivity of catalytic activity and selectivity for contaminant nitrite, NDMA, and diatrizoate removal were investigated on shape- and size-controlled Pd nanoparticles. Results show that TOFs for nitrite, NDMA, and diatrizoate are dependent on coordination numbers of surface Pd sites at low contaminant concentration, but TOFs for nitrite at high concentration are consistent. Selectivity to ammonia for nitrite reduction decreases with increasing surface Pd sites, i.e., decreasing Pd nanoparticle size irrespective of nitrite
concentration, but NDMA reduction is neither shape- nor size-specific, and it exclusively proceeds to ammonia and dimethylamine. Diatrizoate reduction selectivity is also likely to be nonspecific to shape and size, and a series of deiodinated intermediates, 3,5-diacetamidobenzoic acid, and iodide are produced. Hence, this study suggests that contaminant reduction kinetics and selectivity are Pd shape and size dependent, and the dependence varies by contaminant type and concentration.

In summary, Pd-based catalysts can be tailored for enhanced activity, selectivity, and longevity, and catalytic treatment holds the promise for advanced drinking water treatment.
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CHAPTER 1: INTRODUCTION

1.1 General Overview

Catalytic reduction with Pd-based catalysts and H₂ has emerged as a promising technology to remove a suite of persistent contaminants from drinking water or concentrated brine solutions (e.g., brine from ion exchange regeneration) including oxyanions, N-nitrosamines, and halogenated compounds (1). Oxyanions are a diverse class of contaminants often detected in drinking water at concentrations above regulatory threshold levels that are amenable to reductive processes. Oxyanions are often wide-spread, persistent, and mobile in the environment, and those of primary concern are nitrate, perchlorate, and several disinfection byproducts. Nitrate originates from fertilizer run-off (2), and can lead to methemoglobinemia, i.e., “blue-baby syndrome” (3). Its reduction intermediate in natural systems, nitrite, can cause the formation of carcinogenic N-nitroso compounds in the human body (4). Perchlorate is used as an oxidant in rocket fuel, munitions, and blasting materials (5), and adversely affects the thyroid gland (6). Disinfection has been shown to form the oxyanions bromate (e.g., from ozone) (7, 8), chlorite, and chlorate (e.g., from chlorine dioxide) (9, 10). These chemicals are carcinogenic and may adversely affect reproduction and development (11). N-nitrosamines are potent carcinogens (12), and are usually resulted from rocket engine test waste and disinfection byproducts (13, 14). Halogenated compounds, such as trichloroethylene (TCE), perchloroethylene (PCE), polychlorinated biphenyls (PCBs), and diatrizoate, have diverse sources, and they are used as solvents for metal rinsing and dry cleaning, coolants, insulating fluids, and X-ray contrast media.
Halogenated compounds pose adverse effects to human beings, and they are toxic, endocrine disruptive, and carcinogenic (16, 17).

Other traditional physiochemical and biological treatment processes have been evaluated for removing oxyanions, N-nitrosoamines, and halogenated compounds from drinking water. These are electrodialysis, ion exchange, reverse osmosis, adsorption onto activated carbon, air stripping, advanced oxidation, photolysis, and biological reduction (1). Physical separation processes (i.e., electrodialysis, ion exchange, reverse osmosis, adsorption, air stripping) typically generate concentrated brine solutions, which require further disposal. UV photolysis for removing N-nitrosamines is costly and energy intensive (13). Biological processes are sensitive to changes in water quality (18, 19), and there are concerns that amended electron donors will promote pathogen growth and lead to greater disinfection byproduct formation (20). As an advanced water treatment strategy, catalytic reduction overcomes aforementioned concerns. However, there are a number of challenges to address before Pd-based catalytic processes are widely accepted, including greater catalyst activity, longevity, and selectivity.

Previous research has demonstrated nitrate reduction with Pd-In (21-24), Pd-Cu (25-29), and Pd-Sn (27, 30) bimetallic catalysts, chlorate and perchlorate reduction with Pd-Re bimetallic catalysts (31, 32), nitrite, bromate, diatrizoate reduction with Pd-only catalysts (7, 8, 15), and N-nitrosodimethylamine (NDMA) reduction Pd-In and Pd-only catalysts (33, 34). An economic analysis from a recent pilot study indicates trichloroethylene reduction with a Pd-only on activated carbon catalyst is less expensive compared to conventional treatment with activated
The economic advantage of catalytic treatment depends primarily on catalyst cost and life. Catalyst cost is a function of market conditions, and of catalyst activity per unit mass of precious metal. Trichloroethylene reduction rates are at least an order of magnitude greater than those for oxyanions and NDMA (1, 25, 31, 36), indicating significant cost savings are possible for oxyanion or NDMA catalytic treatment if more active catalysts can be developed. Catalyst life depends primarily on catalyst stability during fouling and oxidative regeneration. Pd on activated carbon catalysts and Pd-In on γ-alumina catalysts have both been shown to be robust to multiple cycles of fouling and regeneration with a strong oxidant (35, 37, 38). However, small amounts of Pd leaching occur during oxidative regeneration even for these catalysts (22), so minimizing catalyst fouling is important. Also, it is not clear if other bimetallic Pd-based catalysts are as robust as Pd and Pd-In catalysts. Cu has been shown to readily leach during oxidative regeneration using sodium hypochlorite (22), and Re appears to leach under oxidizing conditions (32).

Catalyst selectivity for the desired end products also affects the viability of this technology. Among the oxyanions, selectivity towards dinitrogen is very important for nitrate reduction. Nitrate initially transforms to nitrite, which then transforms through one or more intermediates to either dinitrogen or ammonia. Possible intermediates are nitric oxide and nitrous oxide (39), and it is not clear how or if their formation affects selectivity.
1.2 Research Objectives

The overall goal of this thesis work is to develop novel Pd-based catalysts with enhanced performance (i.e., activity, selectivity, and sustainability) to treat oxyanions, N-nitrosamines, and halogenated compounds in drinking water. The primary probe contaminants in this study are nitrate and nitrite as oxyanions, NDMA as an N-nitrosamine, and diatrizoate as a halogenated compound. However, other typical oxyanions (i.e., bromate, chlorate, perchlorate) are considered as well. The specific objectives of this thesis are to:

1. Demonstrate that Pd-based catalysts can effectively treat a suite of oxyanions, NDMA, and diatrizoate, and explore the effects of cocontaminant azo dyes on their catalytic reduction kinetics.

Nitrate, nitrite, bromate, chlorate, perchlorate, NDMA, and diatrizoate have all been shown to be amenable to reduction with Pd-based catalysts (1, 8, 15, 31, 33, 34, 40). Azo dyes are potential cocontaminants in source water for drinking water supply, and they may either enhance or inhibit catalytic reduction kinetics for oxyanions, NDMA, and diatrizoate. In this work, the effects of selected azo dyes on catalytic reduction kinetics for nitrate, nitrite, perchlorate, chlorate, bromate, NDMA, and diatrizoate were evaluated, and the mechanism was explored. Methyl orange (MO) was initially selected as a probe azo dye to evaluate the impacts to the reduction rates of selected contaminants. Next, nitrate was selected as a probe contaminant, and the impacts of a suite of azo dyes on nitrate reduction kinetics were evaluated. Corresponding reduction kinetics were related to different physical and chemical properties of dyes to explore enhancement mechanisms,
including hydrogenation energies calculated from density functional theory, and a kinetic model based on Brønsted-Evans-Polanyi (BEP) theory was developed for mechanistic interpretation.

2. Characterize Pd nanoparticle locations on novel carbon nanofiber (CNF) supports, and explore the effects of Pd nanoparticle size and location on nitrite reduction activity and selectivity.

CNFs have unique structural, electronic, adsorption, mechanical, and thermal properties (41), and they have been used for several catalytic reactions including tetrachloroethylene hydrodechlorination (42), H₂S oxidation (43), selective cinnamaldehyde hydrogenation (44), and electrocatalytic reaction in fuel cells (45). Metal nanoparticles were able to be loaded on external or internal surfaces on vapor grown hollow CNFs, and different catalytic performances were observed because of locations of metal nanoparticles (44). However, it is challenging to quantify the amount of metal nanoparticles loaded inside versus outside. Metal nanoparticle size and locations were tuned on CNFs by wetness impregnation (46), and their effects on catalytic performance was not systematically explored. In this work, Pd CNF catalysts with primarily inside loading, primarily outside loading, and proportional inside plus outside loading but similar Pd nanoparticle size were prepared. Pd CNF catalysts with primarily inside loading but small, medium, and large Pd nanoparticle sizes were also synthesized. The locations of Pd nanoparticles were characterized by a geometric method developed based on two-dimensional transmission electron microscopic analysis. Next, the effects of Pd nanoparticle size and location on nitrite reduction kinetics and selectivity were evaluated. To evaluate the potential for CNF catalysts being used in water treatment, the performance of Pd CNF catalysts was compared with
conventional Pd catalysts (i.e., Pd on activated carbon or alumina), and the longevity was evaluated by multiple-cycle nitrite reduction.

3. **Discover the structure-sensitivity of nitrite, NDMA, and diatrizoate reduction on Pd with shape- and size-controlled nanoparticles.**

The effects of shape and size have been studied for a series of structure-sensitive reactions, such as hydrogenation (47-49), oxidation (49), cross-coupling (50), and electron transfer reactions (50), by taking advantages of synthesis of shape-controlled nanoparticles as model catalysts. In this work, a suite of poly(vinyl-pyrrollidone) (PVP) capped Pd nanoparticles: cubes, octahedra, cuboctahedra, and rods with various sizes were prepared, and the effects of surface Pd coordination and packing on reduction activity and selectivity for nitrite, NDMA, and diatrizoate were evaluated. The stability of Pd nanoparticle catalysts was also evaluated by characterizing the size and shape change after reaction.

1.3 **Outline of Thesis**

Chapter 2 contains the work published in *Environ. Sci. Technol.* entitled “Enhancement of Oxyanion and Diatrizoate Reduction Kinetics Using Selected Azo Dyes on Pd-based Catalysts” with co-authors Brian P. Chaplin, John R. Shapley, Nathaniel P. Menendez, Dorrell C. McCalman, William F. Schneider, and Charles J. Werth in 2010. This work addresses research objective 1, illustrates the enhancement of MO to a suite of contaminants on a variety of Pd-based catalysts, and proposed a hydrogen atom shuttling mechanism for enhancement on nitrate
reduction. Chapter 3 contains the work published in *J. Phys. Chem. Lett.* entitled “A New Geometric Method Based on 2D Transmission Electron Microscopy for Analysis of Interior versus Exterior Pd Loading on Hollow Carbon Nanofibers” with co-authors Chongmin Wang, Arda Genç, and Charles J. Werth in 2011. This work addresses “characterizing Pd nanoparticle locations on novel carbon nanofiber (CNF) supports” of research objective 2, and developed a geometric method to quantify the amount of nanoparticles loaded internally versus externally on tubular support. Chapter 4 contains the work published in *Environ. Sci. Technol.* entitled “Enhanced Activity and Selectivity of Carbon Nanofiber Supported Pd Catalysts for Nitrite Reduction” with co-authors Jong Kwon Choe, John R. Shapley, and Charles J. Werth in 2012. This work addresses “exploration the effects of Pd nanoparticle size and location on nitrite reduction activity and selectivity” of research objective 2, and comprehensively studied the effects of CNF aggregate size, Pd nanoparticle size, and Pd nanoparticle locations on nitrite reduction kinetics and selectivity towards ammonia. It also evaluated catalytic performance in comparison to conventional activated carbon and alumina supported Pd catalysts, and explored catalyst longevity during multiple nitrite reduction cycles. Chapter 5 contains a manuscript in preparation for *J. Am. Chem. Soc.* entitled “Structure sensitivity study of waterborne contaminant hydrogenation using shape- and size- controlled Pd nanoparticles”. This work addresses research objective 3, and explored effects of Pd shape and size on reduction kinetics and selectivities for nitrite, NDMA, and diatrizoate. Chapter 6 contains major conclusions, engineering application, and future research directions.

1.4 References


CHAPTER 2: ENHANCEMENT OF OXYANION AND DIATRIZOATE REDUCTION KINETICS USING SELECTED AZO DYES ON PD-BASED CATALYSTS

2.1 Abstract

Azo dyes are wide-spread pollutants and potential co-contaminants for nitrate; I evaluated their effect on catalytic reduction of a suite of oxyanions, diatrizoate, and N-nitrosodimethylamine (NDMA). The azo dye methyl orange significantly enhanced (≤ factor of 5.24) the catalytic reduction kinetics of nitrate, nitrite, bromate, perchlorate, chlorate, and diatrizoate with several different Pd-based catalysts; NDMA reduction was not enhanced. Nitrate was selected as a probe contaminant, and a variety of azo dyes (methyl orange, methyl red, fast yellow AB, metanil yellow, acid orange 7, congo red, eriochrome black T, acid red 27, acid yellow 11, and acid yellow 17) were evaluated for their ability to enhance reduction. Hydrogenation energies of azo dyes were calculated using density functional theory and a volcano relationship between hydrogenation energies and reduction rate enhancement was observed. A kinetic model based on Brønsted–Evans–Polanyi (BEP) theory matched the volcano relationship, and suggests sorbed azo dyes enhance reduction kinetics through hydrogen atom shuttling between reduced azo dyes (i.e., hydrazo dyes) and oxyanions or diatrizoate. This is the first research that has identified this synergetic effect, and it has implications for designing more efficient catalysts and reducing costs for Pd in water treatment systems.

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2.2 Introduction

Pd-based catalytic reduction with hydrogen has emerged as a promising approach to treat a variety of contaminants including nitrate (NO$_3^-$) (1-7), N-nitrosodimethylamine (NDMA) (8, 9), perchlorate (ClO$_4^-$) (10), and trichloroethylene (TCE) (11-13). Relevant Pd-based catalysts for these contaminants include Pd (11, 12), Pd-In (1, 2, 4, 9), Pd-Cu (3, 7), Pd-Sn (7, 14), and Pd-Re (10). The economic feasibility of Pd-based catalysts was recently demonstrated in a pilot study by Davie et al. (13); Pd-based catalytic treatment of TCE in groundwater at Edwards Air Force Base California was potentially less expensive than treatment with activated carbon ($8/1000$ gal versus $10-336/1000$ gal). Also, activated carbon and other competing technologies such as ion exchange, electrolysis, and reverse osmosis produce concentrated residues that require subsequent treatment or disposal. Another promising alternative, biological treatment, is less robust to system interruptions and engenders concerns for pathogens in drinking water (13, 15).

Catalytic reduction can be affected by the presence of multiple contaminants. They may compete for reactive sites or hydrogen on the catalyst surface and lower reduction rates (16), or they may provide synergistic effects that enhance reduction rates (17). In this work the effects of selected azo dyes on catalytic reduction rates for a suite of natural water pollutants were investigated; including nitrate, nitrite, perchlorate, chlorate, bromate, NDMA, and diatrizoate. The suite of pollutants was selected because of their presence in drinking water resources, and their negative ecological and health impacts (18-28). Nitrate and nitrite come from fertilizers (29); perchlorate is used as an oxidant in rocket fuel, munitions, or blasting materials (23); chlorate, bromate, and NDMA are associated with disinfection processes in water treatment (30-32); diatrizoate occurs...
in hospital wastewater and is an iodinated X-ray contrast reagent (33). Azo dyes were chosen as the co-contaminants of interest because in initial studies they enhanced catalytic reduction rates of oxyanion pollutants. Some azo dyes, along with some azo dye products after water treatment (amines and other derivatives), have carcinogenic and mutagenic properties (34-36). They are widely used in industrial processes such as textile, leather, printing, plastic, food, paint, cosmetics, and pharmaceutical industries (37). Their frequent occurrence in surface and ground waters is well documented, especially in developing countries such as Brazil, China, and India; their occurrence in agricultural regions of developing countries where nitrate is present has also been observed (38-42).

The objectives of this study are to explore the effect of selected azo dyes on the enhancement of catalytic reduction rates for nitrate, nitrite, perchlorate, chlorate, bromate, NDMA, and diatrizoate, and to elucidate the mechanism of this enhancement. Methyl orange (MO) was initially selected as a probe azo dye to evaluate reaction rate enhancement of the selected contaminants. Next, nitrate was selected as a probe contaminant, and a suite of azo dyes were evaluated; these were MO, methyl red (MR), fast yellow AB (FYAB), metanil yellow (MY), acid orange 7 (AO7), congo red (CR), eriochrome black T (EBT), acid red 27 (AR27), acid yellow 11 (AY11), and acid yellow 17 (AY17) (dye structures are provided in Figure 2.1). Corresponding rates of reduction were compared to different dye properties to explore enhancement mechanisms, including hydrogenation energies calculated from density functional theory, and a kinetic model based on Brønsted–Evans–Polanyi (BEP) theory was developed for mechanistic interpretation. This is the first research that has identified the synergetic effects of
some azo dyes on co-contaminant reduction in catalytic systems, and it provides new insights for developing novel catalysts with higher activity.

![Figure 2.1 Structures and molecular formulas of selected azo dyes: (a) Methyl orange (MO); (b) Methyl red (MR); (c) Fast yellow AB (FYAB); (d) Metanil yellow (MY); (e) Acid orange 7 (AO7); (f) Congo red (CR); (g) Eriochrome black T (EBT); (h) Acid red 27 (AR27); (i) Acid yellow 11 (AY11); and (j) Acid yellow 17 (AY17).]

2.3 Materials and Methods

All chemicals except azo dyes were reagent grade (>99% purity) and were purchased from Fisher (NaNO₃, NaNO₂), Alfar-Aesar (methanol, sulfanilic acid) or Sigma-Aldrich (KBrO₃, KClO₃, NDMA, sodium diatrizoate dihydrate, NaClO₄·H₂O, Na₂HPO₄·2H₂O, NaH₂PO₄, NH₄ReO₄, In(NO₃)₃·5H₂O). Azo dyes were technical grade (percent purity is reported as available) and were purchased from Acros (acid red 27 >85% purity, congo red >91% purity,
metanil yellow >98% purity, methyl red, acid orange 7, acid yellow 11, acid yellow 17), Alfar-Aesar (methyl orange) or TCI (eriochrome black T). The primary impurities in azo dyes are their parent amines, based on study of Direct Black 38 and Pigment Yellow 12 (43); small amounts of dispersants (e.g., polymers, surfactants) are also likely. It will also show that amines of the azo dye MO do not affect reaction rate enhancement. All chemicals were used without further purification. Ultra-high purity hydrogen (H₂-99.999%) was supplied by Matheson Tri-Gas (Joliet, IL). Nanopure water (18 MΩ•cm; purified from deionized water in Barnstead NANOpure system) was used to prepare all solutions.

A 5 wt% Pd on g-Al₂O₃ catalyst was purchased from Sigma-Aldrich. It was wet sieved to obtain particles less than 38 µm, which is referred to as Pd hereafter. The Pd was used for nitrite, bromate, and diatrizoate reduction. The incipient wetness method was used to prepare a 5 wt% Pd-0.5 wt% In on γ-Al₂O₃ catalyst (referred to as Pd-In hereafter) as previously described (4). The Pd-In was used for nitrate, nitrite, bromate, and NDMA reduction. A Pd-Cu traditional catalyst (referred to as Pd-Cu T) and a Pd-Cu colloidal catalyst (referred to as Pd-Cu C) on γ-Al₂O₃ were prepared by the incipient wetness method and the colloidal method, respectively, both described by Guy et al. (44). Both Pd-Cu T and Pd-Cu C were used for nitrate reduction. A Pd-Re/activated carbon catalyst (referred to as Pd-Re) was prepared by hydrogen reduction of perrhenate on 5 wt% Pd on activated carbon. The Pd on activated carbon was supplied from Sigma-Aldrich, and it was wet sieved to obtain particles less than 125 µm before use. It was then dispersed in an aqueous solution, adjusted to pH=2.68 with H₃PO₄, and ammonium perrhenate was added to the solution with hydrogen sparging for 5 hours. The freshly prepared Pd-Re was used for chlorate and perchlorate reduction.
Catalytic reduction experiments were performed in a 500 mL five-neck reaction flask at 21±0.3 °C with continuous H₂ sparging (300 mL/min) and stirring at ca. 500 rpm. The same setup was used by Frierdich (45) and Knitt (46). Control experiments demonstrated contaminant reduction kinetics were not limited by hydrogen supply or external mass transfer. The reaction flask was initially filled with 400 ml of nanopure water, and then amended with pre-weighed catalyst. The reactor was sealed with silicon rubber stoppers, and pre-sparged with H₂ for 20 minutes at 300 mL/min to reduce the oxidized catalyst surface and remove dissolved oxygen. A target contaminant was added alone or with an azo dye. The pH of solution was maintained at either 5.00 or 2.68 (for perchlorate and chlorate) by adding small amounts of HCl or H₃PO₄ using a pH-stat (TIM 856, Radiometer Analytical). During reaction, 2-3 mL aqueous samples were taken at regular time intervals, filtered using 0.45 μm PTFE syringe filter (Cole-Parmer), and stored in a refrigerator at 4 °C before analysis. To evaluate the time scale over which azo dyes can enhance oxyanion reduction kinetics, an experiment was performed using the same reactor setup but nitrate was spiked into the system every 20 minutes to create the same initial concentration (2.35 mM) nine times. Catalytic reduction experiments for selected contaminants have been successfully performed at other pH values including neutral, and using buffers including CO₂ (3, 14). The experimental conditions in this work were chosen to simplify interpretation of the mechanisms that affect reduction rate enhancement.

Nitrate, nitrite, bromate, and chlorate were analyzed using ion chromatography (Dionex ICS-2000; Dionex IonPac AS18 column; 36 mM KOH as eluent; 1 mL/min eluent flow rate; 25 μL injection loop). Perchlorate was also analyzed by ion chromatography (Dionex ICS-2000;
Dionex IonPac AS16 column; 36 mM KOH as eluent; 1 mL/min eluent flow rate; 1000 µL injection loop) (10). NDMA, diatrizoate, MO and its reduced product, sulfanilic acid (SA), were analyzed by high performance liquid chromatography (Shimadzu Prominence LC-20AT). Separation was achieved by a Dionex Acclaim 120 C18 (3 µm Analytical, 4.6 x 100 mm) column maintained at 40 °C. For NDMA analysis, the eluent was an 80/20 (V/V) water/methanol mixture at 1 mL/min (45). For diatrizoate analysis, the eluent was a mixture of 20 mM phosphate buffer (pH=7), 5 mM triethylamine and 5% (V%) methanol at 1 mL/min (46). The MO and SA were analyzed with the following eluents: a 10 mM phosphate buffer (pH=7) /nanopure water maintained for 2.5 minutes, a 0.5 minute transition to a 60/40 methanol/nanopure water mix maintained for 5 minutes, a 0.5 minute transition back to the 10 mM phosphate buffer (pH=7) maintained for 3.5 minutes. NDMA, diatrizoate, MO, and SA were detected at 226 nm (45), 237 nm (46), 463 nm, and 254 nm, respectively, with a photodiode array detector. Ammonia was measured with an ammonia gas sensitive probe (Orion 9512), after adjusting the pH of the samples to 13 by adding NaOH.

Contaminant concentrations during catalytic reduction followed pseudo-first-order behavior for degradation of at least half of initial concentrations, so first order rate constants were determined for all reaction experiments and used for comparison. First order rate constants were determined from linear regressions of relative concentrations on a natural log scale plotted versus time. Pseudo first order rate constants have been used to compare initial reaction rates for many different catalytic reduction experiments (4, 8, 10, 11, 46). Each reduction experiment (except for time scale evaluation of MO enhancement on nitrate) was repeated twice, and 95% confidence intervals were calculated for reduction rate constants.
2.4 Results and Discussion

2.4.1 Effects of Methyl Orange on Oxyanion, Diatrizoate, and NDMA Reduction

First order rate constants for catalytic reduction of the study pollutants in both the presence and absence of MO are illustrated in Figure 2.2. Rate constants for nitrate, nitrite, and perchlorate in the absence of MO are in the range of those reported in the literature (1, 3, 4, 10); however, reduction rates of diatrizoate and NDMA are slightly lower (55% and 66% lower, respectively) than reported (8, 46). For diatrizoate, this may be due to the lack of catalyst activation by hydration (46). To the best of its knowledge, this is the first time that bromate reduction kinetics has been reported using Pd-based catalysts. Rapid bromate reduction on Pd-based catalysts was mentioned in an earlier study, but no data was provided (30). The reaction rates of bromate are comparable to those of nitrite under the same conditions. Reduction pathways of oxyanions were proposed to be successive oxygen atom transfers with deoxygenation (10, 14, 30) (e.g., nitrate/nitrite, bromate, and chlorate/perchlorate were reduced to form dinitrogen, bromide, and chloride, respectively); while successive deiodination was proposed for diatrizoate reduction (46). The proposed reduction pathway for NDMA is N-N bond cleavage to form dimethylamine and N\textsubscript{2} or ammonia (45). First order rate constants for all oxyanions (nitrate, nitrite, bromate, chlorate, and perchlorate) and diatrizoate were enhanced in the presence of MO. Although the same concentration of MO (15.3 µM) was applied, it had a broad range of enhancement factors for oxyanions on Pd-based catalysts, ranging from 1.10 for perchlorate on Pd-Re to 5.24 for nitrate on Pd-In. However, rate constants for NDMA were less in the presence of MO.
Figure 2.2 Reduction kinetics of nitrate (NO$_3^-$), nitrite (NO$_2^-$), bromate (BrO$_3^-$), chlorate (ClO$_3^-$), perchlorate (ClO$_4^-$), diatrizoate, and N-nitrosodimethylamine (NDMA) on Pd-based catalysts in the presence or absence of methyl orange (MO) addition. The different Pd-based catalysts (e.g., Pd-In, Pd-Cu T, Pd-Cu C, Pd-Re) are described in Materials and Methods. Data values above each pair of bars represent the rate constant enhancement factors, which are rate constants with MO addition divided by those without MO addition. Error bars represent 95% confidence intervals.

The initial concentration of MO (15.3 µM) was small compared to initial oxyanion concentrations (2.35 mM), and many azo dyes are known to reduce on Pd-based catalysts in the presence of hydrogen (47). The first reduction step of MO is proposed to be hydrogenation of the azo group to form reduced MO (dihydro MO); the second step is cleavage of MO at the azo
group to form equimolar amounts of the two amines sulfanilic acid (SA) and dimethyl-p-phenylenediamine (DMPPD); the third and subsequent steps include reduction of the SA, DMPPD, and their transformation products (48). MO reduction and SA production on the Pd-In catalyst used for nitrate reduction were measured. More than 99% of the MO was removed from solution after 5 minutes, and initial production of SA was almost stoichiometric (88% of transformed MO). At the same time, SA decayed slowly with a half life of 3.23 h (Figure A.1 of Appendix A). Adsorption tests of MO and SA indicated their adsorption on the catalysts were negligible (<3%). In contrast, 83% of nitrate remained after 5 minutes, and nitrate reduction enhancement occurred over the entire nitrate reduction period. This suggests that small amounts of MO (<12% of initial mass) and/or its reduction intermediates, either in bulk solution or even less amounts sorbed, cause enhancement of oxyanion reduction.

The presence of MO was shown to inhibit NDMA reduction. NDMA reduction is proposed to go through cleavage of the N-N bond (45); the mechanism of MO reduction to SA and DMPPD is similar (i.e., first the N-N double bond is reduced, and then the N-N single bond is cleaved). Similar reduction pathways may result in competition for the reductant (atomic hydrogen) and/or the same active locations on the catalyst (e.g., edge or terrace sites), and result in inhibition of NDMA reduction.

Oxyanion and halogenated contaminant reduction rate enhancement in the presence of MO was observed on all Pd-based catalysts tested (i.e., Pd, Pd-In, Pd-Cu T, Pd-Cu C, and Pd-Re). The mechanisms for contaminant reduction differ on each catalyst, and therefore suggest that the mechanism of enhancement is not metal specific and may be widely applicable to oxyanion and
halogenated contaminant reduction on a variety of catalysts. For example, nitrate reduction is thought to occur on In or Cu, with hydrogen spillover from Pd; nitrite and bromate reduction is thought to occur on Pd, while chlorate and perchlorate reduction occurs on Re with hydrogen spillover from Pd. In or Cu is necessary for nitrate reduction, while Re is critical for chlorate and perchlorate reduction. No reaction occurs in the absence of Pd and H$_2$. The extent of rate enhancement, defined by the enhancement factors in Figure 2.2, varies widely for the same contaminant on different catalysts. For example, the enhancement factors for nitrate reduction on Pd-In was 2.74 times greater than that on Pd-Cu T. This indicates that catalysts properties (e.g., surface area, metal dispersion, and bimetallic distribution) affect reaction rate enhancement.

2.4.2 Mechanisms of Oxyanion and Diatrizoate Reduction Enhancement by Selected Azo Dyes

Mechanisms of azo dye-mediated reaction rate enhancement of oxyanions and diatrizoate are explored using nitrate as the probe contaminant and MO as the model azo dye. Several lines of evidence suggest that azo dye-mediated rate enhancement occurs by the adsorption of the azo dye to the catalyst surface. The MO transformation products SA and DMPPD were each combined with nitrate individually to evaluate if reaction rate enhancement occurred. Nitrate reduction rates are not enhanced in the presence of either SA or DMPPD, indicating that MO, and/or the reduced intermediate of MO, rather than amines is responsible for reduction enhancement of oxyanions and diatrizoate.

Nitrate reduction rates were evaluated at different MO initial concentrations. First order rate constants increase sharply between a MO concentration of zero and 0.546 µM; beyond the latter
concentration (0.546-27.0 µM) they are relatively stable with enhancement factors between 4 and 6 (Figure A.2 of Appendix A). The initial nitrate concentration (2.35 mM) in all cases was much greater than the initial MO concentration (0.153-27.0 µM, the initial concentration ratios of nitrate to MO vary from 87.1 to 1.54×10⁴). Hence, reaction rate enhancement only requires trace levels of MO (relative to nitrate), and is insensitive to aqueous MO concentrations above some threshold. This observation suggests that only trace amounts of MO, and/or its reduced form are responsible for rate enhancement.

First order rate constants were measured for nine sequential nitrate reduction experiments. Nitrate was spiked in the reactor in 20 minute intervals with either MO addition at time zero only or without MO addition. First order rate constants decrease for each sequential experiment with and without MO; they decrease from 4.30×10⁻² min⁻¹ to 1.10×10⁻² min⁻¹ over nine sequential experiments with MO, and from 7.77×10⁻³ min⁻¹ to 2.49×10⁻³ min⁻¹ without MO (Figure A.3 of Appendix A). During nitrate reduction, OH⁻ is produced and HCl addition is necessary to control pH. Either increasing concentrations of these ions (3), or changes in catalyst morphology and configuration (2) negatively impact reactivity. Regardless of the reason, rate constants with MO are always greater than those without MO. This results in an enhancement factor for nitrate reduction that is relatively constant (varies from 4 to 7) over 180 minutes and nine sequential nitrate additions, even though MO in solution reached non-detect limits in less than 10 minutes. This result suggests that trace amounts of sorbed MO, and/or its reduced form, are stable over long periods, and result in reduction rate enhancement for nitrate.
Mechanisms of reaction rate enhancement are further explored using a suite of azo dyes (i.e., MO, MR, FYAB, MY, AO7, CR, EBT, AR27, AY11, and AY17) and nitrate as the probe contaminant. All azo dyes except CR have one azo bond and were initially at 15.3 µM; CR has two azo bonds and was initially at 7.5 µM. As illustrated in Figure 2.3, reaction rate enhancement of nitrate was observed with MO, MR, FYAB, MY, AO7, and CR, but not with EBT, AR27, AY11, and AY17.

**Figure 2.3** Correlation between hydrogenation energies (HE) of different azo dyes and nitrate reduction rate constants. Error bars represent 95% confidence intervals. Solid cubic symbols represent data used to fit the volcano curve, while open cubic symbols represent exceptions. The dashed line represents the kinetic model fit of the data.
Various azo dye physical and chemical properties were explored to search for correlations with nitrate reduction rate enhancement. Diffusion coefficient, logK_{ow} and average molecular charge estimated using the SPARC database ([http://ibmlc2.chem.uga.edu/sparc/](http://ibmlc2.chem.uga.edu/sparc/)) were uncorrelated with nitrate reduction rate enhancement (Table A.4 of Appendix A). Mass-transfer limitations and overall dye polarity thus do not appreciably affect or contribute to the observed rate enhancement.

As noted above, the azo group (-N=N-) is readily reduced by hydrogen; to investigate the potential contributions of this redox process to nitrate reduction rate enhancement, we used first-principles density functional theory (DFT) methods to calculate azo dye hydrogenation energies (HE):

\[
\text{Ph} \text{N} = \text{N} \text{Ph} + \text{H}_2 \rightleftharpoons \text{Ph} \text{N} = \text{NH} \text{Ph}
\]

Optimized reactant and product structures and energies were calculated at the B3LYP/6-311G** level using the Gaussian code (49), and results are plotted in Figure 2.3. The conformations of azo groups in dyes with lower energy were considered; therefore all azo dyes were taken to adopt a trans conformation except for AY17 with the cis conformation. Aniline, amine, phenol, and nitro groups were taken to be neutral and sulfonic and carboxylic acid groups to be deprotonated, consistent with expectation at pH 5 (Table A.5 of Appendix A). The products all possess pyramidal hydrazo nitrogens and exhibit the same two dominant conformations. Again the HE corresponding to the lowest energy conformer is reported in each case.

In Figure 2.3, the reduction rate constant is plotted against the calculated HE. The results follow a volcano curve, in which enhancement is small for the most difficult (e.g., EBT, AY17) and
most easy (e.g., FYAB) to hydrogenate dyes, while enhancement is greatest for MO, which has an intermediate HE. This suggests that azo dyes and their hydrazo forms which gain and donate hydrogen atoms most easily enhance nitrate reduction. These results suggest a model in which the enhancement is connected with the ability of sorbed azo dyes to reversibly “shuttle” hydrogen between catalyst and the relevant contaminants (i.e., oxyanions or diatrizoate). A volcano relationship between catalyst activity and dissociative chemisorption energy of reactants on catalyst surface is commonly associated with heterogeneous catalytic reactions (50).

CR and MR are notable exceptions to the volcano trend. CR is a double-azo dye with first (-93 kJ/mol -N=N-) and second (-79 kJ/mol -N=N-) HE’s comparable to MO. However, it is larger than single-azo dyes and steric hindrance may restrict its reduction on or near the catalyst surface, thus diminishing its potential for enhancement of nitrate reduction kinetics. In contrast to CR, MR has a much greater observed enhancement than expected for its quite negative HE. MR has an ortho carboxylate group, and intramolecular hydrogen bonding contributes significantly to the stability of the hydrogenated product. This intramolecular effect is expected to be less significant in aqueous solution. Moving the carboxylate to the meta (HE= -107 kJ/mol -N=N-) or para (HE= -83 kJ/mol -N=N-) position eliminates this spurious effect and places MR closer to the volcano curve of Figure 2.3.

The volcano behavior can be explained in terms of a simple kinetic model that takes advantage of the Brønsted–Evans–Polanyi (BEP) relation between reaction energies and rate constants (50). All data except for CR and MR are applied to develop and fit the kinetic model. The overall
reaction includes two steps: reduction of azo dyes with hydrogen oxidation, and oxidation of hydrazo dyes with nitrate reduction.

1. \textit{azo dye} + H\textsubscript{2} \xrightleftharpoons{Pd-In} \textit{hydrazo dye}

2. \textit{hydrazo dye} + NO\textsubscript{3}\textsuperscript{-} \xrightleftharpoons{Pd-In} \textit{azo dye} + NO\textsubscript{2}\textsuperscript{-} + H\textsubscript{2}O

It is assumed that the overall nitrate reduction rate is limited either by reaction 1 or by reaction 2. However, because nitrate is still reduced at some background rate on the Pd-In catalyst in the absence of an azo dye, and because an azo dye can either enhance or have no effect on the reaction rate, the final expression for the overall nitrate reduction rate can be written as:

\[ r = \max(r_b, \min(r_1, r_2)) \]  \hspace{1cm} (1)

In this expression, \( r \) is the overall nitrate reduction rate (\text{mol/(L\cdot min)}), \( r_b \) is the background nitrate reduction rate (\text{mol/(L\cdot min)}), \( r_1 \) and \( r_2 \) are rates of reaction 1 and 2 (\text{mol/(L\cdot min)}).

Nitrate reduction rate constant rather than the reduction rate was calculated in this study, and nitrate reduction follows pseudo-first-order behavior for at least half of its decay. Consequently, nitrate reduction rate constant \( k_{NO_3^-} \) at time zero can represent the initial reduction rate constant, and it is derived as:

\[ k_{NO_3^-} = \frac{r}{[NO_3^-]_0} = \begin{cases} 
  k_b = \frac{r_b}{[NO_3^-]_0}, & \text{when } \min(r_1, r_2) \leq r_b \\
  \nu_1 e^{-\frac{E_{H2}+\beta}{RT} [azo]_0[H_2]_0} \frac{[azo]_0[H_2]_0}{[NO_3^-]_0}, & \text{when } r_b < r_1 \leq r_2 \\
  \nu_2 e^{-\frac{E_{H2}+\beta}{RT} [azo]_0[H_2]_0} \frac{[azo]_0[H_2]_0}{[NO_3^-]_0}, & \text{when } r_b < r_2 < r_1 
\end{cases} \]  \hspace{1cm} (2)
In this equation, HE is the hydrogenation energy value of azo dyes (kJ/mol), \( \alpha \) is the transfer coefficient, \( \beta \) is the intrinsic activation barrier (kJ/mol), and \( \nu \) is the preexponential factor (L/(mol·min)). \([\text{NO}_3^-]_0\) and \([\text{azo}]_{s0}\) are nitrate and sorbed azo dye concentration at time zero (mol/L), respectively; \([\text{H}_2]_0\) is the saturated hydrogen concentration (0.773 mM) at 21±0.3 °C, 1 atm. R is the gas constant (8.31 J/(K·mol)), and T is the temperature in Kelvin (294 K). Full details of the model derivation are in Appendix A.

In order to fit the kinetic model to the data, a value of \( \beta \) in the range of literature values (50 kJ/mol -N=N-, ca. 0.5 eV) (50) was selected, natural log \( k_{NO_3^-} \) versus HE (equation S2.18 of Appendix A) was plotted, \( \alpha \) was adjusted to match the slope of the data, and \( \nu \) was adjusted to match the intercept. It is recognized that the range of \( \beta \) values in the literature are large, and other possible sets of parameter values will match the data. The model results are plotted as a dashed line in Figure 2.3. Model data inputs and fitting parameters are summarized in Table A.6 of Appendix A. The kinetic model shows volcano behavior, and supports the hypothesis that azo dyes enhance contaminant reaction rates by reversibly shuttling hydrogen between catalyst and contaminants.

Enhancement factors observed for oxyanions and diatrizoate using MO but not SA or DMPPD, the volcano relationship between azo dye hydrogenation energies and reduction rate enhancement factors for nitrate, and corresponding agreement of this relationship with the theoretical kinetic model, all support the reduction rate enhancement mechanism proposed in Figure 2.4. Here, Pd-based catalysts dissociate hydrogen and promote reduction of both the oxyanion or diatrizoate pollutants, and azo dyes to hydrazo dyes. The hydrazo dyes subsequently
oxidize back to azo dyes, and in the process reduce oxyanions or diatrizoate. Experimental results with nitrate and the azo dye MO suggest that shuttling between the hydrazo dye and co-contaminant (i.e., oxyanion or diatrizoate) occurs in the presence of trace amounts of sorbed dye that persist on the catalyst surface after azo dyes are no longer detected in solution. This is the first time that azo dyes have been identified to promote reduction rate enhancement of oxyanions and diatrizoate, or implicated in a hydrogen atom shuttling mechanism. NDMA does not appear to participate in this hydrogen shuttling mechanism, and this may be due to its shared reaction mechanism with azo dyes (N-N bond cleavage) that results in competition for hydrogen and/or shared locations on the catalyst surface where reaction occurs.

Figure 2.4 Proposed hydrogen atom shuttling mechanism. Oxyanion and diatrizoate reduction occur on the Pd-based catalyst surface either through direct hydrogenation, or through hydrogen atom shuttling via the azo/hydrazo dye redox couple. Sorbed azo dyes can be reduced and form corresponding hydrazo dyes on catalyst surface, while
Hydrazo dyes can enhance oxyanion and diatrizoate reduction with the aid of catalyst. Excess azo dyes not sorbed to the catalyst surface decay and form amines.

2.4.3 Environmental Implication

Capital costs and operational lifetime are two key factors that affect economic viability of Pd-based catalytic treatment technologies (13). In this work, selected azo dyes enhance reduction rate constants by up to a factor of 5.24 for a suite of oxyanions and for diatrizoate. This suggests that the amount of Pd-based catalyst required for catalytic treatment of these drinking water pollutants will be lower when azo dyes are present. As previously noted, azo dyes are common surface water and groundwater pollutants in developing countries, and are found in agricultural watersheds where nitrate is also present. However, azo dyes are not commonly associated with the other contaminants evaluated in this study. Since many azo dyes, azo dye products (e.g., amines), and added dispersants are carcinogenic and/or mutagenic (34-36), adding them to water to enhance oxyanion or diatrizoate reduction kinetics is likely not prudent. An alternative approach to take advantage of reaction rate enhancement is to bind azo dyes or functional groups to catalyst supports. Azo dyes can be immobilized on activated carbon through a diazonium reaction (51, 52), and on silica or alumina by grafting with silane coupling (53) and a single stage Mannich reaction (54, 55). However, care must be taken to ensure that azo dyes are not mobilized into solution. Results from this study open up a new avenue of research that may lead to more active Pd-based catalysts for pollutant reduction, and decreased capital costs for Pd-based treatment systems.
2.5 References


(20) ATSDR. Toxicological profile for N-nitrosodimethylamine; Agency for Toxic Substances and Disease Registry (ATSDR), U.S. Public Health Service in collaboration with the U.S. Environmental Protection Agency: Washington, DC, 1989.


CHAPTER 3: A NEW GEOMETRIC METHOD BASED ON TWO-DIMENSIONAL TRANSMISSION ELECTRON MICROSCOPY FOR ANALYSIS OF INTERIOR VERSUS EXTERIOR Pd LOADING ON HOLLOW CARBON NANOFIBERS

3.1 Abstract

Hollow carbon nanofibers (CNFs) are being explored as catalyst supports because of their unique properties. Internal versus external loading of metal nanoparticles impacts catalytic performance; a fast and accurate geometric analysis method based on 2D TEM images was developed to estimate Pd internal versus external loading percentages. Three different Pd-loaded CNF catalysts were prepared using methods reported in the literature to yield different amounts of Pd inside loading. Results indicate the percentage of inside loaded Pd increases as expected in the three samples (from 22.7±17.8%, to 47.2±22.8%, to 71.4±19.7%, based on Pd nanoparticle number). The percent inside loading values for one segment of a Pd-loaded CNF was compared between using this method and 3D scanning transmission electron microscopy (3D TEM), and adequate agreement was observed (27.8% vs. 32.7%). This geometric analysis method is proposed as a more straightforward and fast way to evaluate metal nanoparticle on tubular supports.

3.2 Introduction

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Carbon nanofibers (CNFs) are a class of carbonaceous materials composed of graphene layers; they have attracted significant scientific and industrial interest for electronic (1), polymer (2), and catalytic (3) applications due to their unique structural, electronic, adsorption, mechanical, and thermal properties (3). Hollow CNFs are one type of CNFs first discovered in 1952 (4), which are ribbon-like nanofibers with graphene layers conically stacked parallel to the fiber axis, with interior pore sizes several tens of nanometers across. Hollow CNFs have shown promising results as active metal supports in a number of catalytic processes, including tetrachloroethylene hydrodechlorination (5), $\text{H}_2\text{S}$ oxidation (6), selective cinnamaldehyde hydrogenation (7), and electrocatalytic reaction in fuel cells (8). High activities of hollow CNF-supported catalysts compared to conventionally-supported catalysts (e.g., activated carbon, alumina) have been attributed to less coke formation, faster reactant mass transfer, higher metal dispersion, confinement effects inside pores, and favorable electronic properties resulting from curved graphene layers. These factors are motivating researchers to explore differences in performance and characteristics of catalysts with internal versus external loadings of active metals. A formidable challenge of this research is to quantify the amount of internal versus external metal loading on hollow CNFs.

Transmission electron microscopy (TEM) is the most widely used technique to characterize metals on catalyst supports; it often provides straightforward information on metal nanoparticle size, and support and metal nanoparticle morphology. However, the two-dimensional projections provided by TEM do not readily distinguish active metals loaded inside and outside hollow CNFs (9, 10). To overcome this limitation, electron tomography (3D TEM) has been used to visualize the location of metal nanoparticles on zeolites (11, 12), mesoporous silica (13), and
CNFs (10, 14). For CNFs, it has provided quantitative information on interior versus exterior metal loading. Electron tomography is conceptually straightforward; a specimen is placed on a high tilt sample holder, and multiple 2D images are taken with various tilt angles at the same spot to reconstruct a 3D tomographic model. The model illustrates the localization of metal nanoparticles on porous supports. Significant limitations of electron tomography are the much longer acquisition and analysis times compared to 2D imaging, reconstruction artifacts (missing wedge) due to the limited specimen tilt (±70°), the associated challenge of obtaining a statistically significant number of images, the lower resolution (1.5-2.5 nm) compared to 2D high resolution TEM (0.5 nm), and access to the relatively few TEM instruments configured for 3D tomography (10, 12, 15).

Herein, a relatively simple and fast way to quantify metal nanoparticle loadings inside and outside CNF pores is developed. The method relies on standard 2D TEM images, and geometrical calculations assume that CNFs are perfectly cylindrical with uniform inner and outer diameters, and that metal nanoparticles have uniform dimensions and spatial distribution on internal and external CNF surfaces. The outer and inner diameter of individual CNFs change less than 10% along their axis based on measurements, and uniform metal nanoparticle sizes and distributions are facilitated by functionalizing CNF surfaces with hydrophilic functional groups (3). The method allows many 2D TEM images to be analyzed (e.g., 40 individual CNFs for each sample were analyzed), and provides interior versus exterior loading values with uncertainty estimates. The method is applied to CNFs loaded with Pd nanoparticles, and results from this new method are compared with those from electron tomography and find adequate agreement.
3.3 Results and Discussion

**Figure 3.1** 2D transmission electron microscopic (TEM, a) and high angle annular dark field (HAADF) scanning transmission electron microscopic (STEM, b) images of 5Pd/CNFs. Pd nanoparticles are shown as the dark dots and the bright dots in TEM and STEM images, respectively. The yellow rectangle in the STEM image highlights the region used for 3D TEM analysis. Transversal slices of the reconstructed carbon nanofiber volume (c and d) indicating the location of Pd particles on interior and exterior surfaces of CNFs.
Three different Pd on CNF catalysts were prepared, one with primarily inside loaded Pd, one with proportionally both inside and outside loaded Pd, and one with primarily outside loaded Pd (10, 14). Details of preparation methods are included in Appendix B. The Pd wt % in all cases is 5 %, so the three samples are named 5Pd/CNFs-in, 5Pd/CNFs, and 5Pd/CNFs-out. The Pd nanoparticle diameters for these samples are 3.06±1.43 nm, 4.34±2.19 nm, and 2.54±1.33 nm, respectively, based on the analysis of approximately 3,000 Pd nanoparticles for each sample. A TEM Image of Pd loaded on 5Pd/CNFs is shown in Figure 3.1a. The dark spots represent Pd nanoparticles, and CNF supports are clearly visible with walls and internal hollow channels.

The percentages of inside/outside loaded Pd on CNFs were analyzed by developing a geometric relationship between 3D Pd localization and the 2D projection on TEM images; a schematic illustration of a CNF cross section with Pd nanoparticles, and corresponding TEM image, are shown in Scheme 3.1. Before TEM imaging, a small amount of each prepared catalyst sample was ultrasonicated in ethanol, and an aliquot of sample suspension was loaded on a copper grid for TEM imaging. Ultrasonication helps to uniformly disperse CNFs in solution (10, 16), so the CNFs loaded onto the copper grid are representative of the whole sample. During TEM imaging, the axes of selected CNFs lied perpendicular to the electron beam when CNFs were not tilted due to their large aspect ratio (i.e., length-to-diameter ratio, ranging from 30 to many thousands (17)). 40 representative individual CNFs with various diameters were randomly chosen from a much larger number of individual CNFs on the copper grid, because individual CNFs have different internal/external diameters and lengths. All of them were clearly observed with both Pd nanoparticles and CNF walls. For each CNF, a short cylindrical segment (with length L ca. 100 nm) to represent the whole CNF (whole CNF lengths varied from several to a dozen microns)
was selected for analysis; each short segment had sufficient Pd nanoparticles (i.e., 50-100) for statistical analysis.

**Scheme 3.1** Geometric relationship between Pd nanoparticle localizations and their projections in a 2D transmission electron microscopic (TEM) image. Cross-sectional schematic of a Pd loaded CNF is shown; O is the center of the CNF cross section, OB is the outer radius of the CNF, the horizontal line OA is the inner radius of the CNF (i.e., radius of CNF hollow channel), and OA is perpendicular to AB. θ is the angle between OB and AB, and it is also the angle between OB and beam lines. Inside and outside loaded Pd nanoparticles are depicted as gray and black dots, respectively. The projections of Pd nanoparticles on CNF walls are the ones exclusively loaded outside (highlighted by the blue region), and the projections of Pd nanoparticles in the CNF internal channel include those either loaded inside or outside (highlighted by yellow region).

The dispersion of Pd nanoparticles on internal versus external surfaces was calculated based on the number (i.e., n, the number of Pd nanoparticle per CNF surface area, nm⁻²), surface area (i.e., a, the total surface area of Pd nanoparticle per CNF surface area), and mass (i.e., m, the total
mass of Pd nanoparticle per CNF surface area, g nm\(^{-2}\)) of Pd nanoparticles, all normalized by CNF surface area. The corresponding equations are given by:

\[ n_{in} = \frac{N_{in}}{S_{in}} = \frac{N_{in}}{\pi dL}; \tag{3.1} \]

\[ n_{out} = \frac{N_{out}}{S_{out}} = \frac{N_{out}}{\pi DL}; \tag{3.2} \]

\[ a_{in} = \frac{A_{in}}{S_{in}} = \frac{\sum \pi d_{pd}^2}{\pi dL}; \tag{3.3} \]

\[ a_{out} = \frac{A_{out}}{S_{out}} = \frac{\sum \pi d_{pd}^2}{\pi DL}; \tag{3.4} \]

\[ m_{in} = \frac{M_{in}}{S_{in}} = \frac{\sum \frac{1}{6} \pi d_{pd}^3 \rho_{pd}}{\pi dL}; \tag{3.5} \]

\[ m_{out} = \frac{M_{out}}{S_{out}} = \frac{\sum \frac{1}{6} \pi d_{pd}^3 \rho_{pd}}{\pi DL}; \tag{3.6} \]

where \(N_{in}\) and \(N_{out}\), \(A_{in}\) (nm\(^2\)) and \(A_{out}\) (nm\(^2\)), and \(M_{in}\) (g) and \(M_{out}\) (g) are the total number, total surface area, and total mass of Pd nanoparticles loaded on interior and exterior surfaces, respectively. \(S_{in}\) (nm\(^2\)) and \(S_{out}\) (nm\(^2\)) represent the interior and exterior surface areas of a CNF segment with length \(L\), and \(D\) (nm) and \(d\) (nm) are the outer and inner CNF diameters. The parameter \(\rho_{pd}\) is the density of Pd metal (12.023 g cm\(^{-3}\)), and \(d_{pd}\) (nm) is the diameter of a Pd nanoparticle. It is assumed that Pd nanoparticles are spherical, and corresponding diameters are calculated based on their projection areas (\(\text{Area}_{pd}\), nm\(^2\)) by:

\[ d_{pd} = 2 \sqrt{\frac{\text{Area}_{pd}}{\pi}}. \tag{3.7} \]
The spherical nanoparticle assumption is appropriate because the most stable form of Pd nanoparticles is a truncated octahedron with nearly spherical shape (18). The projected Pd nanoparticle numbers on the outer wall \( (N'_{\text{out}}) \) and internal channel \( (N'_{\text{in}}) \) for one CNF segment from the 2D TEM image are counted; and the total surface area and total mass of all projected Pd nanoparticles on the outer wall \( (A'_{\text{out}}, \text{nm}^2, \text{and} \ M'_{\text{out}}, \text{g}) \) and internal channel \( (A'_{\text{in}}, \text{nm}^2, \text{and} \ M'_{\text{in}}, \text{g}) \) of the CNF segment are also calculated based on individual Pd nanoparticle diameters \( d_{\text{Pd}} \).

From the geometric relationship in Scheme 3.1, the projections of Pd nanoparticles on the CNF outer wall are the ones exclusively loaded on the exterior surface (blue region in Scheme 3.1), whereas the projections of Pd nanoparticles on the CNF inside channel include Pd loaded on both interior and exterior surfaces (yellow region in Scheme 3.1). The number, total surface area, and total mass of Pd nanoparticles are proportional to the occupied external CNF surface, assuming Pd is uniformly distributed. The counted number or calculated total surface area and total mass of Pd nanoparticles whose projections are on CNF walls or internal channel are estimated for one CNF segment by:

\[
N'_{\text{in}} = \pi dL_{\text{in}} + 2D\theta L_{\text{out}}; \quad (3.8)
\]

\[
N'_{\text{out}} = (\pi DL - 2D\theta L)n_{\text{out}}; \quad (3.9)
\]

\[
A'_{\text{in}} = \pi dD_{\text{in}} + 2D\theta a_{\text{out}}; \quad (3.10)
\]

\[
A'_{\text{out}} = (\pi DL - 2D\theta L)a_{\text{out}}; \quad (3.11)
\]

\[
M'_{\text{in}} = \pi dM_{\text{in}} + 2D\theta m_{\text{out}}; \quad (3.12)
\]

\[
M'_{\text{out}} = (\pi DL - 2D\theta L)m_{\text{out}}; \quad (3.13)
\]

Where \( \theta \) is the angle between the outer radius OB and electron beam in Scheme 3.1, and is calculated by:
\[ \theta = \arcsin \frac{d}{D}. \quad (3.14) \]

The assumption of negligible CNF diameter variation leads to a fixed \( \theta \) for one CNF segment. To minimize errors, triplicates were performed for \( D \) and \( d \) measurement at three different locations of a CNF segment, and the mean values are used for calculation.

Finally the inside and outside Pd loading percentages for one individual CNF with respect to the number (\( N_{in}\) % and \( N_{out}\) %), surface area (\( A_{in}\) % and \( A_{out}\) %), and mass (\( M_{in}\) % and \( M_{out}\) %) are estimated based on the counted number or calculated surface area and mass of Pd nanoparticles from the corresponding 2D TEM image, and their expressions are:

\[
N_{in}\% = \frac{N_{in}}{N_{in} + N_{out}} = \frac{N_{in}'(\pi - 2\arcsin \frac{d}{D}) - 2N_{out}' \arcsin \frac{d}{D}}{(N_{in}' + N_{out}')(\pi - 2\arcsin \frac{d}{D})}; 
\]

\[
N_{out}\% = \frac{N_{out}}{N_{in} + N_{out}} = \frac{\pi N_{out}'}{(N_{in}' + N_{out}')(\pi - 2\arcsin \frac{d}{D})}; 
\]

\[
A_{in}\% = \frac{A_{in}}{A_{in} + A_{out}} = \frac{A_{in}'(\pi - 2\arcsin \frac{d}{D}) - 2A_{out}' \arcsin \frac{d}{D}}{(A_{in}' + A_{out}')(\pi - 2\arcsin \frac{d}{D})}; 
\]

\[
A_{out}\% = \frac{A_{out}}{A_{in} + A_{out}} = \frac{\pi A_{out}'}{(A_{in}' + A_{out}')(\pi - 2\arcsin \frac{d}{D})}; 
\]

\[
M_{in}\% = \frac{M_{in}}{M_{in} + M_{out}} = \frac{M_{in}'(\pi - 2\arcsin \frac{d}{D}) - 2M_{out}' \arcsin \frac{d}{D}}{(M_{in}' + M_{out}')(\pi - 2\arcsin \frac{d}{D})}; 
\]
\[ M_{\text{out}} \% = \frac{M_{\text{out}}}{M_{\text{in}} + M_{\text{out}}} = \frac{\pi M'_{\text{out}}}{(M'_{\text{in}} + M'_{\text{out}})(\pi - 2 \arcsin \frac{d'}{D})}. \]  

(3.20)

The analysis and calculation for the other representative individual CNFs were repeated, and the mean values and standard deviations for Pd nanoparticle inside and outside loading percentages for 5Pd/CNFs-in, 5Pd/CNFs, and 5Pd/CNFs-out were obtained. The values of Pd loading percentages are shown in Figure 3.2. The sum of Pd inside and outside loadings based on number, surface area, or mass is 100%, and they share the same standard deviation. Hence, in the following discussion only the values of Pd inside loading percentage are addressed.

**Figure 3.2** Pd nanoparticle inside and outside loading percentages of 5Pd/CNFs-in, 5Pd/CNFs, and 5Pd/CNFs-out.

The percentages represent the number, surface area, or mass of Pd nanoparticles loaded on interior or exterior
surfaces of CNFs relative to total values. Calculations based on number are filled with white and labeled as N, based on surface area are filled with light gray and labeled as A, and based on mass are filled with dark gray and labeled as M. Regions that represent inside and outside loadings are filled with blank and oblique line patterns, respectively. Error bars represent standard deviations.

The calculated percentages of inside loaded Pd on 5Pd/CNFs-in, 5Pd/CNFs, and 5Pd/CNFs-out are 71.4±19.7%, 47.2±22.8%, and 22.7±17.8%, respectively, based on number of Pd nanoparticles; 66.4±20.9%, 42.4±28.5%, and 19.5±18.0%, respectively, based on Pd surface area; and 63.3±24.9%, 61.8±32.5%, and 20.0±20.0%, respectively, based on Pd mass. The values of inside Pd loading percentages for 5Pd/CNFs-in in terms of number, surface area, and mass are not statistically different; the same is true for 5Pd/CNFs-out. However, the Pd loading percentages for 5Pd/CNFs based on number and surface area differ from the percentages based on mass. This may result from Pd size variations on interior and exterior CNF surfaces for 5Pd/CNFs, and/or more uniform Pd size distributions for 5Pd/CNFs-in and 5Pd/CNFs-out. CNFs used in this study were graphitized at 3000 °C during production; hence, they are difficult to functionalize with nitric acid and some hydrophobic regions may remain (19). This may contribute to nonuniform Pd nanoparticle formation on inside and outside surfaces. The Pd inside loading percentages agree with the expected trend (based on Pd-loading methods), and also indicate successful preparation of Pd on CNFs.

To further test the validity of this method for evaluating inside versus outside Pd loading on CNFs, 3D scanning transmission electron microscopy (STEM) with high angle annular dark field (HAADF) imaging for one CNF segment from 5Pd/CNFs was performed. Several 2D images were taken at various sample tilting angles, and a video clip was formatted (scale bar 200 nm, Appendix B). One image is shown in Figure 3.1b, and the bright dots and haze parts represent Pd.
nanoparticles and CNF walls, respectively. The yellow rectangle highlights the region of which Pd localization was analyzed. This one CNF segment with Pd was also reconstructed by computer, and its reconstructed transversal slices (Figure 3.1 c and d), whole volume (Figure B.1), and 3D structure were obtained. The Pd location inside and outside CNFs is clear from the reconstructed transversal slices of the CNF segment. Based on the 3D STEM video clip showing Pd on the CNF segment (Appendix B), the number of Pd nanoparticles loaded inside and outside the CNF was counted, and it was determined that 32.7% of Pd nanoparticles were loaded inside. The Pd interior loading percentage on this segment was also analyzed using 2D geometric analysis method, and 27.8% of the Pd nanoparticles were determined to be loaded inside. The difference between these two methods is 15.1%, within the margin of error of the 2D method. In addition, the result of 5Pd/CNFs sample by 2D TEM analysis was compared with the result from Ersen et al. by 3D TEM (10). An almost identical sample preparation method (i.e., by incipient wetness with water), the same CNF support, and the same Pd precursor were shared. Ersen et al. reported that about 50% of Pd nanoparticles were loaded on CNF interior surfaces; this matched result of 47.2±22.8%. These results indicate the 2D geometric method is accurate.

Several key assumptions affect the accuracy of inside/outside loading percentages; these are uniform internal and external diameters of individual CNFs, uniform Pd nanoparticle sizes, and uniform Pd spatial distribution on exterior/interior surfaces. These assumptions are represented by uniformity of key variables in the calculations for loading percentages. The key variables are

\[ \frac{d}{D} \] for loading percentages based on particle number, area, or mass, \[ \frac{N_{in}}{N_{out}} \] for loading percentages based on particle number, \[ \frac{A_{in}}{A_{out}} \] for loading percentages based on particle area, and...
Mean values and standard deviations for these parameters were calculated from all segments analyzed for 5Pd/CNFs. The corresponding effects of uncertainty for these parameters on the uncertainty of inside loading percentages were evaluated via Monte Carlo analysis using the statistical software Crystal Ball (Oracle Corp.).

Mean values and standard deviations for \( \frac{d}{D} \), \( \frac{N_{in}}{N_{out}} \), \( \frac{A_{in}}{A_{out}} \), and \( \frac{M_{in}}{M_{out}} \) are 0.615±0.076, 3.41±2.93, 3.52±4.01, and 4.60±8.27, respectively, where uncertainty for \( \frac{d}{D} \) is best represented by a normal distribution, and uncertainties for the three remaining parameters are best represented by log-normal distributions. Corresponding inside loading percentages are 70.0±14.3% based on particle number, 62.2±17.6% based on particle area, and 65.2±22.0% based on particle mass. While not exhaustive, this uncertainty analysis yields insights into how errors in key parameter values affect inside and outside loading percentages. Additional research exploring the robustness of the method is necessary.

In summary, a new geometric method to analyze the metal nanoparticle localization on hollow CNFs based on 2D TEM images was established, and this method is straightforward and relatively fast. The analysis is not limited to estimating the metal localization on CNFs, but can also be used to estimate the localization of any nanoparticles on other uniform tubular supports (e.g., carbon nanotubes, silicon nanotubes, and titania nanotubes).

3.4 References


CHAPTER 4: ENHANCED ACTIVITY AND SELECTIVITY OF CARBON NANOFIBER SUPPORTED PD CATALYSTS FOR NITRITE REDUCTION\(^3\)

4.1 Abstract

Pd-based catalyst treatment represents an emerging technology that shows promise to remove nitrate and nitrite from drinking water. In this work vapor-grown carbon nanofiber (CNF) supports are used in order to explore the effects of Pd nanoparticle size and interior versus exterior loading on nitrite reduction activity and selectivity (i.e., dinitrogen over ammonia production). Results show that nitrite reduction activity increases by 3.1 fold, and selectivity decreases by 8.0 fold, with decreasing Pd nanoparticle size from 1.4 to 9.6 nm. Both activity and selectivity are not significantly influenced by Pd interior versus exterior CNF loading. Consequently, turnover frequencies (TOFs) among all CNF catalysts are similar, suggesting nitrite reduction is not sensitive to Pd location on CNFs, and Pd structure. CNF based catalysts compare favorably to conventional Pd catalysts (i.e., Pd on activated carbon or alumina) with respect to nitrite reduction activity and selectivity, and they maintain activity over multiple reduction cycles. Hence, the results suggest new insights that an optimum Pd nanoparticle size on CNFs balances faster kinetics with lower ammonia production, that catalysts can be tailored at the nanoscale to improve catalytic performance for nitrite, and that CNFs hold promise as highly effective catalyst supports in drinking water treatment.

4.2 Introduction

Nitrate is one of the most common groundwater and surface water contaminants in the US (1), due to intensive fertilizer use in agriculture (2, 3) and feedlot runoff (4). Nitrate contamination of drinking water resources is a serious health concern because its transformation product nitrite can cause methemoglobinemia (5), or blue baby syndrome, as well as carcinogenic \( \text{N-nitroso} \) compounds in the human body (6). The US EPA has established maximum contaminant levels (MCL) for nitrate and nitrite at 10 mg L\(^{-1}\) as N and 1.0 mg L\(^{-1}\) as N, respectively (7). The most widely used approach to remove nitrate and/or nitrite from drinking water is ion exchange. This approach results in the production of a brine waste which requires further disposal (2). Biological treatment is also possible, but concerns for pathogens and challenges associated with maintaining performance under varying treatment conditions have limited its application (2). Pd-based catalytic reduction has emerged as a promising and potentially more sustainable technology to treat drinking water and ion exchange brines (3, 8-10).

Catalytic nitrate reduction proceeds initially through nitrite and then potentially through nitric oxide and nitrous oxide. The primary product is dinitrogen, but ammonia is also a possible and regulated end product (3, 8, 9, 11, 12). Promoter metals (e.g., Cu, Sn, and In) are necessary to initiate nitrate reduction (8, 9, 11, 13-18), but reduction of nitrite and subsequent intermediates only requires Pd. Concerns regarding the cost of Pd-based catalysis were recently addressed in a pilot study of trichloroethylene (TCE) reduction in groundwater at Edwards Air Force Base in California (19). While these results indicate that Pd-based catalytic treatment can be competitive in terms of both cost and performance, nitrate reduction rates are at least an order of magnitude
less than those for TCE, and maximizing selectivity for dinitrogen versus ammonia is a concern. Hence, new catalysts with higher activity for nitrate reduction, and with greater selectivity for dinitrogen over ammonia for nitrate and nitrite reduction, are needed to promote further development of practical treatment systems.

Various catalyst properties have been found to affect nitrate and nitrite reaction rates, as well as selectivity for dinitrogen, including metal loading, metal nanoparticle size, metal location, and catalyst support electronic properties (8, 9, 14, 20-23). Most previous work has been performed by using conventional catalyst supports, e.g., activated carbon (21), alumina (11, 13-16), and silica (15, 16), although more novel supports have also been used, e.g., TiO$_2$ (24), ZrO$_2$ (22), SnO$_2$ (22, 25), organic resins (26), conducting polymers (23), and carbon nanofiber foam (27, 28). Conventional supports are often thick relative to the size of Pd nanoparticles, and have variable particle sizes, irregular pore structures, and different types of metal binding sites. This makes it difficult to control and characterize the location and size of reactive metals on their surfaces, and therefore to evaluate how these parameters affect catalytic activity and selectivity.

The objectives of this study are to evaluate the effects of Pd nanoparticle size and mass transfer limitations inside pores on nitrite reduction activity and selectivity. Nitrite is selected because it is a downstream intermediate of nitrate reduction, and its reduction activity and selectivity determine overall performance in nitrate reduction. In addition, parameters affecting Pd alone can be studied for nitrite reduction without the complication of a second metal. Vapor-grown carbon nanofibers (CNFs), comprised of stacked angled graphene sheets (5-10° to fiber axis) with a hollow inside tube (29), are used as a model support; they are easy to characterize because
of their linear dimensions and thin walls, and have been used in a number of catalytic studies (30-33).

To address the objectives, nitrite reduction on Pd CNF catalysts with primarily inside loaded CNFs and different Pd nanoparticle sizes was evaluated, as well as on Pd CNF catalysts with either interior or exterior fiber loading but similar Pd nanoparticle sizes. To evaluate the potential for CNF catalysts to be used in water treatment, their nitrite reduction activity and selectivity to those for conventional Pd catalysts (i.e., Pd on activated carbon or alumina) are compared, and CNF catalyst longevity during multiple nitrite reduction treatment cycles is evaluated. This work represents the first report of CNF supported Pd catalysts being prepared with different size Pd nanoparticles, and the first time nitrite reduction activity and selectivity for dinitrogen are correlated with opposite trends to Pd nanoparticle size. The results demonstrate how catalysts can be tailored at the nanoscale to improve catalytic treatment performance for nitrite in drinking water.

4.3 Materials and Methods

4.3.1 Reagents

All chemicals were reagent grade and were purchased from Fisher (NaNO₂ ≥99%, HCl 34%-37%), Sigma-Aldrich (NH₄Cl ≥99%, Pd(NO₃)₂ · 2H₂O ~40% as Pd, nitric acid 70%, acetone ≥99%, m-xylene ≥99%, ethanol ≥99%), or Cambridge Isotope Laboratories (¹⁵N-NaNO₂ ≥98%). They were used without further purification. Tanks of H₂ (99.999%) and N₂ (99.999%) were
purchased from Matheson Tri-Gas (Joliet, IL). All solutions were prepared in nanopure water (18 MΩ cm), purified from deionized water in a Barnstead NANOpure system.

### 4.3.2 Catalyst Preparation and Characterization

A batch of carbon nanofibers (CNFs, PR-24-XT-HHT) was purchased from Pyrograf Products, Inc., and functionalized with hydrophilic moieties by exposure to concentrated nitric acid (68-70 wt %) at 140 °C for 14 h (29, 34). CNF supported 5 wt % Pd catalysts were prepared with proportionally both inside and outside loading (referred to as InOut), primarily inside loading with various Pd sizes (samples with small, medium, and large Pd sizes are referred to as In-S, In-M, and In-L), and primarily outside loading (referred to as Out). The InOut and In-M catalysts were prepared by impregnating CNFs with a Pd(NO$_3$)$_2$ in water solution and a Pd(NO$_3$)$_2$ in acetone/water mixture (1:1, by vol.), respectively. The Out catalyst was prepared by sequentially impregnating CNFs with first m-xylene to block access to internal pores, and then a Pd(NO$_3$)$_2$ water solution. Details of CNF functionalization and preparation of InOut, In-M, and Out are described elsewhere (35, 36), and are summarized in Appendix C.

The In-S catalyst was prepared by dissolving Pd(NO$_3$)$_2$ ·2H$_2$O in 6 mL acetone, and mixing thoroughly with 1 g CNFs in an ice bath to minimize acetone evaporation. The Pd containing acetone solution was drawn inside CNFs by capillary action due to its low surface tension and viscosity. The paste was then dried at 50 °C overnight, calcined at 400 °C in N$_2$ gas flow for 3 h, and reduced at 400 °C in H$_2$ gas flow for 3 h. The In-L catalyst was prepared by heating the In-M catalyst under nitrogen gas at 500 °C for 12 h, and then reducing it under hydrogen gas at 120 °C.
for 1 h. Heating results in Pd agglomeration and the formation of larger Pd nanoparticles, as discussed in the Results and Discussion. Heating has been used previously to agglomerate Pt and Ni nanoparticles on alumina, but not Pd nanoparticles on CNFs (37, 38).

CNF catalysts were typically sonicated for 12 min in solution before use in nitrite reduction tests in order to disperse them. For selected experiments with the InOut catalyst, sonication times were varied from 0.25 to 12 minutes in order to test if large aggregates were broken apart and that intra-aggregate mass transfer limitations were negligible for 12 minute sonication times. The size distribution of InOut aggregates at different sonication times was evaluated using laser scattering particle size analysis, which has been widely used in the literature to evaluate the size distribution of carbon nanotube aggregates (39, 40). This method provides the size distribution of equivalent hydrodynamic diameters, since actual CNF aggregates may not be spherical. Environmental scanning electron microscopy (ESEM, operated at relative humidity 57%) was also used to characterize the size and morphology of InOut aggregates after sonication. ESEM is able to characterize samples in the presence of water, and it provides better insights into sample morphology under representative conditions compared to vacuum conditions required for traditional SEM. Intra-aggregate mass transfer limitations were evaluated using the Weisz-Prater parameter ($C_{WP}$).

Activated carbon (AC) and alumina were also used as supports for Pd catalysts. A 5 wt % Pd on AC and a 5 wt % Pd on alumina, both purchased from Sigma-Aldrich, were wet sieved to obtain particles less than 38 µm in diameter, hereafter referred to as 5Pd/AC and 5Pd/Alumina, respectively.
Pd contents were determined with inductively coupled plasma mass spectrometry (ICP-MS). The Brunauer-Emmett-Teller (BET) surface area and microporosity of supported catalysts were evaluated using nitrogen gas adsorption. Pd nanoparticle size and distribution were determined using transmission electron microscopy (TEM) or scanning transmission electron microscopy (STEM) with ImageJ. TEM images of all CNF catalysts were used to determine Pd nanoparticle sizes, and to determine internal versus external loading percentages by the geometric method described in Shuai et al. (2011) (35). It was previously determined Pd nanoparticle size and location on In-M, InOut, and Out; those for In-S and In-L are newly presented in this work. The interior Pd loading percentage of In-L is identical to that of In-M, because heating did not change Pd inside versus outside loading.

STEM images were used to determine Pd nanoparticle sizes for AC and alumina catalysts. Pd nanoparticles loaded throughout the depth (tens of nanometers) of each CNF were clearly visible using TEM. Pd nanoparticles loaded in AC and alumina were clearly visible only along thin edges of these supports (Figure C.3), but not near support particle centers due to the thickness (microns), and the position of Pd nanoparticles located one behind the other.

In addition to TEM, X-ray powder diffraction (XRD) was used to characterize Pd nanoparticle sizes on all CNF catalysts. Full pattern refinement was performed for XRD diffractograms, and the crystallite size was estimated based on the integral breadth, assuming the intermediate crystallite size broadening modeled by a Voigt function (41). XRD was not used to determine Pd nanoparticle sizes for activated carbon and alumina supported Pd catalysts because of
background interference. In addition to TEM/STEM, CO chemisorption was used to characterize Pd nanoparticles sizes on the InOut CNF catalyst, and the activated carbon and alumina supported Pd catalysts. CO has a strong affinity to Pd, and its chemisorption capacity is used to estimate the number of exposed surface Pd sites (Pd/CO molar ratio=2) (42-45) and hence the dispersion (percent exposed surface Pd atoms) (46). The Pd nanoparticle size was calculated based on the determined dispersion values.

The number of surface Pd sites and the fraction of low coordination Pd sites (i.e., edge and corner sites) on each Pd nanoparticle of CNF catalysts were calculated by assuming cuboctahedral geometry. This geometry is assumed because it is the most stable form of Pd nanoparticles with nearly spherical shape (47), and the overwhelming majority of Pd nanoparticles observed with 2D TEM appear circular. It is important to note that other Pd nanoparticle geometries are likely present in this system, and that the number of Pd surfaces sites and the fraction of low coordination Pd sites will increase with decreasing particle size regardless of Pd geometry (48). Hence, it is emphasized that observed trends use these calculated values but not absolute values.

The order ν of a cuboctahedral nanoparticle (49) is:

\[
\nu = \frac{r}{2r_0} - \frac{1}{2} = \frac{d}{2d_{\text{metal-metal}}} - \frac{1}{2};
\]

(4.1)

where r and d are the nanoparticle radius and diameter (characterized by TEM), respectively. \(r_0\) is atomic radius, \(d_{\text{metal-metal}}\) is the distance between metal atoms (0.275 nm for Pd (46)). 20-40 CNF segments with Pd for each CNF catalyst were analyzed. The number of surface Pd sites (N) exposed to the reactants was calculated based on each image (50):
\[ N = \frac{m \times \text{Pd wt} \%}{M_{\text{Pd}}} \times N_A \times \frac{5 \times \sum_{i=1}^{j} N_{\text{surface},i}}{\sum_{i=1}^{j} N_{\text{total},i}} = \frac{5}{6} \times \frac{m \times \text{Pd wt} \%}{M_{\text{Pd}}} \times N_A \times \frac{\sum_{i=1}^{j} (10v^2+2)}{\sum_{i=1}^{j} \left( \frac{10v^2}{3} + 5v^2 + \frac{11v^2}{3} + 1 \right)}, \]  

(4.2)

where \( m \) is catalyst loading for each reduction experiment (20 mg of Pd plus support), \( M_{\text{Pd}} \) is the atomic weight (106.4 g mol\(^{-1}\)), \( N_A \) is the Avogadro constant (6.022 \times 10^{23} \text{ mol}^{-1} ), \( 5/6 \) is a reduction factor identified from the literature (46) that accounts for the fraction of surface Pd atoms not exposed to the reactants because of direct contact with the support, \( N_{\text{surface},i} \) and \( N_{\text{total},i} \) are the number of surface Pd atoms and the number of total Pd atoms in Pd nanoparticle \( i \), and \( j \) is the total number of Pd nanoparticles in one CNF segment (ca. 50-75 per segment). Pd weight percentage of each catalyst was determined by ICP-MS (Table C.1). It was then assumed that each segment was representative of the whole catalyst sample, and calculated the mean value and standard deviation of \( N \) according to analyzed segments or locations.

The fraction of low coordination sites was also estimated based on nanoparticle order \( v \). Vertices and edges have lower coordination than terraces, and both vertices and edges are designated as low coordination sites. The fraction of low coordination sites (\( F \), i.e., the fraction of edge and vertex atoms in total surface atoms) is calculated by (50):

\[ F = \frac{12}{10v^2+2} + \frac{24(v-1)}{10v^2+2} = \frac{24v-12}{10v^2+2}. \]  

(4.3)

The fraction of low coordination sites was also calculated for every Pd nanoparticle analyzed, and its mean value and standard deviation were statistically calculated from 1,000-3,000 nanoparticles for each CNF catalyst. According to the calculations, the uncertainties of \( N \) and \( F \) resulted from the variation of Pd nanoparticle sizes, which are illustrated in Table C.1. Further details of catalyst preparation and characterization methods are described in Appendix C.
4.3.3 Batch Reaction System and Analytical Methods

The batch reduction experiments were performed in a 500 mL five-neck reaction flask at 21±1 °C with continuous H₂ flow (135 mL/min) and mixing at ca. 500 rpm (51). Approximately 20 mg of catalyst were initially dispersed in 400 mL of nanopure water by sonication in the reactor (i.e., 0.05 g/L as the catalyst loading), and pre-sparged with H₂ for 20 min. Nitrite was then amended to the reactor at time zero to initiate reduction, and the pH of solution was maintained at 5 with HCl by a pH-stat. Samples were taken at regular time intervals, filtered, and stored at 4 °C. Samples for ammonia analysis were taken until ammonia production reached a plateau (i.e., final ammonia production).

It is important to note that different mixing speeds, hydrogen flow rates, and catalyst loadings were initially evaluated for In-S. Nitrite reduction rate constants were constant for mixing speeds greater than 450 rpm and hydrogen flow rates greater than 50 mL/min. Also, nitrite reduction rate constant increased linearly with catalyst loading. These control studies are in Appendix C (Figure C.1), and they indicate that the experimental conditions provide excess hydrogen for reaction and eliminate aqueous/solid mass transfer limitations.

The nitrite anion was analyzed using ion chromatography (Dionex ICS-2000; Dionex IonPac AS19 column; 10 mM KOH as eluent; 1.2 mL/min eluent flow rate; 25 μL injection loop). Ammonia was measured by the Hach salicylate method (low range, 0.02 to 2.50 mg/L NH₃-N, method 10023) using a Hach DR/4000U UV-Vis spectrophotometer.
4.3.4 Data Analysis

Pseudo-first-order rate constants for nitrite reduction were obtained from linear regressions of the natural log of relative concentrations versus time plots. Nitrite follows pseudo-first-order kinetics for decay of at least 70% of the initial concentration, and a large number of pseudo-first-order rate constants are available in the literature for comparison (11, 51-55). The turnover frequency (TOF) for nitrite reduction represents the number of nitrite molecules reduced per site per minute, and it was calculated by dividing the product of the pseudo-first-order rate constant and the initial nitrite concentration by the number of exposed surface Pd sites (N). Pseudo-first-order rate constants and the number of surface Pd sites are represented by lognormal distributions, and the uncertainty of TOF was evaluated by the Monte-Carlo method using Oracle Crystal Ball software.

Ammonia production percentages (NH$_3$% = ammonia produced divided by initial nitrite by mole) were used as a measure of catalytic selectivity for dinitrogen, as in the previous work (11, 13). In addition to ammonia, nitrous oxide and dinitrogen are also produced during nitrite reduction, but they were sparged from solution during reaction. It is shown that the sum of nitrite, nitrous oxide, dinitrogen, and ammonia forms a complete mass balance in a sealed batch reactor (Figure C.2); also, nitrous oxide eventually reduces to dinitrogen exclusively with excess hydrogen (14, 56). Hence, lower ammonia production ratios indicate higher selectivity for dinitrogen and vice versa. It is important to note that nitrous oxide is a potential greenhouse gas and that it is potentially released from an open batch reactor; however it can be completely reduced to dinitrogen in a packed bed reactor (14). Packed bed reactors are typically used in water treatment, but a batch
reactor is used here because it is better suited to evaluating trends and mechanisms among various catalysts (11, 13, 51, 55, 57, 58).

All batch reduction experiments were performed at least twice, except for control experiments performed with CNF aggregates sonicated for time periods below 12 minutes, and standard deviations were calculated for reduction rate constants and ammonia production percentages. The relationship between nitrite reduction rate constants or TOFs and total surface Pd sites for primarily inside loaded CNFs were evaluated using the York method (59), which allows linear regressions of data points with uncertainty in x and y; best-fit regression parameters with standard deviations were calculated.

4.4 Results and Discussion

4.4.1 Elimination of CNF Intra-aggregate Mass Transfer Limitations

Nitrite reduction rate constants (k) and final ammonia production percentages (NH$_3$%) for InOut exposed to ultrasound for time periods from 0.25 to 12 min are shown in Figure 4.1a. The size distribution of CNF aggregates from the laser scattering particle size analyzer versus the same sonication times are shown in Figure 4.1b. The ESEM images after 0.25 min and 12 min sonications are shown in Figure 4.1c and 4.1d. Nitrite reduction rate constants increase from 0.033 min$^{-1}$ to 0.090 min$^{-1}$ with sonication times from 0.25 to 5 minutes, whereas NH$_3$% decreases from 16.9% to 2.1% with the same range of sonication times. Sonication in excess of 5 minutes leads to no significant change in either reduction rate constant or selectivity for NH$_3$%.
The size distribution of CNF aggregates from the laser scattering particle size analyzer shows that the mean aggregate size decreases from $139.1\pm116.4$ $\mu$m to $6.3\pm4.3$ $\mu$m with increasing sonication time from 0.25 to 5 minutes. The mean aggregate size does not significantly change for sonication times in excess of 5 minutes. ESEM results show that aggregate sizes decrease with sonication, and that aggregates transition from compact structures up to 500 $\mu$m across after 0.25 minutes of sonication, to loose more elongated structures less than tens of $\mu$m across after 12 minutes of sonication.

The results suggest that catalyst aggregate size decreases with sonication time, that observed nitrite reduction rates increase and selectivity for ammonia decreases with catalyst aggregate size because intra-aggregate mass transfer limitations decrease, and that beyond 5 minutes of sonication intra-aggregate mass transfer limitations are negligible. Faster nitrite reduction and lower selectivity for ammonia are expected with faster mass transfer, e.g., more nitrite accumulates at reactive Pd sites, resulting in a higher nitrite to hydrogen ratio, and the promotion of N-N pairing and lower ammonia concentrations (28). Also, faster proton mass transfer in smaller aggregates can reduce local pH increases and inhibit ammonia production (22). Faster nitrite reduction and less ammonia production was also demonstrated on smaller activated carbon and alumina catalyst particles (27, 28). This study provides a unique feature that size and morphology of CNF aggregates change with sonication, and that it influences nitrite reduction kinetics and selectivity by mass transfer.
Figure 4.1 (a) Effects of sonication time on first-order rate constant (k) and final ammonia production percentage (NH$_3$%) in nitrite reduction by InOut. Error bars represent standard deviations of replicates. (b) Effects of sonication time on aggregate size distribution of InOut measured by dynamic light scattering. ESEM images of InOut aggregates after 0.25 min sonication (c) and 12 min sonication (d), respectively. The inset in (d) represents the enlarged image of selected region.

Intra-aggregate mass transfer limitations were also evaluated using the Weisz-Prater parameter ($C_{WP}$) (60, 61), defined as:

$$C_{WP} = \frac{R^2 k_{obs} \tau}{D_e \theta},$$

(4.4)

where $k_{obs}$ is observed pseudo-first-order rate constant for nitrite reduction (min$^{-1}$), R is the radius of the catalyst aggregate, $D_e$ is the effective diffusion coefficient of nitrite, $\tau$ is the tortuosity factor of the catalyst aggregate (typically varies from 2-10) (62), $\theta$ is the porosity of
the catalyst aggregate (typically varies from 0.2-0.7) (52), and D is the diffusion coefficient of nitrite in bulk solution (1.91×10^{-9} \text{ m}^2 \text{ s}^{-1}) (63). If $C_{WP}$ is much greater than 1, reaction is significantly limited by intra-aggregate mass transfer; if $C_{WP}$ is much less than 1, intra-aggregate mass transfer is negligible. $C_{WP}$ is conservatively estimated by choosing the smallest $\theta$ (0.2) and largest $\tau$ (10) from the literature, and the largest $k$ value from this work (0.090 min^{-1}). The aggregate diameter is also conservatively chosen at 26.1 $\mu$m because no aggregates larger than 26.1 $\mu$m were detected for the 12-minute sonication time (based on laser scattering particle size analysis). This results in a $C_{WP}$ of 6.7×10^{-3}, which is much less than 1. This result corroborates the assertion that for 12 minutes of sonication time, intra-aggregate mass transfer limitations are negligible.

4.4.2 Dependence of Nitrite Reduction Activity and Selectivity on Pd Nanoparticle Size

Interior loading percentages for In-S, In-M, and In-L are between 71.4±19.7% and 72.2±20.2% based on total Pd nanoparticle numbers. Interior loading percentages for InOut and Out are 47.2±22.8% and 22.7±17.8%, respectively, based on total Pd nanoparticle numbers. Pd nanoparticle sizes for In-S, In-M, In-L, InOut, and Out are 1.4±0.7 nm, 3.1±1.4 nm, 9.6±3.5 nm, 4.3±2.2 nm, and 2.5±1.3 nm, respectively, based on TEM images, and 2.8±0.2 nm, 3.7±0.1 nm, 12.4±0.3 nm, 4.8±0.2 nm, and 3.9±0.3 nm, respectively, based on XRD analysis (Table C.1). TEM images and XRD diffractograms of CNF catalysts are shown in Figures C.3 and C.5. The results show that Pd nanoparticle sizes and internal loading percentages follow expected trends, and that TEM and XRD results are not statistically different except for In-S. The difference for In-S is likely because XRD results are not sensitive to crystallite sizes less than 2 nm (43, 64).
Figure 4.2 (a) First-order rate constant \(k\) versus the number of exposed Pd sites; (b) turnover frequency (TOF) versus Pd nanoparticle diameter; (c) final ammonia production percentage \(\text{NH}_3\%\) versus the number of exposed Pd sites; and (d) final ammonia production percentage \(\text{NH}_3\%\) versus the fraction of low coordination Pd sites. Nitrite reduction tests were performed with CNF supported Pd catalysts. Horizontal and vertical error bars represent the standard deviations of simulation results and experimental replicates, respectively. In (a) and (b), solid orange lines represent best-fit linear regression lines for primarily inside loaded catalysts by the York method (59), and dash lines with gray areas represent the best-fit plus or minus one standard deviation \(\sigma\).

First-order rate constants \(k\) for nitrite reduction are compared to the number of exposed Pd sites in Figure 4.2a, and TOFs for nitrite reduction are compared to Pd nanoparticle diameters (by TEM) in Figure 4.2b. It is noted that the number of exposed Pd sites increases with decreasing Pd nanoparticle diameter. Comparing inside loaded catalysts (i.e., In-S, In-M, and In-L), first-
order rate constants increase linearly ($R^2=0.998$) but TOFs remain relatively constant with increasing Pd nanoparticle diameters. Comparing all catalysts, the average TOFs for the inside plus outside loaded CNF (i.e., InOut) and the outside loaded CNF (i.e., Out) are larger than those for inside loaded CNFs; however, the standard deviation of TOFs for InOut and Out overlap standard deviations for inside loaded catalysts. It is noted that imperfections inside some CNFs are apparent from low-resolution TEM images (Figure C.3); based on TOF values, these do not appear to significantly hinder nitrite mass transfer to inside-loaded Pd sites. Standard deviations for number of exposed Pd sites, and subsequently for TOF that is calculated from number of exposed Pd sites, are up to 30.4% of average values. These variations arise from variations of Pd nanoparticle size using the wetness impregnation approach, and are similar to size variations reported by others using this method (46). Therefore, it is concluded that there is no statistical change for TOF with Pd nanoparticle size variation from 1.4±0.7 nm to 9.6±3.5 nm, and each exposed Pd site (e.g., edge, vertex, terrace) has equal activity for nitrite reduction. It indicates that the specific activities of CNF catalysts (i.e., TOFs) for nitrite reduction are independent of their preparation, and it is a structure-insensitive reaction according to Boudart et al. (65) Guy et al. observed that pseudo-first-order nitrite reduction rate constants were independent of Pd-Cu content for unsupported colloidal Pd-Cu catalysts, suggesting that only a small number of Pd surface atoms (possibly just one or two) are required for reaction (66). However, particle size varied among the catalysts and TOFs were not evaluated, so it is difficult to determine if the reaction was structure-insensitive. In contrast to the results here, the significant effects of particle sizes and low-coordination sites for ethene hydrogenation or carbon-carbon cross coupling by Pd catalysts are consistent with a requirement for a significant ensemble of surface Pd atoms to activate reactants (67, 68).
The final ammonia production percentages (NH$_3$%) for nitrite reduction are compared to the number of exposed Pd sites and the fraction of low coordination Pd sites in Figures 4.2c and 4.2d. Comparing all catalysts, NH$_3$% values increase with increasing number of exposed Pd sites and with the fraction of low coordination Pd sites regardless of whether Pd is loaded inside or outside CNFs ($R^2$=0.926 and 0.952 by linear regression, respectively), and that means NH$_3$% values increase with decreasing Pd nanoparticle size because the number of exposed Pd sites or the fraction of low coordination Pd sites increase monotonously with decreasing Pd nanoparticle size. The increase of ammonia production results from relatively less N-N pairing on Pd nanoparticles. One possible reason is that N-N pairing becomes more difficult on smaller Pd islands with more low coordination sites (i.e., edges and corners) (21). This is supported by results showing that dinitrogen production from nitrate reduction on titanium dioxide supported Pd-Cu bimetallic nanoparticles was greater on 3.51 and 4.22 nm nanoparticles than smaller nanoparticles (24). However, Pd and Cu contents varied among particles making it difficult to distinguish particle size effects on dinitrogen production (24). Another possible reason is that N-N pairing is not favorable on smaller Pd islands because of the decreasing chances for adsorbed N being adjacent to each other. A third possible explanation is that faster nitrite reduction on smaller Pd nanoparticles depletes nitrite and lowers the chance of N-N pairing.

4.4.3 Environmental Implications

CNFs are excellent model catalyst supports to explore nitrite reduction mechanisms because their regular tubular structure allows for better control of deposited Pd location and size, and catalyst
characterization using a variety of spectroscopic tools. Results of this study indicate for the first time that CNF catalysts for nitrite reduction can be tailored to select for high activity by decreasing Pd nanoparticle size or high dinitrogen selectivity by increasing Pd nanoparticle size. Greater activity with decreasing Pd particle size is attributed to the corresponding increase in Pd surface area and Pd structure insensitivity of this reaction. Greater dinitrogen selectivity with increasing Pd particle size may be due to several factors, including more high coordination Pd surface sites that promote N-N pairing (21), more Pd surface area for nitrogen species to adsorb adjacent to each other for N-N pairing, and the presence of more adsorbed nitrogen species due to slower reduction kinetics. The results suggest that Pd nanoparticles size on CNFs can be optimized to achieve the desired combination of activity and selectivity for nitrite reduction in drinking water.

To further evaluate the promise of CNF supported Pd catalysts in water treatment, their activity and selectivity are compared to conventional Pd catalysts, and their sustainability during repeated nitrite reduction experiments is evaluated. The TOF and NH₃% of the inside plus outside CNF catalyst (InOut), 5Pd/AC, and 5Pd/Alumina are shown in Figure 4.3a. TOFs are calculated based on nitrite reduction rate constant (k) and the number of exposed Pd sites determined from CO chemisorption. CO chemisorption results were used because they access all exposed Pd sites, whereas STEM images for AC and alumina were only able to capture Pd on the edges of these supports. The 5Pd/AC and InOut have the highest TOFs (54.8±6.5 min⁻¹ and 44.6±5.0 min⁻¹, respectively), and they are not statistically different; 5Pd/Alumina has a TOF of 4.15±0.02 min⁻¹, and it is 12.2 or 9.8 times less than the TOFs of 5Pd/AC and InOut. However, the amount of final ammonia produced is lower for InOut (1.9%) compared to both 5Pd/AC.
(7.2%) and 5Pd/Alumina (2.3%). These results indicate that CNF supported Pd gives the best combination of nitrite reduction activity and selectivity compared to activated carbon and alumina supported Pd.

Catalyst sustainability was evaluated over three cycles of sequential nitrite reduction using the In-M catalyst, by measuring reduction activity, and Pd content and nanoparticle size before and after treatment. The nitrite reduction activity remained constant during each cycle (i.e., nitrite reduction rate constants are 0.088±0.014 min⁻¹, 0.073±0.008 min⁻¹, and 0.073±0.009 min⁻¹, respectively, Figure 4.3b), and little to no Pd leaching or Pd nanoparticle agglomeration occurred (i.e., 4.8 wt % Pd and 3.1±1.4 nm before reduction, 4.6 wt % Pd and 2.9±0.8 nm after reduction). Hence, the preliminary results suggest the CNF catalysts are stable over multiple treatment cycles during water treatment, but longer tests with real water samples are required in future work.

**Figure 4.3** (a) Turnover frequencies (TOFs) and ammonia production percentages (NH₃%) for nitrite reduction on 5Pd/AC, InOut, and 5Pd/Alumina catalysts. TOFs were calculated based on the number of exposed Pd sites estimated by CO chemisorption. Error bars represent standard deviations of replicates. (b) Longevity test of CNF catalyst In-M for nitrite reduction. The reduction was performed for three cycles.
There are concerns about the relatively high cost of CNFs, the unique CNF handling requirements due to small size, and potential CNF toxicity if released to drinking water. However, advances in industrial scale production of CNFs have resulted in lower prices, and this trend is expected to continue (69). Hence, costs may be competitive with conventional supports in the future. Furthermore, exciting developments in new membrane processes and membrane materials have significantly changed water treatment practices, and hold promise as a way to integrate CNF catalysts into water treatment systems and overcome handling and release concerns (70, 71).

4.5 References


CHAPTER 5: STRUCTURE SENSITIVITY STUDY OF WATERBORNE CONTAMINANT HYDROGENATION USING SHAPE- AND SIZE-CONTROLLED PD NANOPARTICLES

5.1 Abstract

Catalytic reduction with Pd has emerged as a promising technology to remove a suite of contaminants from drinking water, such as oxyanions, disinfection byproducts, and halogenated pollutants, but low activity and poor selectivity for desired end products hinder implementation. To address these challenges, a suite of shape- and size-controlled Pd nanoparticles were synthesized, and the activity and selectivity of three probe contaminants (i.e., nitrite, N-nitrosodimethylamine (NDMA), and diatrizoate) as a function of facet type (e.g., (100), (110), (111)), ratios of low- to high-coordination sites, and ratios of surface sites to total Pd (i.e., dispersion) were evaluated. Reduction results for initial contaminant concentration at 100 µM show that turnover frequencies (TOFs) for nitrite increase 4.7 folds with increasing ratio of (100) Pd sites to surface Pd sites from 0% to 95.3%, and TOFs for NDMA and diatrizoate increase 4.5 folds and 3.6 folds with increasing ratio of terrace Pd site to surface Pd sites from 79.8% to 95.3%, respectively. Results for initial nitrite concentration at 2 mM show that at TOFs are consistent for all shape- and size-controlled Pd nanoparticles. A two-site model based on Langmuir-Hinshelwood mechanism was developed to shed light on the change of structure-sensitivity for nitrite reduction with contaminant concentration, and it suggests that both reaction and adsorption of nitrite and nitric oxide play important roles. The amount of produced ammonia to initial nitrite (i.e., ammonia production percentage), representing the selectivity to ammonia,
decreases 3.9 folds and 3.7 folds for 100 µM and 2 mM nitrite reduction with increasing Pd dispersion from 12.7% to 33.4%, respectively. Selectivity for NDMA reduction is neither shape-nor size-specific, and dimethylamine and ammonia are exclusive products. That diatrizoate reduction on different catalysts likely produces the same deiodinated products suggests its selectivity may be non-shape- and non-size-specific. Moreover, all catalysts but one were stable in shape and size up to 12 days, and iodide liberation in diatrizoate reduction is proposed to be responsible for shape-change of 4 nm octahedral Pd nanoparticles. Hence, this study suggests insights that catalytic reduction performance for waterborne contaminant removal varies with Pd shape and size for the first time, that catalysts can be tailored for better performance, and that Pd catalysts hold the promise to treat a variety of contaminants simultaneously for drinking water.

5.2 Introduction

Pd-based catalytic hydrogenation has emerged as a promising technology to reduce a variety of priority contaminants including oxyanions (e.g., nitrate (1, 2), nitrite (3), bromate (4), chlorate (5), perchlorate (6)), N-nitrosoamines (e.g., N-nitrosodimethylamine (NDMA) (7)), and halogenated compounds (e.g., trichloroethylene (TCE) (8), perchloroethylene (PCE) (9), diatrizoate (10)). These contaminants come from various sources or processes (e.g., fertilizer (11), rocket fuel (12), X-ray contrast media (13), degreasing (14), dry cleaning (14), and disinfection (15-17)), they are ubiquitously present in surface water (12), groundwater (12, 18, 19), or even treated water (20-23), and they can adversely affect human health (e.g., carcinogenicity, mutagenicity, cytotoxicity, genotoxicity) (12, 24-32) or ecological systems (e.g., result in eutrophication) (33, 34). Compared to conventional water treatment technologies such
as ion-exchange, membrane process, and biological treatment, catalytic hydrogenation is a promising technology because it uses hydrogen as a clean reductant, it does not generate brine or a secondary waste stream (35), it is robust to changes in water quality (36, 37), and it can simultaneously remove a suite of contaminants. Although catalytic treatment has been shown to be economically feasible for treating halogenated alkenes in a groundwater (36), reduction rates for other contaminants are often much slower (e.g., nitrate, NDMA, perchlorate), and selectivity for desired end products can be a challenge for some compounds.

Previous efforts to understand and improve catalyst activity and selectivity have explored the effects of water quality parameters (1, 4, 5), catalytic process control parameters (2, 38), and catalyst properties (3, 39-41). Of these, catalyst properties are the most difficult to evaluate because controlling catalyst properties at the atomic scale is challenging. Catalysts contain an active metal (Pd in this study), typically loaded onto a support, and controlling either of these materials at the atomic scale is often beyond current abilities. This is rapidly changing as advances in nanotechnology research are enabling unprecedented control of metal nanoparticle shapes and sizes, and exploration of how these parameters enhance catalytic performance.

Shape-controlled metal nanoparticles have been prepared through liquid-based colloidal methods, using a variety of reactants and reaction conditions, to promote the formation of defined crystallographic orientations (42-45). Nanoparticle growth is controlled either thermodynamically or kinetically at various rates, and a range of reductants, stabilizers, and etching agents are used to promote the formation of nanoparticles with desired shapes and sizes (42). Metal nanoparticle size variations result in a change in the number of surface atoms, and in
the ratios of low/high coordination atoms (e.g., vertex, edge, and terrace (46)). Metal
nanoparticle shape variations lead to a change in morphology and surface atom arrangement (e.g.,
cubes with only (100) terrace atoms, octahedra with (111) terrace atoms, cuboctahedra with both
(100) and (111) terrace atoms, and rods with all (100), (110), and (111) terrace atoms) (42). The
effects of catalyst nanoparticle shape and size on activity have been studied for a series of
structure-sensitive reactions, such as hydrogenation (44, 46, 47), oxidation (44), cross-coupling
(48), and electron transfer (48). However, no studies have explored the impacts of catalyst
nanoparticle shape and size on reduction of waterborne contaminants.

The objective of this study is to explore catalytic structure-sensitivity of Pd for hydrogenation of
three probe contaminants in water. We prepared a series of different shape and size poly(vinyl-
pyrrolidone) (PVP) capped Pd nanoparticles, i.e., cubes, octahedra, cuboctahedra, and rods, in
order to systematically vary the surface area of different facets, the ratio of surface to bulk Pd
atoms, and the ratio of low- to high-coordination surface Pd atoms. The three probes
contaminants are nitrite, NDMA, and diatrizoate; they are all environmentally relevant and
difficult to treat water contaminants characterized by different reduction mechanisms. Nitrite is a
direct intermediate of nitrate, the most common groundwater contaminant in the United States
(18). Nitrite is converted in vivo to N-nitroso compounds, carcinogenic precursors (49). NDMA
is a neutral organic compound unintentionally created during wastewater disinfection; and it is a
carcinogen (28). Diatrizoate is a dissociable organic chemical (pKa=3.4) used as an x-ray
contrast agent; it has no known toxicological properties, but its recalcitrance to degradation may
cause unanticipated health threats (10). Nitrite reduction involves N-O bond cleavage (i.e.,
deoxygenation) and yields the end products dinitrogen and ammonia (2), NDMA reduction
proceeds through N-N bond cleavage and can yield the end products dimethylamine and ammonia (7,50). N,N-dimethylhydrazine (UDMH) or dinitrogen was observed as a NDMA reduction intermediate/product only for nickel catalysts (51, 52), and its presence in Pd catalyst system needs to be clarified. Diatrizoate reduction requires C-I bond cleavage (i.e., dehalogenation), and yields a series of deiodinated intermediates, 3,5-diacetamidobenzoic acid (Dia-H₃), and iodide (10). Details of the contaminant reduction pathways are shown in Scheme 5.1. This work represents the first report of Pd structure-sensitivity for catalytic reduction of waterborne contaminants, and it shows for the first time that structure-sensitivity depends on chemical type and concentration, that stability of nanoparticle catalysts depends on constituents in reaction solution, and that catalyst activity and selectivity can be enhanced with proper Pd nanoparticle shape- and size-selection.

Scheme 5.1 Nitrite, NDMA, and diatrizoate hydrogenation pathways on Pd. Nitrite reduction is involved with sequential deoxygenation, and nitric oxide (NO) is a proposed intermediate (in italic) determining selectivity towards dinitrogen or ammonia (2). Ammonia formation is also proposed to bypass NO route and proceed through nitrite hydrogenation (53). NDMA initiates reduction by N-N bond cleavage and then hydrogenation. Nitrosyl group is proposed as an intermediate (in italic), and it is reduced to ammonia exclusively (7,50). Diatrizoate reduction proceeds through a stepwise deiodination to Dia-H₃ (10).
5.3 Materials and Methods

5.3.1 Reagents

All chemicals were reagent grade and were purchased from Sigma-Aldrich (\(\text{Na}_2\text{PdCl}_4\) \(\sim\) 99.995\%, PVP M\(_w\) \(\sim\) 55,000, KBr \(\geq\) 99.0\%, ethylene glycol \(\geq\) 99\%, citric acid \(\geq\) 99.5\%, acetone \(\geq\) 99\%, methanol \(\geq\) 99.9\%, acetic acid \(\geq\) 99.7\%, sodium acetate \(\geq\) 99.0\%, acetonitrile \(\geq\) 99.9\%, triethylamine \(\geq\) 99\%, \(\text{Na}_2\text{HPO}_4\cdot2\text{H}_2\text{O}\) \(\sim\) 99\%, \(\text{NaH}_2\text{PO}_4\) \(\geq\) 99.0\%, NDMA, dimethylamine hydrochloride i.e., DMA \(\sim\) 99\%, UDMH \(\sim\) 98\%, sodium diatrizoate hydrate \(\geq\) 99\%, 3,5-diacetamidobenzoic acid, i.e., Dia-H\(_3\), \(\text{NH}_4\text{Cl}\) \(\geq\) 99\%, KI \(\geq\) 99.0\%, 1-fluoro-2,4-dinitrobenzene, i.e., DNFB \(\geq\) 99\%, 4-nitrobenzaldehyde, i.e., NBA \(\sim\) 98\%), Fisher (\(\text{NaNO}_2\) \(\geq\) 99\%, \(\text{NaOH}\) \(\geq\) 98\%) or J. T. Baker (L-(+)-ascorbic acid \(\geq\) 99.5\%), or Cambridge Isotope Laboratories (\(^{15}\text{N}-\text{NaNO}_2\) \(\geq\) 98\%, \(^{15}\text{N}-\text{N}_2\) \(\geq\) 98\%, \(^{15}\text{N}_2\)-NDMA \(\geq\) 98\%). Tanks of \(\text{H}_2\) (99.999\%), NO (99.5\%), and \(\text{N}_2\text{O}\) (99.999\%) were purchased from Matheson Tri-Gas (Joliet, IL). All chemicals were used without further purification. All solutions were prepared in nanopure water (18 M\(\Omega\) cm), purified from deionized water in a Barnstead NANOpure system.

5.3.2 Synthesis and Characterization of Pd Nanoparticle Catalysts

Pd cubes, rods, cuboctahedra with small and large sizes, and octahedra with small and large sizes were one-step synthesized based on the protocols published by Xiong et al (54, 55). and Shao et al. (56) with modifications. Briefly, \(\text{Na}_2\text{PdCl}_4\) was the Pd precursor, PVP was used as a stabilizer, and ethylene glycol, ascorbic acid, or citric acid was used as the reductant. KBr was used to promote isotropic growth with (100) or (110) facets for cube or rod preparation, because bromide
preferentially chemisorbs on the (100) facet, alters the surface energies for different facets, and changes the thermodynamic favorability of facet growth (54). The mixture of all reagents was stirred continuously, while heating or refluxing at 80-130 °C for 3h. Synthesized Pd nanoparticle catalysts were precipitated out of solution with acetone, collected with centrifugation, and washed with nanopure water several times to remove excess PVP and other reactants. Finally Pd nanoparticle catalysts were stored in aqueous stock suspensions. Duplicate batches of Pd cubes, cuboctahedra with small size, and octahedra with small and large sizes were prepared, and each of duplicates for one desired shape was separately synthesized with the same protocol.

Reproducibility of Pd nanoparticles with respect to shape, size, and catalytic performance was evaluated. The details of Pd nanoparticle catalyst synthesis are described in Appendix D. To the best of its knowledge, this study is the first to report the one-step synthesis method for large-size octahedra; in previous work epitaxial growth on Pd seeds was reported (46). Large-size octahedra were synthesized with modified protocol for large-size cuboctahedra (55), and a slower mixing rate for Pd precursor and ethylene glycol was used (5 mL h\(^{-1}\) other than 45 mL h\(^{-1}\) for cuboctahedra). Slower mixing reduces the number of nuclei and facilitates the size growth of each nanoparticle. In addition, slower mixing also enhances complete shell formation for octahedra, whereas faster injection induces cuboctahedron production with truncated edges.

Transmission electron microscopy (TEM) with ImageJ was used to determine the shape and size of Pd nanoparticle catalyst. Geometric illustrations of Pd cubes, rods, cuboctahedra, and octahedra are shown in Figure 5.1. Edge lengths or diameters of Pd nanoparticles were measured, and dispersion (i.e., percentage of surface Pd atoms relative to total Pd atoms in bulk), surface fractions of each facet (e.g., surface fraction of (100) facet is the ratio of (100) surface Pd atoms
to total Pd surface atoms), and surface fraction of terrace sites (i.e., surface fraction of high coordination sites, it is the ratio of terrace Pd atoms to total surface Pd atoms) were calculated for each nanoparticle based on geometry (57). The percent number purity, the ratio of the number of Pd nanoparticles with desired shape to the total nanoparticle number, was also evaluated for each sample. About 300 Pd nanoparticles per sample were measured and evaluated for geometric properties and purity. The details of calculations are described in Appendix D.

Figure 5.1 Geometric schematics of Pd cubes, rods, cuboctahedra, and octahedra. Blue, red, yellow, and green atoms represent edge/vertex, (100) site, (110) site, and (111) site, respectively.

X-ray powder diffraction (XRD) was used to characterize the size (in addition to characterization with TEM) and crystallinity of Pd nanoparticle catalysts. Full pattern refinement was performed in TOPAS (Bruker AXS, Inc., version 3) using a Pd CIF file (58), and the crystallite size was estimated based on the integral breadth, assuming the intermediate crystallite size broadening modeled by a Voigt function (59). X-ray photoelectron spectroscopy (XPS) was used to characterize impurities on the surfaces of Pd nanoparticle catalysts after extensive cleaning with
acetone and nanopure water to remove residual PVP, Cl\(^-\), and Br\(^-\). The binding energy scale was referenced to the aliphatic C 1s line at 285.0 eV. Pd catalyst loading for each catalytic run was calculated based on the Pd content of a stock suspension, which was analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Details of characterization methods are described in Appendix D.

5.3.3 Hydrogenation Reaction and Analytical Methods

Hydrogenation experiments were conducted in a 60 mL serum bottle equipped with a Teflon-coated magnetic stir bar and septum sealed stoppers, all at 21±1 °C. The bottles were filled with 20 mL or 40 mL of phosphate buffer (pH=7, buffer concentration is ten times the contaminant concentration), and amended with 0.2 mg of Pd catalysts (i.e., \(10^{-2}\) or \(5 \times 10^{-3}\) g L\(^{-1}\) as catalyst loading). The suspension was sparged with hydrogen for 30 min to remove oxygen in the suspension and headspace, to reduce oxidized catalyst surfaces, and to saturate the headspace and water with hydrogen. To initiate reaction, nitrite, NDMA, or diatrizoate was amended to the suspension at time zero while mixing at 560 rpm. A high and a low initial concentration of nitrite were evaluated. The high concentration was 2 mM; the low concentration was 100 µM, and was chosen to match initial NDMA and diatrizoate concentrations, and to explore structure-sensitivity effects. The initial concentrations of were chosen higher than environmental concentrations observed in drinking water in order to satisfy equipment detection limits and to facilitate accurate analysis. The molar ratio between contaminant and surface Pd atoms ranges from 3.2 to 8.4 for all three contaminants at 100 µM, whereas the molar ratio ranges from 128 to 334 for nitrite at 2 mM. The difference in molar ratios for a set contaminant concentration is due
to variations in shape, size, and corresponding dispersion values for Pd nanoparticle catalysts. During reaction, 0.5 mL of sample was withdrawn by syringe at different time intervals, filtrated through centrifugal filters (Amicon Ultra-0.5, Ultracel-30 Membrane, 30 kDa, Millipore), and stored in a refrigerator at 4 °C before analysis. Dilution by nanopure water is necessary to analyze some samples. Control experiments were performed with various catalyst loadings and mixing rates; they indicate that hydrogen is essential for reaction and is present in excess, and that external mass transfer limitations are insignificant. All batch reactions were performed 3 to 6 times.

The nitrite and iodide anions were analyzed using ion chromatography (Dionex ICS-2000, Dionex IonPac AS18 and AS19 columns). NDMA, DMA, UDMH, diatrizoate, and Dia-H$_3$ were analyzed using high performance liquid chromatography (Shimadzu Prominence LC-20AT, Dionex Acclaim 120 C18 column). Ammonia was measured using the Hach salicylate method (low range, 0.02 to 2.50 mg/L NH$_3$-N, method 10023) and a Hach DR/4000U UV-Vis spectrophotometer. Gas samples were analyzed using gas chromatography-mass spectroscopy (Varian 4000 GC/MS, CP-Molsieve 5Å column) for $^{15}$N labeled nitric oxide, nitrous oxide, and dinitrogen.

5.3.4 Data Analysis

Pseudo-first-order rate constants for nitrite, NDMA, and diatrizoate reduction were obtained from linear regressions of the natural log of relative concentrations versus time plots. All contaminants follow pseudo-first-order kinetics for decay of at least 50% of the initial
concentrations. The turnover frequency (TOF) represents the number of contaminant molecules reduced per site per minute, and it was calculated by dividing the product of the pseudo-first-order rate constant and the initial contaminant concentration by the product of Pd catalyst loading and dispersion (D). Final ammonia production percentages for nitrite reduction (NH$_3$% = moles of ammonia produced after complete reduction divided by moles of initial nitrite) were used as a measure of catalytic selectivity for dinitrogen, as in the previous work (1, 60, 61). We showed that the sum of nitrite, nitrous oxide, dinitrogen, and ammonia forms a complete nitrogen mass balance (Figure D.1). Lower ammonia production ratios indicate higher selectivity for dinitrogen and vice versa.

5.4 Results and Discussion

5.4.1 Synthesis and Characterization of Pd Nanoparticle Catalysts with Controlled Shapes and Sizes

Low magnification and high resolution TEM images of Pd cubes, rods, cuboctahedra, and octahedral are shown in Figure 5.2. Low magnification TEM images were used to characterize Pd nanoparticle shapes and sizes, and to calculate percent number purities. Pd cubes were prepared with >95.5% purity, and their edge lengths are 9.3±2.1 nm and 8.7±1.8 nm for duplicate batches. Pd rods were prepared with >92.2% purity, and their longitudinal and transversal lengths are 13.2±2.4 nm and 4.3±0.8 nm, corresponding to an aspect ratio of 3.0. Both small and large cuboctahedra have almost 100% purity, and their effective diameters are 5.3±1.1 nm and 5.7±1.0 nm for duplicates batches, and 8.6±1.9 nm, respectively. Both small and large octahedra were prepared with >85.1% purity, and their edge lengths were 4.5±0.7 nm and
4.3±0.6 nm for duplicate batches, and 10.7±1.4 nm and 10.5±1.2 nm for duplicate batches, respectively.

**Figure 5.2** Low magnification and high resolution transmission electron microscopic (TEM) images of Pd cubes (a, g), rods (b, h), cuboctahedra (c, d, and i), and octahedra (e, f, and j). c and d are cuboctahedra with small and large size, and e and f are octahedra with small and large size. Lattice spacing is indicated in high resolution images. Enlarged images are shown in Figure D.2.

High resolution TEM was used to characterize Pd nanoparticle lattice spacing, and to confirm their monocrystallinity and crystallographic plane boundaries. Pd nanoparticle crystallinity and size was also characterized by XRD, and a representative diffractogram is shown in Figure 5.3a. All Pd samples share the similar diffractograms, which confirm their crystalline rather than amorphous structures. Pd nanoparticle from XRD are 8.9 nm and 8.7 nm for duplicate batches of prepared cubes, 5.8 nm for rods, 4.9 nm and 4.5 nm for duplicate batches of small cuboctahedra, 8.8 nm for duplicate batches of large cuboctahedra, 3.9 nm and 4.3 nm for duplicate batches of
small octahedra, and 10.5 nm and 10.5 nm for duplicate batches of large octahedra. The values agree adequately with those measured by TEM for all samples but rods, and XRD sizes are in the range of TEM sizes plus and minus uncertainties. Unlike other shapes, rods were prepared with isotropic growth towards one direction; hence, their size characterized by XRD represents some average of longitudinal and transversal dimensions. To compare rod size characterized by TEM and XRD, the edge length for imaginary cubes with the same volume as rods was calculated, and its value 5.9 nm is close to XRD size (5.8 nm).

**Figure 5.3** X-ray powder (XRD) diffractogram and X-ray photoelectron spectrum (XPS) of selected Pd nanoparticle catalyst. Small sized octahedron was selected as representative nanoparticle catalyst, and XRD diffractograms and XPS spectra of other Pd nanoparticle catalysts are similar to the ones showing in the figure.
After extensive cleaning of synthesized nanoparticles by acetone and nanopure water, XPS was used to determine if residual chemicals used during synthesis remained on Pd surfaces. A representative XPS spectrum is shown in Figure 5.3b; all other Pd samples share the similar spectra. Only O, N, C, and Pd were detected; neither Br\textsuperscript{-} nor Cl\textsuperscript{-} was observed. N is used as an indicator to estimate residual stabilizer PVP on the Pd surface, and it agrees with a previous study using similar synthesis protocols and cleaning procedures (46). Different stabilizers can modify the surface properties and impact catalytic behaviors (62-64), therefore the same stabilizer PVP was used to minimize the interference. In addition, quantitative analysis of N to surface Pd ratio is 6.3±3.4, suggesting that the residual amount of PVP is similar across all samples and that more than 90\% of PVP has been removed.

5.4.2 Pd Nanoparticle Catalysts for Nitrite Reduction

Nitrite reduction activity and selectivity for ammonia on Pd nanoparticle catalysts with different shapes and sizes are shown in Figure 5.4. Two initial nitrite concentrations, 100 \(\mu\)M and 2 mM, were evaluated. At low concentration (100 \(\mu\)M), nitrite reduction TOFs increases proportionally with surface fraction of (100) facets (R=0.93), and 95\% confidence intervals of regression also suggest negative correlation. (100) sites on Pd nanoparticles are also more active for oxygen reduction reaction (ORR) than other sites (e.g., (111) sites), and it can be attributed to lower coverage of poisonous surface adsorbed OH on (100) sites and consequently more available sites for reaction (56). Adsorption strengths of nitrite or its reduction intermediate (e.g., nitric oxide) may also be different on different facets, and it can influence nitrite reduction kinetics. Density functional theory simulations results (with GGA-RPBE (Boldface) functional) suggest that nitric
oxide adsorption energies on Pd (100) sites, (111) sites, step sites, and edge sites are -1.64, -1.80, -1.86, and -1.88 eV, respectively, and it supports that affinity of nitric oxide to different Pd sites varies (65). In contrast, nitrite reduction TOFs are not statistically different at high initial nitrite concentration (2 mM). Surface fraction of specific facet is dependent on Pd nanoparticle catalyst shape but not size (Figure D.3d-f), whereas TOF is dependent on catalyst size but not shape.

TOF is a normalized activity in terms of the number of surface sites, and catalyst dispersion decrease linearly with increasing catalyst TEM size from 4.3-10.7 nm for all shapes (Figure D.3a). A specific facet dependent TOF indicates that catalyst activity relies not only on catalyst shape but also on size, whereas a constant TOF indicates that catalyst activity is independent of catalyst shape or facet type. These results suggest that nitrite reduction activity is both shape and size dependent at low concentration, but only size dependent at high concentration. This is the first report that the dependence of reaction activity on nanoparticle catalyst shape and size depends on concentration.

Several factors may contribute to the concentration dependence of nitrite reaction activity on nanoparticle catalyst shape and size; these include pH, residual organic molecules on the Pd surface, and intrinsic reactivity/adsorption on different Pd facets. Reaction solutions were well-buffered during reaction (pH = 7.5±0.2). The majority of stabilizer PVP has been removed during extensive catalyst cleaning procedures, and it is estimated not to inhibit catalyst reduction kinetics (discussed in Appendix D). The variation of intrinsic reactivity and adsorption on different Pd facets may be responsible for the change of dependence on facets at low and high concentrations, and a two-site model based on Langmuir-Hinshelwood mechanism is proposed. Adsorption of reactants, reaction, and desorption of products need all to be considered. As shown
in the scheme 5.1, nitric oxide is proposed to be an important intermediate. Moreover, nitric oxide strongly binds to Pd catalyst surface because of its very negative adsorption energy according to density functional theory simulation (65), and it may accumulate on catalyst surface and compete for available catalyst sites with nitrite adsorption. Dinitrogen, ammonia, and nitrous oxide do not show strong binding compared with nitric oxide (65-67), so their accumulation on Pd surface sites is ignored in the model. Two types of surface Pd sites, (100) sites and non-(100) sites, are designated as sites 1 and sites 2, respectively. The adsorption and reaction of nitrite, nitric oxide, and hydrogen are taken into consideration for the model. For sites 1, it is assumed that the aqueous concentrations of nitrite, nitric oxide, and hydrogen are at equilibrium with surface concentrations, and adsorption constants are written as:

\[
K_{NO_2^{-},*1} = \frac{[\text{*1} - \text{NO}_2^-]}{[\text{*1}][\text{NO}_2^-]}, \quad (5.1)
\]
\[
K_{NO,*,1} = \frac{[\text{*1} - NO]}{[\text{*1}][NO]}, \quad (5.2)
\]
\[
K_{H2,*,1} = \frac{[\text{*1} - H]^2}{[\text{*1}]^2[H_2]}, \quad (5.3)
\]

in which \(K_{X,*,1}\) is equilibrium adsorption constants for X at sites 1 (X=NO\(_2^-\), NO, or H\(_2\)) (L mol\(^{-1}\)), \([*1 - X]\) is surface concentration of X at sites 1 (mol L\(^{-1}\)), [X] is aqueous concentration of X (mol L\(^{-1}\)), and \([*1]\) is the concentration of empty sites 1 (mol L\(^{-1}\)).

The expression of site balance for sites 1 is:

\[
[*1]_0 = [*1] + [*1 - H] + [*1 - NO_2^-] + [*1 - NO]; \quad (5.4)
\]

in which \([*1]_0\) is the total concentration of sites 1 (mol L\(^{-1}\)).

Nitrite reduction rate \((r_{NO_2^-,*1}, \text{mol L}^{-1} \text{min}^{-1})\) at sites 1 can be expressed as:

\[
r_{NO_2^-,*1} = k'_{NO_2^-,*1}[*1 - H][*1 - NO_2^-] = k'_{NO_2^-,*1} \frac{([*1]_0)^2 \sqrt{K_{H2,*1}[H_2]K_{NO_2^-,*1}[NO_2^-]}}{\left(1 + \sqrt{K_{H2,*1}[H_2] + K_{NO_2^-,*1}[NO_2^-] + K_{NO,*1}[NO]}\right)}; \quad (5.5)
\]
in which \( k'_{\text{NO}_2,1} \) is the second order rate constant (L mol\(^{-1}\) min\(^{-1}\)) for nitrite reduction at sites 1.

The value of \( K_{H_2,1} \) has been reported close to zero,\(^{11}\) and it is simplified that \( K_{H_2,1} [H_2] \ll 1 \).

Therefore,

\[
r_{\text{NO}_2,1} = k_{\text{NO}_2,1} \frac{([1]_0)^2 K_{\text{NO}_2,1}[\text{NO}_2^{-}]}{(1+K_{\text{NO}_2,1}[\text{NO}_2^{-}]+K_{\text{NO}_2,1}[\text{NO}])^2};
\]

(5.6)

in which \( k_{\text{NO}_2,1} \) is a rate constant (L mol\(^{-1}\) min\(^{-1}\)), and it is the product of \( k'_{\text{NO}_2,1} \) and \( \sqrt{K_{H_2}^1 [H_2]} \).

Similarly, nitrite reduction rate at sites 2 (\( r_{\text{NO}_2,2} \), mol L\(^{-1}\) min\(^{-1}\)), nitric oxide reduction rate at sites 1 (\( r_{\text{NO},1} \), mol L\(^{-1}\) min\(^{-1}\)) and sites 2 (\( r_{\text{NO},2} \), mol L\(^{-1}\) min\(^{-1}\)) can be expressed as:

\[
r_{\text{NO}_2,2} = k_{\text{NO}_2,2} \frac{([1]+_0)^2 K_{\text{NO}_2,2}[\text{NO}_2^{-}]}{(1+K_{\text{NO}_2,2}[\text{NO}_2^{-}]+K_{\text{NO}_2,2}[\text{NO}])^2};
\]

(5.7)

\[
r_{\text{NO},1} = k_{\text{NO},1} \frac{([1]+_0)^2 K_{\text{NO},1}[\text{NO}]}{(1+K_{\text{NO}_2,1}[\text{NO}_2^{-}]+K_{\text{NO},1}[\text{NO}])^2};
\]

(5.8)

\[
r_{\text{NO},2} = k_{\text{NO},2} \frac{([1]+_0)^2 K_{\text{NO},2}[\text{NO}]}{(1+K_{\text{NO}_2,2}[\text{NO}_2^{-}]+K_{\text{NO},2}[\text{NO}])^2};
\]

(5.9)

in which \( k_{\text{NO}_2,2} \), \( k_{\text{NO},1} \), and \( k_{\text{NO},2} \) are rate constants (L mol\(^{-1}\) min\(^{-1}\)), \([+_2]_0\) is the total concentration of sites 2 (mol L\(^{-1}\)), and \( K_{X,2} \) is equilibrium adsorption constants for \( X \) at sites 2 (\( X=\text{NO}_2^{-}\) or \( \text{NO} \)) (L mol\(^{-1}\)). Site concentration is the number of specific sites per volume of reaction solution, and it is calculated by:

\[
[_1]_0 = \frac{F_1 m D}{M V};
\]

(5.10)

\[
[_2]_0 = \frac{(1-F_1) m D}{M V};
\]

(5.11)

in which \( F_1 \) is the surface fraction of sites 1, \( m \) is Pd weight for each reaction (g), \( D \) is dispersion of Pd nanoparticle catalysts, \( M \) is the atomic weight of Pd (106.4 g mol\(^{-1}\)), and \( V \) is the volume of
reaction solution (L). Finally the concentration variations of nitrite and nitric oxide with time are expressed as:

\[
\frac{d[NO_2^-]}{dt} = -r_{NO_2^-,1} - r_{NO_2^-,2}^*; \quad (5.12)
\]

\[
\frac{d[NO]}{dt} = r_{NO_2^-,1}^* + r_{NO_2^-,2} - r_{NO_2^-} - r_{NO_2^-}^*, \quad (5.13)
\]

We solve the differential equations with initial inputs of reaction rate constants, equilibrium adsorption constants, and nitrite concentrations, obtain degradation of nitrite concentration time course profile, and then calculate pseudo-first-order rate constants and TOFs according to the same methods used in Data Analysis. The differences between experimental TOFs and model TOFs are minimized by iteration with find minimum of constrained nonlinear multivariable function (fmincon) in Matlab (version R2012a, Mathworks). The details of codes and solved parameter values are enclosed in Appendix D, and the model estimated TOFs are plotted in Figure 5.4 (also listed in Table D.2). Linear regression of model estimated TOFs were performed in respect with surface fraction of (100) facet (Figure 5.4), and it is compared with experimental TOFs and corresponding linear regression results. Results show that experimental and model TOFs are not statistically different from each others, because 95% confidence intervals of their linear regressions overlap. Hence, model TOFs match adequately with experimental TOFs. Best-fitted parameters suggest that both reactivity and adsorption influence nitrite reduction kinetics, and that the differences of rate constants or equilibrium adsorption constants for the same reactant (i.e., nitrite or nitric oxide) between sites 1 and 2 range within 10 folds (Table D.1). Reduction rate constants for nitrite are 6.0×10^1-5.7×10^3 folds greater than those for nitric oxide (Table D.1), suggesting that nitric oxide reduction is the rate-limiting step and nitric oxide may build up on catalyst surface. It agrees well with the previous results, showing that pseudo-first-order rate constant for nitric oxide reduction on a Pd-In catalyst is 15.5 fold smaller than that of
nitrite (data not published). Equilibrium adsorption constants for nitric oxide are $1.9 \times 10^4$-$1.7 \times 10^5$ folds greater than those for nitrite (Table D.1), suggesting that nitric oxide binds significantly strongly on Pd surface in comparison to nitrite. Strong binding between nitric oxide and Pd agrees with previous density functional theory simulation results (65), and it agrees with the model hypothesis.

Nitrite reduction selectivity to ammonia depends on the dispersion of Pd nanoparticle catalysts at both low and high concentrations. No correlation between selectivity and specific facet of Pd nanoparticle catalysts was observed. Hence nitrite reduction selectivity to ammonia on Pd is size-dependent rather than shape-dependent. $\text{NH}_3\%$ decreases linearly with increasing dispersion (with $R=0.85$ and 0.69 for 100 $\mu$M and 2 mM nitrite reduction, respectively), and 95% confidence intervals of regressions also suggest negative correlation. It indicates that less ammonia is produced on smaller Pd nanoparticles. This is in contradiction to previously reported results (41, 61), in which more ammonia is produced on smaller Pd nanoparticles. Smaller Pd nanoparticles were believed to facilitate the overhydrogenation of N species (40), to inhibit N-N pairing (61), and to reduce concentration of N species and increase local pH by faster reduction kinetics (61, 68). However, none of previous nitrite/nitrate reduction was done with unsupported Pd nanoparticle catalysts or with defined shape and size. Unique electronic and surface properties of Pd nanoparticles, support-Pd interactions, and local environment near Pd surface may be responsible for the contradiction, and further exploration is required in the future.

Selectivity comparison between low and high initial nitrite concentration also indicates that ammonia production is significant higher with lower nitrite concentration. Up to 100% of nitrogen goes to ammonia for 100 $\mu$M nitrite reduction, but only up to 17.7% of nitrogen ends up
with ammonia production for 2 mM nitrite reduction. It agrees with previous studies, as more nitrogen species on catalyst surface (e.g., higher nitrite concentration) promote N-N pairing rather than overhydrogenation for N-H products.

**Figure 5.4** (a, c) Nitrite reduction turnover frequencies (TOFs) versus surface fraction of (100) facet of Pd nanoparticle catalysts, and (b, d) ammonia production percentages (NH$_3$%) for nitrite reduction versus dispersion of Pd nanoparticle catalysts. Initial nitrite concentration was 100 µM (a, b) and 2 mM (c, d), respectively. Green diamond ♦, red hexagon ●, gray cross □, and blue cube ■ represent experimental data of octahedral, cubocatahedral, rod, and cubic Pd nanoparticle catalysts. Surface fraction of (100) facet of Pd nanoparticle catalysts is the number of (100) atoms to the number of surface Pd atoms, and dispersion of Pd nanoparticle catalysts is the number of surface Pd atoms to the number of total Pd atoms in bulk. Error bars represent standard deviations of replicates. Orange solid lines — are linear regressions of experimental TOFs versus surface fraction of (100) facet or experimental NH$_3$% versus dispersion, and orange dash lines —— and enclosed light yellow region represent the 95% confidence intervals of linear regressions of experimental data. Gray circles ○ represent model data, gray solid lines — are linear regression of model estimated TOFs versus surface fraction of (100) facet, and gray dash lines —— represent the 95% confidence intervals of linear regressions of model data.
5.4.3 Pd Nanoparticle Catalysts for NDMA and Diatrizoate Reduction

NDMA and diatrizoate reduction TOFs on Pd nanoparticle catalysts with different shapes and sizes are shown in Figure 5.5. TOFs for both contaminants increase linearly with increase of surface fraction of terrace sites (with 95% confidence intervals), hence NDMA and diatrizoate reduction activity is only size-dependent, because surface fraction of terrace sites relies on Pd nanoparticle size for all shapes (Figure D.3c). Each NDMA molecule was proposed to bind two to three neighboring Pd atoms during reduction (69), and diatrizoate may also bind to multiple Pd sites because of its large molecular size and abundant moieties and functional groups, such as carboxylic acid group, benzene ring, iodine, and amide group. Benzene hydrogenation was studied on Pt (111) and Pd (111) by density functional theory simulations, and benzene and its hydrogenation intermediates anchor on catalyst surface through multi-sites (70). Large Pd nanoparticles with more terrace sites (Figure D.3c) provide strong and stable multi-site binding to NDMA, diatrizoate, and their reduction intermediates in contrast to edge and vertex sites, therefore faster reduction kinetics were observed.
Figure 5.5 Turnover frequencies (TOFs) for (a) NDMA and (b) diatrizoate reduction versus surface fraction of terrace sites of Pd nanoparticle catalysts. 100 µM contaminants were used as initial concentrations. Green diamond ■, red hexagon □, gray cross ●, and blue cube ▲ represent data of octahedral, cuboctahedral, rod, and cubic Pd nanoparticle catalysts. Surface fraction of terrace sites of Pd nanoparticle catalysts is the number of terrace atoms to the number of surface atoms. Error bars represent standard deviations of replicates. Orange solid lines are linear regressions of TOFs versus surface fraction of terrace sites, and orange dash lines and enclosed light yellow region represent the 95% confidence intervals of linear regressions.

For selectivity, NDMA reduction on Pd nanoparticle catalysts leads to DMA and ammonia production exclusively, regardless of catalyst shape and size. No UDMH was detected during reaction. Carbon and nitrogen mass balance are 99.6±2.4% and 97.0±2.3%, respectively. $^{15}$N$_2$ labeled NDMA was also used for reduction, and no $^{15}$N labeled gaseous products (e.g., nitric
oxide, nitrous oxide, dinitrogen) were observed. It confirms that DMA and ammonia are the only products for NDMA reduction on Pd. Diatrizoate reduction is proposed to proceed through a stepwise deiodination (10), however, only fully deiodinated product Dia-H$_3$ is quantified in the study because of the lack of available standards of other intermediates. At the end of diatrizoate reduction when Dia-H$_3$ concentration is stable (i.e., diatrizoate and other partially deiodinated intermediates disappear from HPLC spectra), the recovery of Dia-H$_3$ and I$^-$ are 88.9±2.7% and 92.1±0.7% (assuming that three I$^-$ liberated from diatrizoate reduction), respectively. It suggests that Dia-H$_3$ is likely the only fully hydrogenated product, and that other partially deiodinated intermediates may also be present.

5.4.4 Shape and Size Stability of Pd Nanoparticle Catalysts

The shape and size stability of Pd nanoparticle catalysts is a concern for the validity of aforementioned data. Pd nanoparticle catalysts may change their shape and size during reaction, especially the dissolution of low coordination atoms at edge and corner sites by Ostwald ripening (48), by interaction with chemicals present in the reaction mixture (71), or by aggregation (72, 73). Catalytic performance can also vary with catalyst shape and size (48). In this study, Pd nanoparticle catalysts did not change shape or size during reaction with nitrite or NDMA over a period of 4 h to 5 d (Figure D.4). The same is true during reaction with diatrizoate even up to 12 d, except for reaction with small octahedra (Figure D.4). Small octahedra ca. 4 nm in size changed shape to sphere-like particles (Figure D.4). During diatrizoate reduction, I$^-$ is liberated; it has been shown to strongly chemisorb to Pd (74). I$^-$ changes Pd nanoparticle shape either by atomic rearranging or by etching. To test this possibility, small octahedra Pd nanoparticles were
exposed to 35 µM of I−, I− and nitrite, or I− and NDMA for 9 h; this is the same concentration of I− released during diatrizoate reduction. Results show that the sample with I−-only changed shape to near-sphere (Figure D.5). No shape-change was observed in when the octahedra Pd nanoparticles were exposed to mixtures of I− and nitrite, or I− and NDMA (Figure D.5). These results suggest that I−, and that nitrite or NDMA compete for adsorption sites on the Pd surface, and that nanoparticle shape may be maintained by amending inert species with sufficient concentration.

5.5 Conclusions

Catalytic reduction with Pd has emerged as a promising technology to remove a suite of persistent contaminants from drinking water, including oxyanions, disinfection byproducts, and halogenated pollutants, but low activity and poor selectivity for desired end products prohibit its application. To address these challenges, a suite of shape- and size-controlled Pd nanoparticles were synthesized, and the effects of shape and size on reduction activity and selectivity for nitrite, NDMA, and diatrizoate were evaluated. Reduction results for initial contaminant concentration at as low as 100 µM show that TOFs for nitrite increase 4.7 folds with increasing surface fraction of (100) facet from 0% to 95.3%, and TOFs for NDMA and diatrizoate increase 4.5 folds and 3.6 folds with increasing surface fraction of terrace sites from 79.8% to 95.3%, respectively. It indicates that TOFs for nitrite, NDMA, and diatrizoate reduction are dependent on coordination number of surface Pd sites at low contaminant concentration. TOF is a normalized activity in terms of the number of surface Pd sites, which is dependent on Pd nanoparticle size; surface fraction of (100) facet and terrace sites are dependent on Pd shape and size, respectively. Hence, activity for nitrite reduction is both shape- and size-dependent but activities for NDMA and
Diatrizoate reduction are only size-dependent at low contaminant concentrations. Results for initial nitrite concentration at 2 mM show that at TOFs are consistent for all shape- and size-controlled Pd nanoparticles, suggesting activity for nitrite reduction is only size-dependent at high contaminant concentration. A two-site model based on Langmuir-Hinshelwood mechanism was developed to shed light on the change of structure-sensitivity for nitrite reduction with contaminant concentration, and it suggests that both reaction and adsorption of nitrite and nitric oxide play important roles. Based on the fitting results, nitric oxide reduction is much slower than nitrite, and its binding to Pd sites is significantly stronger than nitrite.

Ammonia production percentage, representing the selectivity to ammonia, decreases 3.9 folds and 3.7 folds for 100 µM and 2 mM nitrite reduction with increasing Pd dispersion from 12.7% to 33.4%, respectively. It suggests that selectivity for nitrite reduction at both low and high contaminant concentrations are size-dependent. Selectivity for NDMA reduction is neither shape- nor size-specific, and dimethylamine and ammonia are exclusive products; and selectivity for diatrizoate reduction is also likely to be non-shape- and non-size-specific.

The shape and size of Pd nanoparticle catalysts are stable for nitrite and NDMA reduction during a period of 4 h to 5 d, and it holds the truth for diatrizoate reduction up to 12 d except for small octahedra of ca. 4 nm in size, which turned into near-spherical shape after reaction. Iodide was liberated in diatrizoate reduction, and it changes Pd nanoparticle shape either by atomic rearranging or by etching.
In summary, this study suggests insights that catalytic reduction performance for waterborne contaminant removal varies with Pd shape and size for the first time, that catalysts can be tailored for better performance, and that Pd catalysts hold the promise to treat a variety of contaminants simultaneously for drinking water.

5.6 References


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CHAPTER 6: SUMMARY AND CONCLUSIONS

6.1 Summary and Conclusions

The dissertation focuses on the development of sustainable Pd-based catalysts for a suite of contaminant removal, including oxyanions, \( N \)-nitrosodimethylamine (NDMA), and diatrizoate. It evaluates the impacts of water quality (i.e., co-contaminants), catalyst supports, and nanoparticulate metal on catalytic kinetics, selectivities, and longevities for contaminant reduction. Catalyst performance can be tailored based on research results, and Pd-based catalytic reduction holds the promise to remove contaminants from drinking water. Conclusions drawn from the studies are shown in the following sections.

6.1.1 Enhancement of Oxyanion and Diatrizoate Reduction Kinetics using Selected Azo Dyes on Pd-based Catalysts

- Co-contaminant azo dye methyl orange enhances oxyanions (i.e., nitrate, nitrite, bromate, chlorate, and perchlorate) and diatrizoate reduction kinetics significantly.
- The enhancement of a suite of azo dyes for nitrate reduction kinetics varies with dye hydrogenation energies, and a kinetic model based on Brønsted–Evans–Polanyi (BEP) theory was developed to match experimental results.
- A hydrogen atom shuttling mechanism was proposed to explain the enhancement. Sorbed azo dyes and reduced hydrazo dyes shuttle hydrogen atoms for oxyanions or diatrizoate reduction.
This research has identified for the first time the synergetic effect of azo dyes on oxyanion and diatrizoate reduction on Pd-based catalysts.

6.1.2 A New Geometric Method Based on Two-Dimensional Transmission Electron Microscopy for Analysis of Interior versus Exterior Pd Loading on Hollow Carbon Nanofibers

A fast and accurate geometric analysis method based on two-dimensional transmission electron microscopic (2D TEM) images to estimate Pd internal versus external loading percentages on carbon nanofibers (CNFs) was development.

Three different CNF supported Pd catalysts were prepared using literature reported methods, and different amounts of Pd inside loading were yielded. Results show that the percentage of inside loaded Pd varies as expected.

The interior loading percentage of one segment of a Pd-loaded CNF was characterized by both 2D TEM and 3D scanning transmission electron microscopy (3D TEM), and adequate agreement was observed.

6.1.3 Enhanced Activity and Selectivity of Carbon Nanofiber Supported Pd Catalysts for Nitrite Reduction

Nitrite reduction activity and selectivity are not significantly influenced by Pd interior versus exterior CNF loading.
Nitrite reduction turnover frequencies (TOFs) among all CNF catalysts are consistent, suggesting catalytic activity is higher for catalysts with smaller Pd nanoparticles, and suggesting nitrite reduction is not structure sensitive.

Nitrite reduction selectivity to dinitrogen increases with increasing Pd nanoparticle size.

This is the first study to report an optimum Pd nanoparticle size balances faster nitrite reduction kinetics and higher selectivity to dinitrogen.

CNF Pd catalysts have better performance compared to conventional Pd catalysts (i.e., Pd on activated carbon or alumina) in terms of nitrite reduction activity and selectivity, and they maintain consistent activity over multiple reduction cycles.

6.1.4 Structure Sensitivity Study of Waterborne Contaminant Hydrogenation using Shape- and Size-Controlled Pd Nanoparticles

TOFs for nitrite, NDMA, and diatrizoate reduction are dependent on coordination numbers of surface Pd sites at low contaminant concentration (100 µM). Nitrite reduction is more active on (100) facet, whereas NDMA and diatrizoate reduction are more active on terrace sites rather than on edge/vertex sites. At low contaminant concentration, overall activity for nitrite reduction is both shape- and size-dependent, but overall activities for NDMA and diatrizoate reduction are only size-dependent.

TOFs for nitrite reduction are consistent for any shaped- or sized-Pd nanoparticles at high concentration, suggesting overall activity is only size-dependent.
A two-site model based on Langmuir-Hinshelwood mechanism was developed to explain the change of structure-sensitivity with nitrite concentration, and both reaction and adsorption properties of nitrite and nitric oxide are responsible.

Selectivity to ammonia for nitrite reduction decreases with increasing surface Pd sites for both low and high nitrite concentrations, suggesting selectivity is only size-dependent. Selectivity for NDMA reduction is neither shape- nor size-specific, and ammonia and dimethylamine are the only products. Selectivity for diatrizoate is also likely not shape- and size-specific, and a series of deiodinated intermediates, 3,5-diacetamidobenzoic acid, and iodide are produced.

This reports for the first time that reduction kinetics and selectivities of waterborne contaminants are shape- and size-dependent on Pd nanoparticles, and the dependence varies with contaminant type and concentration.

6.2 Engineering Application

The key findings in this dissertation help develop sustainable Pd-based catalysts for persistent contaminants removal from drinking water, and it promotes the implementation of this technology. For using the groundwater as source for drinking, a variety of contaminants potentially exist in groundwater and they require removal. Halogenated compounds, especially chlorinated ethane (e.g., trichloroethylene, perchloroethylene), are able to be reduced by catalytic treatment with fast reduction kinetics at first. Next, recalcitrant nitrate, perchlorate, and NDMA can be removed, but the enhancement of catalytic activity per mass is needed to reduce the cost and enhance sustainability. Azo dyes, or other azo compounds, may present in the groundwater
as co-contaminants; they significantly enhance catalytic reduction kinetics. It reduces the cost for removal of persistent contaminants, and pushes the application in practice forward. Even if azo dyes are not present as co-contaminants, we can still take the advantages from their enhancement on catalytic kinetics. Azo dyes, or other azo compounds, can be functionalized on supported Pd-based catalysts and anchored on supports (e.g., carbon, silica). Covalent bonding prevents azo group leaching and potential pollution to treated water, and it also maintains catalytic activity for extended lifetime.

CNF supported catalysts show unique properties and enhance catalytic performance significantly for nitrite reduction. They can be used not only for monometal loading but also for bimetal loading, and they can also be used to remove a series of contaminants besides nitrite. CNFs are explored as filtration media, such as membrane, for removal of waterborne contaminants and air contaminants. The integration of catalytic process and physical separation, by using catalyst loaded CNFs for filtration, is advantageous compared with either filtration or catalytic treatment alone. Filtration concentrates the low level contaminants on media surface, and it enhances catalytic performance by fully utilizing available catalytic active sites. Catalytic treatment reduces contaminants to innocuous products; it saves efforts for filtration media regeneration and contaminant disposal, and it prolongs the lifetime for filtration media. Integration of catalytic reduction and filtration also broadens the application of CNFs, because it overcomes handling, leaching, and deactivation issues.

Structure-sensitivity for contaminant reduction depends on contaminant type and contaminant concentration. It is important to tune catalyst properties accordingly to enhance reduction
kinetics for target contaminants. It is important to consider both activity and selectivity to dinitrogen for nitrite and nitrate reduction, and an optimum Pd nanoparticle size exists to balance fast reduction kinetics and high selectivity. A case-by-case catalyst design is necessary to achieve the best performance of catalytic reduction, and it reduces the cost and improves the sustainability of this technology.

Catalytic treatment is not only applicable for fresh water treatment but also for ion-exchange brine regeneration. Ion-exchange resin designed for nitrate and perchlorate removal, requires regeneration by concentrated sodium chloride brine before it loses its capacity. The brine after regeneration carries high concentration of nitrate (ca. 5,000 mg/L as nitrate), and needs disposal. The preparation of new brine and brine disposal after use are costly, energy intensive, and environmental unfriendly. Implementation of catalytic treatment for brine regeneration is promising because it reduces contaminants, reuses brine, lowers cost and environmental impacts, and improves the sustainability of ion-exchange.

6.3 Future Directions

The results and conclusions presented in this dissertation indicate several future research directions. Improvement of fouling resistance, hybrid systems for contaminant removal, and production of valuable products from waste should be considered in the future.

Pd-based catalysts suffer from poisoning of reduced sulfur species and natural organic matter. Improving fouling resistance is necessary for application in practice. Results from this
dissertation have shown that Pd nanoparticles are loaded inside CNFs, and the protection from CNFs will probably improve fouling resistance. Pd nanoparticles and with promoter metal, are able to be loaded inside CNFs, carbon nanotubes, or mesoporous silica with smaller pores, and it will repulse foulants by size exclusion or hydrophilic/hydrophobic interactions.

Hybrid systems for contaminant removal will have synergistic effects, and will have better performance than single treatment technology. Catalytic treatment uses hydrogen as the reductant, and it is always produced from fossil fuels. Besides, hydrogen is stored in pressured tank, which requires additional handling and raises concerns for safety. Electrolyzer generates hydrogen in situ, and it overcomes the aforementioned limitations. In addition, the hydrogen production is able to be tuned by adjusting the voltage and current for electrolyzer. It is especially convenient for on site use. We also can load Pd-based catalysts on cathodes, and perform electrocatalytic reduction for contaminant removal. Electrooxidation and electroreduction may be coupled, and can be used for advanced water treatment. Advanced oxidation removes the majority of organic contaminants by mineralization, and the following reduction removes oxidative contaminants or persistent contaminants to oxidation. This integration will precede the performance of oxidation or reduction alone, and it will be promising for small-scaled drinking water treatment for removing a variety of contaminants.

Production of valuable products from waste enhances the sustainability of a certain technology, and it also reduces the cost, energy use, and environmental impacts. Ammonia is considered as an undesired product in nitrate or nitrite reduction for drinking water treatment. However, it is a valuable product for making fertilizers, pharmaceuticals, and other industrial products. Ion-
exchange brine has high concentration of nitrate, and it is a great source of nitrogen. It can be used to produce ammonia rather than dinitrogen, and ammonia can be separated from brine for further industrial use. Reduction of nitrate or nitrite to ammonia is operated under ambient temperature and pressure, and it bypasses dinitrogen reduction pathway, which is energy intensive. Dinitrogen is stable under ambient conditions, and it requires high temperature and catalysts to activate for reaction.
Appendix A contains azo dye hydrogenation energy calculation and kinetic model development. It also contains figures and tables that are referred to in the text of the main manuscript.

A.1 Control Experiments

Control experiments were performed, including nitrate reduction in the presence or absence of H₂, catalyst (Pd-In), and azo dye methyl orange (MO). Results indicate that H₂ and catalyst are essential for nitrate reduction, regardless of whether the azo dye MO is added. Control experiments with different hydrogen supply and mixing rates were also performed, and results prove that contaminant reduction kinetics were not limited by hydrogen supply (300 mL/min) or external mass transfer (mixing rate at ca. 500 rpm) under the operation conditions in this study.

Adsorption tests for methyl orange (MO) and sulfanilic acid (SA) on a supported Pd-catalyst was performed in an inert atmosphere of N₂. No observable adsorption (<3%) of MO and SA was observed.

A.2 Hydrogenation Energy Calculation

All computational chemistry calculations were performed at the B3LYP/6-311G** level using the Gaussian code, based on first-principles density functional theory (DFT) methods. Optimized structures and energies were calculated for azobenzene, its relative variants, azo dyes and their
reduced hydrazo forms. The hydrogenation energy (HE) for azo dye to form hydrazo dye was calculated as:

\[
HE = E_{\text{hydrazo dye}} - E_{\text{azo dye}} - E_{H_2}
\]

(A.1)

for single-azo dyes;

and HE was calculated as:

\[
HE = 0.5 \times (E_{\text{hydrazo dye}} - E_{\text{azo dye}} - 2 \times E_{H_2})
\]

(A.2)

for double-azo dyes (congo red only in this research). The unit of HE is kJ per mol azo groups (kJ/mol -N=N-).

A.3 Kinetic Model Development

This volcano behavior can be explained in terms of a simple kinetic model that takes advantage of the Brønsted–Evans–Polanyi (BEP) relation between reaction energies and rate constants (1). All data except for CR and MR are applied to develop and fit the kinetic model. The overall reaction includes two steps: reduction of azo dyes with hydrogen oxidation, and oxidation of hydrazo dyes with nitrate reduction.

R1. azo dye + H₂ + NO₃⁻ \(\text{Pd-In} \rightleftharpoons\) hydrazo dye + NO₃⁻

R2. hydrazo dye + NO₃⁻ \(\text{Pd-In} \rightleftharpoons\) azo dye + NO₂⁻ + H₂O

The forward and reverse reaction rate constants for reaction R1 are defined as \(k_1\) (L/(mol·min)) and \(k_{-1}\) (min⁻¹), respectively; and for reaction R2, \(k_2\) (L/(mol·min)) and \(k_{-2}\) (L/(mol·min)), respectively.
Based on previous study and the preliminary experiments of this study, nitrate catalytic reduction to form nitrite can only occur with the second promoter metal (e.g. In, Cu, Sn) present, and this process limits the overall nitrate reduction kinetics. For this reason, it is assumed that azo dyes mainly enhanced the step of nitrate reduction to nitrite, and only this step is considered in kinetic model.

The rates of reaction R1 and R2, \( r_1 \) and \( r_2 \) (mol/(L·min)), can be derived as:

\[
\begin{align*}
 r_1 &= k_1[^{\text{azo}}][^H_2] - k_{-1}[^{\text{hydrazo}}]
 \quad \text{(A.3)} \\
 r_2 &= k_2[^{\text{hydrazo}}][NO_3^-] - k_{-2}[^{\text{azo}}][NO_2^-]
 \quad \text{(A.4)}
\end{align*}
\]

\([^{\text{azo}}], [^{H_2}], [^{\text{hydrazo}}], [NO_3^-], \) and \([NO_2^-] \) (mol/L) refer to the aqueous concentration of azo dye, hydrogen, hydrazo dye, nitrate, and nitrite, respectively.

As stated above, nitrate reduction rate constant before degradation of at least half of its initial concentration was calculated; according to this, nitrate reduction rate at time zero was considered to simplify this problem. At time zero, the forward reaction rate is substantially higher than its corresponding reverse reaction \( k_1[^{\text{azo}}][^{H_2}] \gg k_{-1}[^{\text{hydrazo}}] \) and \( k_2[^{\text{hydrazo}}][NO_3^-] \gg k_{-2}[^{\text{azo}}][NO_2^-] \). Hydrogen is saturated in aqueous solution under operation conditions (21±0.3 °C, 1 atm) and its concentration \([^{H_2}]_0 \) is 0.773 mM; nitrate concentration at time zero, \([NO_3^-]_0 \), is 2.35 mM. Consequently reaction rates \( r_1 \) and \( r_2 \) can be expressed as:

\[
\begin{align*}
 r_1 &= k_1[^{\text{azo}}][^{H_2}]_0
 \quad \text{(A.5)} \\
 r_2 &= k_2[^{\text{hydrazo}}][NO_3^-]_0
 \quad \text{(A.6)}
\end{align*}
\]
From the Arrhenius equation, it is known that rate constants $k_1$ and $k_2$ can be expressed as:

\[ k_1 = \nu_1 e^{E_{a1}/RT} \]  \hspace{1cm} (A.7)  
\[ k_2 = \nu_2 e^{E_{a2}/RT} \]  \hspace{1cm} (A.8)

in which $\nu_1$ and $\nu_2$ are pre-exponential factors (L/(mol·min)), $R$ is the gas constant (8.31 J/(K·mol)), $T$ is the temperature in Kelvin (294 K in this study), and $E_{a1}$ and $E_{a2}$ (kJ/mol) refer to the activation energies in reaction R1 and reaction R2, respectively. Absolute quantum mechanical energies (kJ/mol) of reacting species ($E(\text{NO}_3^-)$, $E(\text{azo})$, $E(\text{H}_2)$, $E(\text{hydrazo})$, $E(\text{NO}_2^-)$, and $E(\text{H}_2\text{O})$), energy change in reactions ($DE_1$, also as $HE$, and $DE_2$), and activation energies ($E_{a1}$ and $E_{a2}$) are schematically listed in Figure A.4. Before reaction R1, total quantum mechanical energy of all reactants is $E(\text{NO}_3^-)+E(\text{azo})+E(\text{H}_2)$. $E(\text{NO}_3^-)$ is considered here to balance the species in both reaction R1 and R2. After reaction R1 and before reaction R2, total quantum mechanical energy of all reactants/products is $E(\text{NO}_3^-)+E(\text{hydrazo})$. When reaction R2 is finished, total quantum mechanical energy of all products is $E(\text{NO}_2^-)+E(\text{H}_2\text{O})+E(\text{azo})$. The energy change in reaction R1 and reaction R2, $DE_1$ (HE) and $DE_2$, is $E(\text{hydrazo})-E(\text{azo})-E(\text{H}_2)$ and $E(\text{NO}_2^-)+E(\text{H}_2\text{O})+E(\text{azo})-E(\text{NO}_3^-)-E(\text{hydrazo})$, respectively. The assumption is made based on the BEP relation that the activation energy in each reaction step ($E_{a1}$ and $E_{a2}$) is linearly proportional to their corresponding quantum mechanical energy change ($HE$ and $DE_2$). Because the total energy change of nitrate reduction to nitrite ($DE$) is a fixed number and $DE= HE+DE_2$, thus $E_{a2}$ can also be linearly correlated with $HE$. Based on this assumption, $E_{a1}$ and $E_{a2}$ can be expressed as:

\[ E_{a1} = \alpha_1 HE + \beta_1 \]  \hspace{1cm} (A.9)  
\[ E_{a2} = \alpha_2 HE + \beta_2 \]  \hspace{1cm} (A.10)
Here $\alpha$ is transfer coefficient and $\beta$ is intrinsic activation barrier (kJ/mol). Since $E_{a1}$ and $E_{a2}$ represent the activation energies of two reverse reactions, which involve hydrogen addition and release, they should be negatively interrelated. When they are correlated with the same HE as a reference, $\alpha_1$ and $\alpha_2$ have opposite signs.

It is assumed that the overall nitrate reduction rate is limited either by reaction R1 or by reaction R2. However, because in the absence of azo dye nitrate can still be reduced on the Pd-In catalyst with a background rate and the addition of azo dye can either enhance or have no effect on this rate, the final expression of overall nitrate reduction rate can be written as:

$$r = \max (r_b, \min(r_1, r_2))$$

(A.11)

In this expression, $r_b$ is the reaction rate without azo dye addition (mol/(L·min)).

By combining equations (A.5)-(A.10) the following expressions are got:

$$r_1 = v_1e^{-(\alpha_1HE+\beta\nu)/RT}[azo][H_2]_0$$

(A.12)

$$r_2 = v_2e^{-(\alpha_2HE+\beta\nu)/RT}[hydrazo][NO_3^-]_0$$

(A.13)

It is further proposed that the sorbed dyes are responsible for reaction rate enhancement and cycle between azo and hydrazo groups, hence [azo] and [hydrazo] in equations (A.12) and (A.13) are sorbed dye concentrations, $[azo]_s$ and $[hydrazo]_s$, respectively. Assuming all azo dyes and their reduced hydrazo forms in this test have identical affinity to the same catalyst, and considering their initial concentrations before reduction are the same (15.3 $\mu$M), the sorbed azo dye concentrations at time zero, $[azo]_{s0}$, are identical. When reaction R1, azo dye reduction with hydrogen oxidation, limits the overall reaction rate, all sorbed azo dyes are in their oxidized...
forms initially. In this scenario, [azo] (= [azo]₀) in equation (A.12) equals to [azo]₀. Then equation (A.12) can be derived as:

\[
\min(r_1, r_2) = r_1 = v_1e^{-(\alpha_1HE + \beta_1)/RT} [azo]_0[H_2]_0
\]  \hspace{1cm} (A.14)

When reaction R2, hydrazo dye oxidation with nitrate reduction, limits the reaction rate, all pre-
sorbed azo dyes turn into their reduced hydrazo forms. In this case, [hydrazo] (= [hydrazo]₀) in
equation (A.13) equals to [azo]₀.

\[
\min(r_1, r_2) = r_2 = v_2e^{-(\alpha_2HE + \beta_2)/RT} [azo]_0[NO_3^-]_0
\]  \hspace{1cm} (A.15)

The final expression of the kinetic model can be expressed as:

\[
\begin{align*}
    r &= \begin{cases} 
    r_b, & \text{when } \min(r_1, r_2) \leq r_b \\
    r_1 = v_1e^{-(\alpha_1HE + \beta_1)/RT} [azo]_0[H_2]_0, & \text{when } r_b < r_1 \leq r_2 \\
    r_2 = v_2e^{-(\alpha_2HE + \beta_2)/RT} [azo]_0[NO_3^-]_0, & \text{when } r_b < r_2 < r_1
    \end{cases}
\end{align*}
\]  \hspace{1cm} (A.16)

Furthermore, the nitrate reduction rate constant rather than reduction rate was calculated in this
study, and nitrate reduction follows pseudo-first-order behavior before at least half of its decay.

Consequently, nitrate reduction rate constant \( k_{NO_3} \) at time zero can represent the initial reduction
rate constant, and it can be written as:

\[
\begin{align*}
    k_{NO_3} &= \frac{r}{[NO_3^-]_0} = \begin{cases} 
    k_b = \frac{r_b}{[NO_3^-]_0}, & \text{when } \min(r_1, r_2) \leq r_b \\
    v_1e^{-(\alpha_1HE + \beta_1)/RT} [azo]_0[H_2]_0, & \text{when } r_b < r_1 \leq r_2 \\
    v_2e^{-(\alpha_2HE + \beta_2)/RT} [azo]_0, & \text{when } r_b < r_2 < r_1
    \end{cases}
\end{align*}
\]  \hspace{1cm} (A.17)
In order to fit the kinetic model to the data, a value of $\beta$ in the range of literature values $(50\text{kJ/mol -N=N-, ca. 0.5eV})$ (1) was selected, natural log $k_{NO_3}$ versus HE (according to equation A.18) was plotted, $\alpha$ was adjusted to match the slope of the data, and $\nu$ was adjusted to match the intercept. The corresponding best fit values are listed in Table A.6.

$$\ln(k_{NO_3}) = \begin{cases} 
\ln\left(\frac{r_b}{[NO_3^-]_0}\right), & \text{when } \min(r_1, r_2) \leq r_b \\
-\frac{\alpha_1}{RT} HE - \frac{\beta_1}{RT} + \ln(v_1) + \ln\left(\frac{[azo]_0[H_2]_0}{[NO_3^-]_0}\right), & \text{when } r_b < r_1 \leq r_2 \\
-\frac{\alpha_2}{RT} HE - \frac{\beta_2}{RT} + \ln(v_2) + \ln([azo]_0), & \text{when } r_b < r_2 < r_1
\end{cases}$$  \hspace{1cm} (A.18)

It is recognized that the range of $\beta$ values in the literature are large, and other possible sets of parameter values will match the data. The model results using the data in Table A.6 are plotted as a dashed line in Figure 2.3. The line shows volcano behavior, and supports the hypothesis that azo dyes enhance contaminant reaction rates by reversibly shuttling hydrogen between catalyst and contaminants.

**A.4 Schemes of Immobilizing Azo Dyes on Catalysts**

Schemes of immobilizing azo dyes on different catalyst support are listed below, including activated carbon, other carbon based supports, alumina, and silica.
**Scheme A.1** Scheme of azo dye immobilization onto activated carbon or other carbon based catalyst supports by the diazonium reaction.

**Scheme A.2** Scheme of azo dyes immobilization onto alumina or silica catalyst supports by silane coupling and a single stage Mannich reaction.
Supporting Figures

Figure A.1 (a) Nitrate reduction on Pd-In with different methyl orange (MO) concentrations. (b) Product distribution of nitrate reduction on Pd-In with MO addition. A proposed nitrate catalytic reduction pathway with [H] is shown. (c) MO reduction on Pd-In with nitrate co-existing. The proposed MO catalytic reduction pathway with [H] is shown. 5 wt% Pd-0.5 wt% In (Pd-In) catalyst was used at loadings of 0.08 g/L for all experiments. Nitrate initial concentration was 2.35 mM for all experiments. MO initial concentrations were 0.153 µM, 1.53 µM, and 14.4 µM for (a); while 6.11 µM for (b) and (c), respectively. Details are in Table A.2.
Figure A.2 Nitrate reduction kinetics with different methyl orange (MO) concentrations. 5 wt% Pd-0.5 wt% In (Pd-In) catalyst was used at loadings of 0.08 g/L. Initial nitrate concentrations were 2.35 mM. Error bars represent 95% confidence intervals. Details are in Table A.2.
Figure A.3 Nitrate reduction kinetics and methyl orange (MO) enhancement in successive reduction cycles on Pd-In. 15.3 µM MO was only added at time zero, while nitrate was added every 20 minutes and its initial concentration of each cycle was maintained at ca. 2.35 mM after each injection. 5 wt% Pd-0.5 wt% In (Pd-In) catalyst was used at a loading of 0.08 g/L. Enhancement factors are rate constants with MO addition divided by those without MO addition.
Figure A.4 Potential energy diagram for nitrate reduction with the aid of azo/hydrazo dyes as atomic hydrogen shuttle. $E(\text{NO}_3^-)$, $E(\text{azo})$, $E(\text{H}_2)$, $E(\text{hydrazo})$, $E(\text{NO}_2^-)$, and $E(\text{H}_2\text{O})$ refer to absolute quantum mechanical energy of nitrate, azo dyes, hydrogen, hydrazo dyes, and water, respectively. Before reaction R1, total quantum mechanical energy of all reactants is $E(\text{NO}_3^-)+E(\text{azo})+E(\text{H}_2)$. After reaction R1 and before reaction R2, total quantum mechanical energy of all reactants/products is $E(\text{NO}_3^-)+E(\text{hydrazo})$. When reaction R2 is finished, total quantum mechanical energy of all products is $E(\text{NO}_2^-)+E(\text{H}_2\text{O})+E(\text{azo})$.

$E$ is the total quantum mechanical energy change of nitrate reduction to nitrite and it is a fixed number, no matter how $E(\text{azo})$ and $E(\text{hydrazo})$ change. It equals to the sum of $E_1$ and $E_2$. $E_1$ and $E_2$ represent the quantum mechanical energy change of azo dye reduction with hydrogen oxidation and nitrate reduction with hydrazo dye oxidation, reactions R1 and R2, respectively. $E_1$ is also referred to as the hydrogenation energy (HE) of azo dyes in discussion. $E_1$ (HE) and $E_2$ equals to $E(\text{hydrazo})-E(\text{azo})-E(\text{H}_2)$ and $E(\text{NO}_2^-)+E(\text{H}_2\text{O})+E(\text{azo})-E(\text{NO}_3^-)-E(\text{hydrazo})$. $E_{a1}$ and $E_{a2}$ are the activation energies of reactions R1 and R2.
A.6 Supporting Tables

Table A.1 Oxyanion, Diatrizoate, and NDMA Reduction Rates without and with Methyl Orange (MO) on Pd-based Catalysts

<table>
<thead>
<tr>
<th>Target Contaminant</th>
<th>Contaminant Initial Conc.(^b) (mM)</th>
<th>Catalyst</th>
<th>Catalyst Metal Weight Percentage(^b)</th>
<th>Catalyst Loading(^b) (g/L)</th>
<th>MO Initial Conc.(^b) (μM)</th>
<th>(k_{obs})^(^c) (min(^{-1})) Without MO</th>
<th>(k_{obs}) With MO</th>
<th>Enhancement Factor(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>2.35</td>
<td>Pd-In</td>
<td>5 wt % Pd-0.5 wt % In(^e)</td>
<td>0.08</td>
<td>15.3</td>
<td>7.27×10(^{-2}) (8.3×10(^{-3}))</td>
<td>3.81×10(^{-2}) (3.5×10(^{-3}))</td>
<td>5.2</td>
</tr>
<tr>
<td>Nitrate</td>
<td>2.35</td>
<td>Pd-Cu T</td>
<td>5 wt % Pd-1.3 wt % Cu, prepared by traditional method(^e)</td>
<td>0.08</td>
<td>15.3</td>
<td>7.10×10(^{-3}) (4.0×10(^{-4}))</td>
<td>9.97×10(^{-3}) (4.9×10(^{-4}))</td>
<td>1.4</td>
</tr>
<tr>
<td>Nitrate</td>
<td>2.35</td>
<td>Pd-Cu C</td>
<td>5 wt % Pd-1.3 wt % Cu, prepared by colloid method(^e)</td>
<td>0.08</td>
<td>15.3</td>
<td>7.02×10(^{-3}) (2.6×10(^{-4}))</td>
<td>1.30×10(^{-2}) (6×10(^{-4}))</td>
<td>1.9</td>
</tr>
<tr>
<td>Nitrite</td>
<td>2.35</td>
<td>Pd</td>
<td>5 wt % Pd(^e)</td>
<td>0.08</td>
<td>15.3</td>
<td>1.77×10(^{-2}) (2.2×10(^{-3}))</td>
<td>4.21×10(^{-2}) (1.9×10(^{-3}))</td>
<td>2.4</td>
</tr>
<tr>
<td>Nitrite</td>
<td>2.35</td>
<td>Pd-In</td>
<td>5 wt % Pd-0.5 wt % In(^e)</td>
<td>0.08</td>
<td>15.3</td>
<td>3.05×10(^{-2}) (3.5×10(^{-3}))</td>
<td>5.34×10(^{-2}) (8.9×10(^{-3}))</td>
<td>1.8</td>
</tr>
<tr>
<td>Bromate</td>
<td>2.35</td>
<td>Pd</td>
<td>5 wt % Pd</td>
<td>0.08</td>
<td>15.3</td>
<td>2.28×10(^{-2}) (1.0×10(^{-3}))</td>
<td>6.63×10(^{-2}) (6.3×10(^{-3}))</td>
<td>2.9</td>
</tr>
<tr>
<td>Bromate</td>
<td>2.35</td>
<td>Pd-In</td>
<td>5 wt % Pd-0.5 wt % In(^e)</td>
<td>0.08</td>
<td>15.3</td>
<td>4.11×10(^{-3}) (4.2×10(^{-4}))</td>
<td>9.59×10(^{-3}) (7.6×10(^{-4}))</td>
<td>2.3</td>
</tr>
<tr>
<td>Chlorate</td>
<td>2.35</td>
<td>Pd-Re</td>
<td>5 wt % Pd-12 wt % Re(^e)</td>
<td>0.1</td>
<td>15.3</td>
<td>1.84×10(^{-2}) (7×10(^{-4}))</td>
<td>3.46×10(^{-2}) (7×10(^{-4}))</td>
<td>1.9</td>
</tr>
<tr>
<td>Perchlorate</td>
<td>0.02</td>
<td>Pd-Re</td>
<td>5 wt % Pd-12 wt % Re(^e)</td>
<td>2</td>
<td>15.3</td>
<td>5.27×10(^{-3}) (1.0×10(^{-4}))</td>
<td>5.79×10(^{-3}) (1.3×10(^{-4}))</td>
<td>1.1</td>
</tr>
<tr>
<td>Diatrizoate</td>
<td>2.35</td>
<td>Pd</td>
<td>5 wt % Pd</td>
<td>0.4</td>
<td>15.3</td>
<td>2.84×10(^{-3}) (2.9×10(^{-4}))</td>
<td>4.35×10(^{-3}) (4.4×10(^{-4}))</td>
<td>1.5</td>
</tr>
<tr>
<td>NDMA</td>
<td>0.1</td>
<td>Pd-In, 1</td>
<td>5 wt % Pd-0.5 wt % In(^e)</td>
<td>0.4</td>
<td>15.3</td>
<td>3.01×10(^{-3}) (1.0×10(^{-4}))</td>
<td>1.66×10(^{-3}) (1.1×10(^{-4}))</td>
<td>0.57</td>
</tr>
<tr>
<td>NDMA</td>
<td>0.49</td>
<td>Pd-In, 2</td>
<td>5 wt % Pd-0.5 wt % In(^e)</td>
<td>0.08</td>
<td>15.3</td>
<td>3.97×10(^{-3}) (6.1×10(^{-5}))</td>
<td>2.04×10(^{-3}) (1.3×10(^{-5}))</td>
<td>0.51</td>
</tr>
</tbody>
</table>

\(^a\) pH was maintained at 5.00 for nitrate, nitrite, bromate, diatrizoate, and NDMA reduction, while at 2.68 for chlorate and perchlorate reduction. \(^b\) Theoretical values for catalyst metal weight percentage, catalyst loadings, contaminant initial conc., and methyl orange (MO) initial conc. \(^c\) Values in parentheses represent ±95% confidence intervals for observed rate constant (\(k_{obs}\)). \(^d\) Enhancement factor is \(k_{obs}\) in the presence of MO divided by that in the absence of MO. \(^e\) Detailed information is included in Materials and Methods.
### Table A.2 Nitrate Reduction Rates with Different Concentrations of Methyl Orange (MO) on Pd-In Catalyst\(^a\)

<table>
<thead>
<tr>
<th>MO Initial Conc.(^b) ((\mu)M)</th>
<th>(k_{\text{obs}})(^c) (min(^{-1}))</th>
<th>(k_{\text{obs}}) Enhancement Factor(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.27(\times)10(^{-3}) (8.3(\times)10(^{-4}))</td>
<td>1.0</td>
</tr>
<tr>
<td>0.153</td>
<td>1.40(\times)10(^{-2}) (7(\times)10(^{-3}))</td>
<td>1.9</td>
</tr>
<tr>
<td>0.546</td>
<td>3.15(\times)10(^{-2}) (2.7(\times)10(^{-3}))</td>
<td>4.3</td>
</tr>
<tr>
<td>1.53</td>
<td>3.21(\times)10(^{-2}) (6(\times)10(^{-4}))</td>
<td>4.4</td>
</tr>
<tr>
<td>2.86</td>
<td>3.21(\times)10(^{-2}) (6(\times)10(^{-4}))</td>
<td>4.4</td>
</tr>
<tr>
<td>5.31</td>
<td>3.98(\times)10(^{-2}) (4.6(\times)10(^{-3}))</td>
<td>5.5</td>
</tr>
<tr>
<td>14.4</td>
<td>3.81(\times)10(^{-5}) (6(\times)10(^{-4}))</td>
<td>5.2</td>
</tr>
<tr>
<td>21.9</td>
<td>4.23(\times)10(^{-2}) (2.6(\times)10(^{-4}))</td>
<td>5.8</td>
</tr>
<tr>
<td>27.0</td>
<td>3.94(\times)10(^{-2}) (2.9(\times)10(^{-4}))</td>
<td>5.4</td>
</tr>
</tbody>
</table>

\(^a\) 5 wt % Pd-0.5 wt % In (Pd-In) catalyst was applied with loading of 0.08 g/L, and pH was maintain at 5.00 by pH stat. Nitrate initial conc. was 2.35 mM for all experiments. \(^b\) Measured MO initial conc. by HPLC. \(^c\) Values in parentheses represent ±95% confidence intervals for observed rate constant (\(k_{\text{obs}}\)). \(^d\) Enhancement factor is \(k_{\text{obs}}\) in the presence of MO divided by that in the absence of MO.

### Table A.3 Nitrate Reduction Rates with Different Azo Dyes on Pd-In Catalyst\(^b\)

<table>
<thead>
<tr>
<th>Azo Dye</th>
<th>Azo Dye Initial Conc.(^b) ((\mu)M)</th>
<th>(k_{\text{obs}})(^c) (min(^{-1}))</th>
<th>(k_{\text{obs}}) Enhancement Factor(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/A(^d)</td>
<td>0</td>
<td>7.27(\times)10(^{-3}) (8.3(\times)10(^{-4}))</td>
<td>1.0</td>
</tr>
<tr>
<td>Methyl Orange</td>
<td>15.3</td>
<td>3.81(\times)10(^{-2}) (3.5(\times)10(^{-3}))</td>
<td>5.2</td>
</tr>
<tr>
<td>Methyl Red</td>
<td>15.3</td>
<td>2.67(\times)10(^{-2}) (6(\times)10(^{-4}))</td>
<td>3.7</td>
</tr>
<tr>
<td>Fast Yellow AB</td>
<td>15.3</td>
<td>2.35(\times)10(^{-2}) (2.7(\times)10(^{-3}))</td>
<td>3.2</td>
</tr>
<tr>
<td>Metanil Yellow</td>
<td>15.3</td>
<td>1.78(\times)10(^{-2}) (5(\times)10(^{-4}))</td>
<td>2.5</td>
</tr>
<tr>
<td>Acid Orange 7 or Orange II</td>
<td>15.3</td>
<td>1.18(\times)10(^{-2}) (4(\times)10(^{-4}))</td>
<td>1.6</td>
</tr>
<tr>
<td>Congo Red</td>
<td>7.65</td>
<td>1.08(\times)10(^{-2}) (5(\times)10(^{-4}))</td>
<td>1.5</td>
</tr>
<tr>
<td>Eriochrome Black T</td>
<td>15.3</td>
<td>6.40(\times)10(^{-3}) (9(\times)10(^{-5}))</td>
<td>0.88</td>
</tr>
<tr>
<td>Acid Red 27 or Amaranth</td>
<td>15.3</td>
<td>6.14(\times)10(^{-3}) (1.8(\times)10(^{-4}))</td>
<td>0.85</td>
</tr>
<tr>
<td>Acid Yellow 11</td>
<td>15.3</td>
<td>5.93(\times)10(^{-3}) (1.7(\times)10(^{-4}))</td>
<td>0.82</td>
</tr>
<tr>
<td>Acid Yellow 17</td>
<td>15.3</td>
<td>5.16(\times)10(^{-3}) (2.0(\times)10(^{-4}))</td>
<td>0.71</td>
</tr>
</tbody>
</table>

\(^a\) 5 wt % Pd-0.5 wt % In (Pd-In) catalyst was applied with loading of 0.08 g/L, and pH was maintain at 5.00 by pH stat. Nitrate initial conc. was 2.35 mM for all experiments. \(^b\) Values in parentheses represent ±95% confidence intervals for observed rate constant (\(k_{\text{obs}}\)). \(^c\) Enhancement factor is \(k_{\text{obs}}\) in the presence of azo dye divided by that in the absence of azo dye. \(^d\) N/A stands for control experiment without azo dye addition.
### Table A.4 Properties of Selected Azo Dyes

<table>
<thead>
<tr>
<th>Azo Dye</th>
<th>$k_{obs}$ Enhancement Factor on Nitrate Reduction(^ a )</th>
<th>Number of Azo Bonds per Molecule</th>
<th>Diffusion Coefficient $10^5 \times D^b$ (cm(^2)/s)</th>
<th>logK(_{ow})(^ c )</th>
<th>Average Molecular Charge(^ d )</th>
<th>Hydrogenation Energy(^ e ) (kJ/mol –N=N–)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Orange</td>
<td>5.3</td>
<td>1</td>
<td>5.65</td>
<td>2.1</td>
<td>-0.98</td>
<td>-86</td>
</tr>
<tr>
<td>Methyl Red</td>
<td>3.7</td>
<td>1</td>
<td>5.51</td>
<td>4.18</td>
<td>-0.85</td>
<td>-179</td>
</tr>
<tr>
<td>Fast Yellow AB</td>
<td>3.2</td>
<td>1</td>
<td>6.26</td>
<td>-0.86</td>
<td>-1.95</td>
<td>-69</td>
</tr>
<tr>
<td>Metanil Yellow</td>
<td>2.5</td>
<td>1</td>
<td>5.34</td>
<td>3.32</td>
<td>-1</td>
<td>-100</td>
</tr>
<tr>
<td>Acid Orange 7 or Orange II</td>
<td>1.6</td>
<td>1</td>
<td>5.81, 5.63</td>
<td>3, 3.69</td>
<td>-1</td>
<td>-106</td>
</tr>
<tr>
<td>Congo Red</td>
<td>1.5</td>
<td>2</td>
<td>3.95</td>
<td>6.09</td>
<td>-2</td>
<td>-86</td>
</tr>
<tr>
<td>Eriochrome Black T</td>
<td>0.88</td>
<td>1</td>
<td>5.08, 4.88, 4.86</td>
<td>3.91, 4.88, 5.23</td>
<td>-1.29</td>
<td>-127</td>
</tr>
<tr>
<td>Acid Red 27 or Amaranth</td>
<td>0.85</td>
<td>1</td>
<td>5.03, 4.9</td>
<td>0.6, 0.59</td>
<td>-3</td>
<td>-106</td>
</tr>
<tr>
<td>Acid Yellow 11</td>
<td>0.82</td>
<td>1</td>
<td>5.42</td>
<td>1</td>
<td>-1</td>
<td>-120</td>
</tr>
<tr>
<td>Acid Yellow 17</td>
<td>0.71</td>
<td>1</td>
<td>4.99</td>
<td>1.05</td>
<td>-2</td>
<td>-147</td>
</tr>
</tbody>
</table>

\(^ a \) Enhancement factor is the observed rate constant ($k_{obs}$) in the presence of azo dye divided by that in the absence of azo dye for the Pd-In catalyst. Details are included in Table S3.  
\(^ b,c,d \) Diffusion coefficient, logK\(_{ow}\), and average molecular charge were calculated online by using SPARC database (http://ibmlc2.chem.uga.edu/sparc/).  
\(^ b,c \) The reason why one azo dye has multiple diffusion coefficient and logK\(_{ow}\) values is because this azo dye has several different configurations simultaneously.  
\(^ d \) SPARC database was applied to estimate the pKa of azo dyes.  
Average molecular charge represents average charge per azo dye, and it was calculated based on pKa when pH=5.00.  
\(^ e \) Hydrogenation energy (HE) was calculated at the B3LYP/6-311G** level using the Gaussian code, based on first-principles density functional theory (DFT) methods.  
Details are included in hydrogenation energy calculation part of Supporting Information.
### Table A.5 Key Features of Azo Molecule Hydrogenation Calculations

<table>
<thead>
<tr>
<th>Unreduced Azo Molecule</th>
<th>Reduced Hydrazo Form</th>
<th>Hydrogenation Energy$^b$ (kJ/mol –N=N–)</th>
</tr>
</thead>
<tbody>
<tr>
<td>azobenzene parent</td>
<td><img src="image1" alt="Azobenzene parent" /></td>
<td>-103</td>
</tr>
<tr>
<td>1.25Å</td>
<td><img src="image2" alt="Hydrazo Form" /></td>
<td></td>
</tr>
<tr>
<td>ortho substituted nitro variant</td>
<td><img src="image3" alt="ortho substituted nitro variant" /></td>
<td>-180</td>
</tr>
<tr>
<td>Hydrogen bond</td>
<td>1.87Å, 117°, 120°, 119° Planar across hydrazo group</td>
<td></td>
</tr>
<tr>
<td>para substituted amine variant</td>
<td><img src="image4" alt="para substituted amine variant" /></td>
<td>-75</td>
</tr>
<tr>
<td>methyl red (MR)</td>
<td><img src="image5" alt="methyl red (MR)" /></td>
<td>-179</td>
</tr>
</tbody>
</table>

$^a$In the ball-stick model, balls and sticks represent atoms and covalent bonds, respectively. Gray, white, blue, and red balls represent carbon, hydrogen, nitrogen, and oxygen atoms, respectively.

$^b$Hydrogenation energy (HE) was calculated at the B3LYP/6-311G** level using the Gaussian code, based on first-principles density functional theory (DFT) methods. Details are included in hydrogenation energy calculation part of Supporting Information.
Table A.6 Predicted Values of Parameters in Kinetic Model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>294 K</td>
</tr>
<tr>
<td>[azo]₀₀</td>
<td>0.153 μMᵃ</td>
</tr>
<tr>
<td>[H₂]₀</td>
<td>0.773 mMᵇ</td>
</tr>
<tr>
<td>[NO₃]⁻₀</td>
<td>2.35 mM</td>
</tr>
<tr>
<td>kₗ</td>
<td>7.27×10⁻³ min⁻¹</td>
</tr>
<tr>
<td>α₁</td>
<td>0.0697</td>
</tr>
<tr>
<td>β₁</td>
<td>50.0 kJ/mol</td>
</tr>
<tr>
<td>ν₁</td>
<td>4.99×10⁻¹³ L/(mol min)</td>
</tr>
<tr>
<td>α₂</td>
<td>-0.142</td>
</tr>
<tr>
<td>β₂</td>
<td>50.0 kJ/mol</td>
</tr>
<tr>
<td>ν₂</td>
<td>2.79×10⁻¹⁶ L/(mol min)</td>
</tr>
</tbody>
</table>

ᵃ We assume that 1% of azo dyes are sorbed to the catalyst, and the sorbed azo dyes shuttle hydrogen atoms via the azo/hydrazo group redox couple. ᵇ Saturated H₂ concentration in water (21±0.3 °C and 1 atm).

A.7 References

APPENDIX B: SUPPORTING INFORMATION FOR CHAPTER 3

Detailed procedures of catalyst preparation and 2D and 3D TEM analysis are included in Appendix B. 3D TEM analysis of a CNF segment by sample tilting and its corresponding 3D reconstruction are also included in Appendix B as images.

B.1 Experimental Methods

Reagents. All chemicals were reagent grade and were purchased from Sigma-Aldrich (Pd(NO$_3$)$_2$·2H$_2$O ~40% as Pd, nitric acid 70%, acetone ≥99%, m-xylene ≥99%, ethanol ≥99%). They were used without further purification. Tanks of H$_2$ (99.999%) and N$_2$ (99.999%) were purchased from Matheson Tri-Gas (Joliet, IL). All solutions were prepared in nanopure water (18 MΩ cm), purified from deionized water in Barnstead NANOpure system.

Sample Preparation. A batch of hollow CNFs (PR-24-XT-HHT, 20-70 nm inner diameter, 40-110 nm outer diameter, several to a dozen microns in length) was purchased from Pyrograf Products, Inc., and a thorough study of its characterization was performed by Tessonnier et al. (1) Firstly it was functionalized with hydrophilic moieties by adapting the method suggested by Pan et al. (2) CNFs were refluxed in concentrated nitric acid (68-70 wt %) at 140 °C for 14 h, and next the oxidized CNFs were filtered, rinsed with nanopure water until the filtrate reached neutral pH, and dried at 120 °C overnight. This procedure has also been shown to remove metallic impurities (3). CNF supported 5 wt % Pd catalysts were then prepared with proportionally both inside and outside loading, primarily inside loading, and primarily outside
loading, following methods described by Ersen et al. (4) and Tessonnier et al. (5) and are referred to as 5Pd/CNFs, 5Pd/CNFs-in, and 5Pd/CNFs-out. The pore volume of CNFs was determined to be 6 mL/g initially. Pd was loaded proportionally both inside and outside CNFs using incipient wetness with water as the solvent. Pd was loaded primarily inside CNFs by substituting acetone for water in wet impregnation. Pre-weighed Pd(NO$_3$)$_2$·2H$_2$O was dissolved in 4 mL acetone/nanopure water (1:1, by vol.) mixture, and mixed thoroughly with 1 g CNFs. The paste was maintained in an ice bath during mixing to slow acetone evaporation. Acetone with Pd was drawn inside CNFs by capillary action because of its low surface tension and viscosity. Next, 3 mL of nanopure water was added to rinse the exterior surfaces of CNFs. Pd was loaded primarily outside CNFs by first filling and protecting CNF interior spaces with m-xylene, and then loading Pd on external surfaces with water via wet impregnation. The m-xylene was used because of its low surface tension, low viscosity, and immiscibility with water.

Approximately 1 g of CNFs were wetted by 6 mL m-xylene thoroughly, then Pd(NO$_3$)$_2$·2H$_2$O was dissolved in 4 mL nanopure water, and the solution was mixed with CNF m-xylene paste. All catalyst pastes were dried at 50 °C overnight, calcined at 400 °C in N$_2$ gas flow for 3 h, and reduced at 400 °C in H$_2$ gas flow for 3 h before use.

Sample Characterization. Pd nanoparticle size and localization were determined using transmission electron microscopy (TEM) with ImageJ software. TEM analysis was carried out on a JEOL 2100 Cryo transmission electron microscope working at 200 kV accelerating voltage with a point resolution of 0.27 nm. For TEM observation, the samples were dispersed in ethanol for 10 min by ultrasonication (Branson Ultrasonics Corp.), and several drops were deposited onto an ultrathin holey carbon membrane copper grid (Ted Pella, Inc.). About 3,000 Pd
nanoparticles from 40 individual CNFs of each sample were imaged and analyzed for size and localization.

The scanning transmission electron microscopy (STEM) with high angle annular dark field (HAADF) electron tomography data set was acquired using a single axis tilting of the specimen at ± 70° range with an interval of 1°. The experiment was carried out using a Titan 80-300 operated at 300 kV, fitted with a probe forming lens spherical aberration corrector, which gives a resolution of ~ 0.1 nm for the STEM imaging. The reconstruction was performed using a weighted back projection method where a weighting filter was employed to balance the frequency distribution.
B.2 Supporting Figures

Figure B.1 3D reconstruction of the carbon nanofiber volume with Pd loaded inside and outside (sample 5Pd/CNFs). The carbon nanofiber is represented by dark red, and the Pd nanoparticles are represented by green.
Figure B.2 3D iso-surface visualization of Pd nanoparticles (represented by green) perpendicular to the tube axis (parallel to tilt axis) of 5Pd/CNFs. Note: elongation of Pd nanoparticles is a TEM tomography artifact due to the missing wedge.

B.3 References


APPENDIX C: SUPPORTING INFORMATION FOR CHAPTER 4

Appendix C includes physical, chemical, and morphological characterizations of Pd catalysts on activated carbon (AC), carbon nanofiber (CNF), and alumina supports, as well as the details of experimental methodology and data analysis.

C.1 Materials and Methods

C.1.1 Catalyst Preparation and Characterization

A batch of vapor-grown CNFs (PR-24-XT-HHT, 20-70 nm inner diameter, 40-110 nm outer diameter, several to a dozen microns in length) was purchased from Pyrograf Products, Inc., and was functionalized with hydrophilic groups using the method described by Pan et al. (1) Briefly, CNFs were refluxed in concentrated nitric acid (68-70 wt %) at 140 °C for 14 h, and then the oxidized CNFs were filtered, rinsed with nanopure water until the filtrate reached neutral pH, and dried at 120 °C in the oven overnight. This procedure also removes metallic impurities (2). CNF supported 5 wt % Pd catalysts were prepared with proportionally both inside and outside loading, primarily inside loading, and primarily outside loading, following methods suggested by Ersen et al. (3) and Tessonnier et al. (4), and are referred to as InOut, In-M, and Out, respectively. The pore volume of CNFs was determined to be 6 mL/g, and Pd nanoparticles were loaded proportionally both inside and outside CNFs by incipient wetness using water as the solvent.
Pd nanoparticles were loaded primarily inside CNFs by wet impregnation using acetone as the solvent. Pd(NO$_3$)$_2$·2H$_2$O, as the Pd precursor, was dissolved in 4 mL of an acetone/nanopure water (1:1, by vol.) mixture, and mixed thoroughly with 1 g of CNFs in an ice bath. The ice bath was used to slow acetone evaporation. The acetone/water mixture with Pd was drawn inside CNFs by capillary force because of its low viscosity and surface tension. Next, 3 mL of nanopure water was added to wash the Pd precursor off the exterior surfaces of CNFs.

Pd nanoparticles were loaded primarily outside CNFs by first occupying and protecting CNF inner spaces with m-xylene, and then loading Pd nanoparticles on outside surfaces with water by wet impregnation. The m-xylene was used because of its low viscosity, low surface tension, and immiscibility with water. 1 g of CNFs were impregnated with 6 mL m-xylene thoroughly, then Pd(NO$_3$)$_2$·2H$_2$O was dissolved in 4 mL nanopure water, and the Pd precursor solution was mixed with the CNF m-xylene paste. All catalyst pastes were dried at 50 °C overnight, calcined at 400 °C in N$_2$ gas flow for 3 h, and reduced at 400 °C in H$_2$ gas flow for 3 h before use.

The size distribution of InOut aggregates at different sonication times was measured using a laser scattering particle size analyzer (Horiba Instruments Incorporated, LA-300). Approximately 2 mg of InOut was sonicated in 40 mL nanopure water for different times from 0.25 to 12 minutes, and then the suspension was analyzed immediately. An environmental scanning electron microscope (ESEM, FEI company, Philips XL30 ESEM-FEG) was used to characterize the size and morphology of InOut aggregates after sonication for 0.25 min and 12 min. The ESEM was operated at 20.0 kV with an ultimate resolution of 2 nm. An aliquot of the InOut aggregate water
suspension was loaded on the Peltier stage, and the chamber of ESEM was evacuated to 3.5 torr at 4 °C. The corresponding relative humidity was 57%.

Activated carbon (AC) and alumina were used as supports for Pd catalysts. A 5 wt % Pd on AC and a 5 wt % Pd on alumina, both purchased from Sigma-Aldrich, were wet sieved to obtain particles less than 38 µm in diameter, and hereafter referred to as 5Pd/AC and 5Pd/Alumina, respectively.

Pd percentages of catalysts were analyzed by PerkinElmer SCIEX - ELAN DRCe inductively coupled plasma mass spectrometer (ICP-MS). The Brunauer-Emmett-Teller (BET) surface area and micropore area of 5Pd/AC, InOut, and 5Pd/Alumina were determined experimentally by standard nitrogen adsorption (77 K) on a Micromeritics ASAP 2010 surface area analyzer. The zeta potential of supported catalysts was determined using a Zetasizer Nano ZS90 (Malvern Instruments, UK) to indicate the surface charge under experimental conditions. Pd catalysts were suspended in a 2 mM NaNO₂ solution, and pH was adjusted to 5. The zeta potential measurements were conducted at room temperature (21 °C), and were repeated 9 to 12 times for each sample. Morphology of CNF supported Pd catalysts were characterized by high resolution JEOL 2100 Cryo transmission electron microscope (TEM) operated at 200 kV with a point resolution of 0.27 nm. For TEM observation, the samples were dispersed in ethanol for 10 min by ultrasonication (Branson Ultrasonics Corp.), and several drops were deposited onto an ultrathin holey carbon membrane copper grid (Ted Pella, Inc.). About 1,000-3,000 Pd nanoparticles from 20-40 individual CNF segments of each sample were imaged and analyzed for size and localization with ImageJ. Morphology of AC and alumina supported Pd-only
catalysts were characterized by high resolution JEOL 2010F transmission electron microscope (TEM) with high angle annular dark field scanning mode (HAADF-STEM) operated at 200 kV, and the HAADF resolution is 0.18 nm. The samples were also dispersed in ethanol for 10 min by ultrasonication (Branson Ultrasonics Corp.), and several drops were deposited onto an ultrathin holey carbon membrane copper grid (Ted Pella, Inc.). At least 300 Pd nanoparticles from at least 10 locations were imaged and analyzed for size with ImageJ.

X-ray powder diffraction (XRD) was also used to characterize Pd nanoparticle size. Powder XRD data were collected on a Bruker General Area Detector Diffraction System (GADDS) equipped with a four-circle diffractometer and HiStar multiwire area detector. A Bruker M18XHF$^{22}$ rotating anode generator operating at 50 kV and 40 mA supplied the graphite monochromated incident beam. The sample was loaded without modification into a 0.7mm special glass capillary and exposed for 900 seconds for each of 5 frames. Scatter from the glass capillary was removed by coincidence correction before merging the five frames for integration from 30-100 degrees 2θ. A background pattern for the plain CNFs was collected and removed from those samples that had this substrate. The final spectrum was truncated to remove boundary anomalies, normalized to facilitate pattern matching, and the baseline was corrected using a fourth or fifth order Chebyshev polynomial. Full pattern refinement was performed in TOPAS (Bruker AXS, Inc., version 3) using a Pd CIF file (5), and the crystallite size was estimated based on the integral breadth, assuming the intermediate crystallite size broadening modeled by a Voigt function (6).
CO chemisorption was performed using a static volumetric technique (Micromeritics ASAP 2020-Chemi), and it is used to estimate Pd dispersion and nanoparticle size. The thermal treatment procedure was performed as follows: (1) the sample was dried in the oven at 120 °C overnight to remove the moisture; (2) the sample was loaded inside the U-tube and heated in He at 110 °C for 30 min (with a heating rate 10 °C min\(^{-1}\)); (3) the sample was reduced in H\(_2\) at 120 °C for 3 h, and then evacuated at the same temperature for 2 h; (4) finally the sample was cooled down to 35 °C in 30 min and CO chemisorption analysis was performed. The chemisorption stoichiometry, expressed as the Pd/CO molar ratio, was assumed to be 2 (7-10).

Pd dispersion (D) is calculated by:

\[
D = \frac{PV_{CO} \times 2 \times \frac{6}{5}}{Pd\text{ wt}\%} = \frac{12PV_{CO}M_{pd}}{5RT \times Pd\text{ wt}\%};
\]

(C.1)

in which P and T are standard pressure (100 kPa) and standard temperature (273.15 K), \(V_{CO}\) is the adsorbed CO per gram catalyst under STP, R is the gas constant (8.31 J mol\(^{-1}\) K\(^{-1}\)), the factor 6/5 is a reduction factor identified from the literature (11) that accounts for the fraction of surface Pd atoms in direct contact with supports not measured by CO chemisorption, Pd wt % is the Pd weight percentage, and \(M_{pd}\) is the atomic weight of Pd (106.4 g mol\(^{-1}\)). Pd nanoparticle size (d as diameter) is estimated based on dispersion assuming cuboctahedral shape, and it is calculated by:

\[
D = \frac{10v^2 + 2}{10\frac{v^3}{3} + 5v^2 + 11\frac{v}{3} + 1};
\]

(C.2)

and \(d = (2v + 1)d_{metal-metal}\);

(C.3)

in which v is the average order of cuboctahedral nanoparticles, and \(d_{metal-metal}\) is the distance between metal atoms (0.275 nm for Pd (11)).
C.1.2 Experimental Reactor System

The experimental setup for batch reduction experiments follows Shuai et al. (12) Briefly, the reduction experiments were performed in a 500 mL five-neck reaction flask at 21±1 °C with continuous H₂ flow (135 mL/min) and mixing at ca. 500 rpm. Different mixing speeds of 300, 400, 450, and 500 rpm were evaluated, and hydrogen addition rates of 6.5, 24.5, 50, 95, and 135 mL/min were also evaluated. Nitrite reduction rates increased by 49.2% from 300 to 400 rpm, and increased by 27.6% from 400 to 450 rpm, but did not significantly change with the increase from 450 to 500 rpm (Figure C.1a). Similarly, 98.2% and 13.5% enhancement was observed for nitrite reduction rates from 6.5 to 24.5 to 50 mL/min, but further increase to 95 and to 135 mL/min leads to a marginal increase of reduction rate (Figure C.1b). Hence, 500 rpm and 135 mL/min were used in this study. Catalyst loading experiments indicated that pseudo-first-order rate constant for nitrite reduction was linear for catalyst loadings between 0 and 0.1 g/L (Figure C.1c), and 0.05 g/L catalyst loading was selected in this study. It indicates that excess hydrogen for reaction was provided and aqueous/solid mass transfer limitations were eliminated.

The reaction flask was filled with 400 mL of nanopure water, and then amended with 20 mg catalyst. To disperse the catalysts in water, catalysts were sonicated for 12 min with an ultrasonic cleaner (Cole-Parmer) before reaction. The reactor was sealed with silicon rubber stoppers, and pre-sparged with H₂ for 20 min at 135 mL/min to reduce the oxidized catalyst surface and remove dissolved oxygen. When the reaction began, 2 mM nitrite was amended to the reaction solution at time zero. The pH of solution was maintained at 5 by adding small amounts of HCl.
using a pH-stat (TIM 856, Radiometer Analytical). During reaction, 2-3 mL aqueous samples were taken at regular time intervals, filtered using a 0.45 µm PTFE syringe filter (Cole-Parmer), and stored in a refrigerator at 4 °C before analysis. Samples for ammonia analysis were taken until ammonia production reached a plateau (i.e., final ammonia production). Control experiments showed ammonia adsorption onto all supports (i.e., AC, alumina, and CNFs) was negligible, and ammonia production reached steady state at least 26 h, 3 h, and 24 h after the reaction started for AC, alumina, and CNF supported catalysts, respectively.

A control test was also performed with the InOut catalyst to evaluate if air trapped in CNFs before sonication limited access to Pd and led to reduced activity and selectivity. The test was performed identically to the batch methods described above, except that the flask with CNFs was first evacuated before being filled with water to eliminate trapped air. The corresponding nitrite reduction rate constant was 0.0061 min⁻¹, which is only 7.1% of the nitrite reduction rate constant after 12 min sonication (i.e., 0.086 min⁻¹). This indicates that air trapped inside CNFs is not responsible for the reduced activity and selectivity.

Nitrogen mass balance experiment was carried out in a sealed serum bottle (60 mL) at room temperate (21±1 °C). Approximately 10 mg of In-S was dispersed in a 40 mL phosphate buffer (10 mM, pH=7) by ultrasonication for 12 min, and then the catalyst suspension was sparged with hydrogen for 30 min (135 mL/min) to fully reduce the oxidized catalyst surface and remove dissolved oxygen in solution. When the reaction began, stable isotope ¹⁵N labeled nitrite (1mM) was amended at time zero. The reaction solution was mixed by a magnetic stirrer at ca. 500 rpm, and the gas samples and liquid samples were taken at different time intervals. Gas samples were
analyzed by gas chromatography-mass spectroscopy (GC-MS) for nitric oxide, nitrous oxide, and dinitrogen. A Varian 4000 GC/MS equipped with a CP-Molsieve 5Å column was used to separate the gas products. The oven was maintained at 165 °C, and the flow rate of the helium carrier gas was 1 mL/min. Charge-to-mass ratios of 31, 46, and 30 were selected to represent and analyze ionized nitric oxide, nitrous oxide, and dinitrogen, respectively; nitric oxide was not detected for all gas samples. Liquid samples were filtered using a 0.1 µm PTFE syringe filter, and then analyzed by ion chromatography (IC) and the Hach salicylate method for nitrite and ammonia, respectively. Details of IC and the Hach salicylate method are described in Chapter 4.
C.2 Supporting Figures

Figure C.1 Nitrite reduction rate constants vs. (a) mixing speeds, (b) hydrogen flow rates, and (c) catalyst loadings (linear regression line shown). In-S was used as the catalyst, and the red circles indicate the values chosen in this study. Error bars represent 95% confidence intervals, and orange dash lines with gray area represent 95% confidence intervals of linear regression.
Figure C.2 Nitrogen mass balance in nitrite reduction with In-S. Stable isotope $^{15}$N labeled nitrite (1 mM) was used as the probe contaminant and nitrite, nitrous oxide, dinitrogen, and ammonia was measured at the entire time course. The theoretical nitrogen loading was 40 µmol, and it is indicated in the figure.
Figure C.3 Scanning transmission electron microscopic (STEM) images of (a) 5Pd/AC and (b) 5Pd/Alumina; transmission electron microscopic (TEM) images of (c) In-S, (d) In-M, (e) In-L, (f) InOut, and (g) Out. The bright dots in STEM images and the dark dots in TEM images represent Pd nanoparticles.
Figure C.3 (cont.)
Figure C.3 (cont.)
Figure C.4 Photos of InOut aggregates after 0.25 min and 12 min sonication, respectively.
Figure C.5 XRD diffractograms of Pd CNF catalysts.
C.3 Supporting Tables

Table C.1 Properties of Pd catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd wt % (ICP-MS)</th>
<th>Pd nanoparticle size (nm)</th>
<th>Pd nanoparticle size (nm)</th>
<th>Pd nanoparticle size (nm)</th>
<th>Pd nanoparticle internal loading percentage based on number (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-S</td>
<td>4.1</td>
<td>1.4±0.7</td>
<td>2.8±0.2</td>
<td>N/A</td>
<td>72.2±20.2</td>
</tr>
<tr>
<td>In-M</td>
<td>4.8</td>
<td>3.1±1.4</td>
<td>3.7±0.1</td>
<td>N/A</td>
<td>71.4±19.7</td>
</tr>
<tr>
<td>In-L</td>
<td>5.1</td>
<td>9.6±3.5</td>
<td>12.4±0.3</td>
<td>N/A</td>
<td>71.4±19.7</td>
</tr>
<tr>
<td>InOut</td>
<td>4.7</td>
<td>4.3±2.2</td>
<td>4.8±0.2</td>
<td>7.2</td>
<td>47.2±22.8</td>
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<tr>
<td>Out</td>
<td>4.7</td>
<td>2.5±1.3</td>
<td>3.9±0.3</td>
<td>N/A</td>
<td>22.7±17.8</td>
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<tr>
<td>5Pd/AC</td>
<td>5.4</td>
<td>2.0±0.4</td>
<td>N/A</td>
<td>5.1</td>
<td>N/A</td>
</tr>
<tr>
<td>5Pd/Alumina</td>
<td>5.6</td>
<td>3.1±0.8</td>
<td>N/A</td>
<td>3.1</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table C.1 (cont.)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET area (m² g⁻¹)</th>
<th>Micropore area (m² g⁻¹)</th>
<th>Micropore area percentage (%)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Zeta potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-S</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>In-M</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>In-L</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>InOut</td>
<td>69.9</td>
<td>5.0</td>
<td>7.1</td>
<td>0.14</td>
<td>-43.0±2.4</td>
</tr>
<tr>
<td>Out</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>5Pd/AC</td>
<td>895.1</td>
<td>523.5</td>
<td>58.5</td>
<td>0.75</td>
<td>-35.7±1.1</td>
</tr>
<tr>
<td>5Pd/Alumina</td>
<td>101.8</td>
<td>3.1</td>
<td>3.1</td>
<td>0.21</td>
<td>31.2±0.4</td>
</tr>
</tbody>
</table>

a Micropore area was approximated by the t-plot method. b Micropore area percentage is the ratio between micropore area and BET area. c Yun Shen in Department of Civil and Environmental Engineering, University of Illinois at Urbana-Champaign performed the analysis.
C.4 References


APPENDIX D: SUPPORTING INFORMATION FOR CHAPTER 5

Appendix D contains synthesis and characterization of Pd nanoparticle catalysts, control experiments for nitrite reduction, analytical methods for reactants and products, relationships between total surface sites or specific sites and nanoparticle size, TEM images of Pd nanoparticle catalysts before and after reduction, and Matlab codes and solved parameter values.

D.1 Methods

D.1.1 Synthesis of Pd Nanoparticle Catalysts

For Pd cube synthesis, 57 mg of Na$_2$PdCl$_4$ was thoroughly dissolved in 3 mL of nanopure water by extensive mixing for at least 1 h, meanwhile 105 mg of PVP, 300 mg of KBr, and 60 mg of ascorbic acid were dissolved in 8 mL of nanopure water. The PVP-KBr-ascorbic acid solution was transferred to a reaction vial, stirred at 380 rpm, and pre-heated in an oil bath at 80 °C for 5 min, and then Na$_2$PdCl$_4$ solution was amended quickly. The reaction solution was kept stirring at 380 rpm and maintained at 80 °C in air for 3 h, and the sample was collected after naturally cooled down. An excess amount of acetone was used (at least 22 mL, acetone/reaction solution≥2 by vol) to precipitate the nanoparticles, and next nanoparticles were separated by centrifugation and washed by nanopure water for several times to remove excess PVP and other reactants.

For Pd rod synthesis, 5 mL of ethylene glycol was pre-heated in a three-neck flask (equipped with a reflux condenser and a Teflon-coated stir bar) at 130 °C for at least 1 h. Meanwhile, 64.8
mg of Na₂PdCl₄ and 800 mg of KBr were dissolved in 4 mL of nanopure water, and 122 mg of PVP was dissolved 4 mL of ethylene glycol, respectively. 3 mL of each Na₂PdCl₄-KBr solution and PVP solution was injected simultaneously by a syringe pump into the flask at a flow rate of 45 mL h⁻¹ (in 4 min). The reaction solution was stirred at 380 rpm and maintained at 130 °C in air for 3 h, and the sample was collected after naturally cooled down. An excess amount of acetone was used (at least 22 mL, acetone/reaction solution ≥ 2 by vol) to precipitate the nanoparticles, and next nanoparticles were separated by centrifugation and washed by nanopure water for several times to remove excess PVP and other reactants.

For small Pd cuboctahedron synthesis, 57 mg of Na₂PdCl₄ was thoroughly dissolved in 3 mL of nanopure water by extensive mixing for at least 1 h, and 105 mg of PVP, 60 mg of citric acid, and 60 mg of ascorbic acid were dissolved in 8 mL of nanopure water, respectively. The PVP-citric acid-ascorbic acid solution was transferred to a three-neck flask (equipped with a reflux condenser and a Teflon-coated stir bar), and pre-heated in an oil bath at 120 °C for 5 min, and then Na₂PdCl₄ solution was amended in 30 s. The reaction solution was stirred at 380 rpm and maintained at 120 °C in air for 3 h, and the sample was collected after naturally cooled down. An excess amount of acetone was used (at least 22 mL, acetone/reaction solution ≥ 2 by vol) to precipitate the nanoparticles, and next nanoparticles were separated by centrifugation and washed by nanopure water for several times to remove excess PVP and other reactants.

For large Pd cuboctahedron synthesis, 5 mL of ethylene glycol was pre-heated in a three-neck flask (equipped with a reflux condenser and a Teflon-coated stir bar) at 110 °C for at least 1 h. Meanwhile, 184.5 mg of Na₂PdCl₄ was thoroughly dissolved in 4 mL of ethylene glycol by
extensive mixing for at least 1 h, and 106.7 mg of PVP was dissolved in 4 mL of ethylene glycol, respectively. 3 mL of each Na₂PdCl₄ solution and PVP solution was injected simultaneously by a syringe pump into the reaction vial at a flow rate of 45 mL h⁻¹ (in 4 min). The reaction solution was stirred at 380 rpm and maintained at 110 °C in air for 3 h, and the sample was collected after naturally cooled down. An excess amount of acetone was used (at least 22 mL, acetone/reaction solution ≥ 2 by vol) to precipitate the nanoparticles, and next nanoparticles were separated by centrifugation and washed by nanopure water for several times to remove excess PVP and other reactants.

For small Pd octahedron synthesis, 57 mg of Na₂PdCl₄ was thoroughly dissolved in 3 mL of nanopure water by extensive mixing for at least 1 h, and 105 mg of PVP and 180 mg of citric acid were dissolved in a mixture containing 5 mL of nanopure water and 3 mL of ethanol, respectively. The PVP-citric acid solution was transferred to a three-neck flask (equipped with a reflux condenser and a Teflon-coated stir bar), and pre-heated in an oil bath at 80 °C for 5 min, and then Na₂PdCl₄ solution was amended in 30 s. The reaction solution was stirred at 380 rpm and maintained at 80 °C in air for 3 h, and the sample was collected after naturally cooled down. An excess amount of acetone was used (at least 22 mL, acetone/reaction solution ≥ 2 by vol) to precipitate the nanoparticles, and next nanoparticles were separated by centrifugation and washed by nanopure water for several times to remove excess PVP and other reactants.

For large Pd octahedron synthesis, 5 mL of ethylene glycol was pre-heated in a reaction vial at 110 °C for at least 1 h with stirring at 380 rpm. Meanwhile, 184.5 mg of Na₂PdCl₄ was thoroughly dissolved in 4 mL of ethylene glycol by extensive mixing for at least 1 h, and 106.7
mg of PVP was dissolved in 4 mL of ethylene glycol, respectively. 3 mL of each Na₂PdCl₄ solution and PVP solution was injected simultaneously by a syringe pump into the reaction vial at a flow rate of 5 mL h⁻¹ (in 36 min). The reaction solution was stirred at 380 rpm and maintained at 110 °C in air for 3 h, and the sample was collected after naturally cooled down. An excess amount of acetone was used (at least 22 mL, acetone/reaction solution≥2 by vol) to precipitate the nanoparticles, and next nanoparticles were separated by centrifugation and washed by nanopure water for several times to remove excess PVP and other reactants.

For all Pd nanoparticle catalyst synthesis, great attention should be paid to cross-contamination. Spatulas, vials, flasks, and any other containers should be clean. Single-used spatulas and vials are recommended, and glass flasks and Teflon-coated stir bars should be cleaned by aqua regia to remove attached Pd nanoparticles. Any metal lined or coated caps or containers should be avoided, because that reduction of palladate by metals may interfere the final shapes and sizes of nanoparticles.

**D.1.2 Characterization of Pd Nanoparticle Catalysts**

The shape and size of Pd nanoparticle catalyst were characterized by transmission electron microscopy (TEM), using high resolution JEOL 2100 Cryo transmission electron microscope (TEM) operated at 200 kV with a point resolution of 0.27 nm. For TEM observation, the several drops of samples were deposited onto an ultrathin holey carbon membrane copper grid (Ted Pella, Inc.). About 300 Pd nanoparticles of each sample were imaged and analyzed by ImageJ. The geometric schematics of Pd cubes, rods, cuboctahedra, and octahedra are shown in Figure
5.1. Edge lengths (L, nm) of cubes (i.e., cub) and octahedra (i.e., oct) and diameters (d, nm) of cuboctahedra (i.e., cot) were measured, and the number of Pd atoms on edge (m) was calculated based on geometric schematics (1):

\[ m_{\text{cub}} = \frac{L - d_{\text{metal-metal}}}{\sqrt{2}d_{\text{metal-metal}}} + 1; \]  

(D.1)

\[ m_{\text{oct}} = \frac{L}{d_{\text{metal-metal}}}; \]  

(D.2)

\[ m_{\text{cot}} = \frac{d}{\sqrt{10}d_{\text{metal-metal}}}; \]  

(D.3)

where \( d_{\text{metal-metal}} \) is the distance between face-centered cubic metal atoms (0.275 nm for Pd (2)). Dispersion (D, i.e., number fraction of surface to total atoms), surface fraction of specific terrace sites (\( F^{(100)} \) for (100) terrace), surface fraction of low coordination sites (\( F_{\text{low}} \), i.e., edge and vertex sites), and surface fraction of terrace sites (\( F_{\text{terrace}} \), i.e., high coordination sites) were calculated, and they can be expressed as:

\[ D_{\text{cub}} = \frac{N_{S}}{N_{T}} = \frac{12m_{\text{cub}}^{2} - 24m_{\text{cub}} + 14}{4m_{\text{cub}}^{2} - 6m_{\text{cub}}^{2} + 3m_{\text{cub}}}; \]  

(D.4)

\[ D_{\text{oct}} = \frac{N_{S}}{N_{T}} = \frac{12m_{\text{oct}}^{2} - 24m_{\text{oct}} + 18}{2m_{\text{oct}}^{2} + m_{\text{oct}}}; \]  

(D.5)

\[ D_{\text{cot}} = \frac{N_{S}}{N_{T}} = \frac{30m_{\text{cot}}^{2} - 60m_{\text{cot}} + 32}{16m_{\text{cot}}^{2} - 33m_{\text{cot}}^{2} + 24m_{\text{cot}} - 6}; \]  

(D.6)

\[ F_{\text{cub}}^{(100)} = \frac{N_{S}^{(100)}}{N_{S}} = \frac{6m_{\text{cub}}^{2} - 18m_{\text{cub}} + 15}{6m_{\text{cub}}^{2} - 12m_{\text{cub}} + 7}; \]  

(D.7)

\[ F_{\text{oct}}^{(100)} = \frac{N_{S}^{(100)}}{N_{S}} = 0; \]  

(D.8)

\[ F_{\text{cot}}^{(100)} = \frac{N_{S}^{(100)}}{N_{S}} = \frac{3m_{\text{cot}}^{2} - 12m_{\text{cot}} + 12}{15m_{\text{cot}}^{2} - 30m_{\text{cot}} + 16}; \]  

(D.9)

\[ F_{\text{low}}^{\text{cub}} = \frac{N_{E} + N_{V}}{N_{S}} = \frac{6m_{\text{cub}} - 8}{6m_{\text{cub}}^{2} - 12m_{\text{cub}} + 7}; \]  

(D.10)

\[ F_{\text{low}}^{\text{oct}} = \frac{N_{E} + N_{V}}{N_{S}} = \frac{6m_{\text{oct}} - 9}{2m_{\text{oct}}^{2} - 4m_{\text{oct}} + 3}; \]  

(D.11)
where \( N_S, N_T, N_{(100)}, N_E, \) and \( N_V \) represent the number of surface atoms, total atoms, (100) terrace atoms, edge atoms, and vertex atoms on Pd nanoparticle catalysts. Pd rods are octagonal rods majorly encompassed with (100) and (110) facets, containing a small fraction of truncated sides with (110) and (111) facets near both ends (3). For convenient estimation of \( D, F_{(100)}, F_{low}, \) and \( F_{terrace} \) for rods, the geometry of rods was simplified to regular octagonal rods. The sides contain four (100) and four (110) facets, and the ends are (100) facets (as shown in Figure 5.1b). The edge lengths for side and end were measured as \( k \) (nm) and \( h \) (nm), respectively. Next, the total edge length (i.e., \( TEL, \text{nm} \)), total (100) or (110) terrace area (i.e., \( TA, \text{nm}^2 \)), and volume (\( V, \text{nm}^3 \)) of rods are calculated by:

\[
TEL = 8k + \frac{16h}{\sqrt{2+1}}; \tag{D.16}
\]

\[
TA_{(100)} = \frac{4kh+h^2}{\sqrt{2+1}}; \tag{D.17}
\]

\[
TA_{(110)} = \frac{4kh}{\sqrt{2+1}}; \tag{D.18}
\]

\[
V = \frac{2kh^2}{\sqrt{2+1}}. \tag{D.19}
\]

Pd linear density for edges (i.e., \( LD \)), Pd planar density for (100) and (110) terraces (i.e., \( PLD \)), and Pd packing density (i.e., \( PAD \)) describe the number of Pd atoms per length on the edges, per area on the sides, and per volume, respectively. They are expressed by:
\[ LD = \frac{1}{\sqrt{2}d_{\text{metal-metal}}}; \]  
\[ PLD_{(100)} = \frac{1}{d_{\text{metal-metal}}^2}; \]  
\[ PLD_{(110)} = \frac{1}{\sqrt{2}d_{\text{metal-metal}}^2}; \]  
\[ PAD = \frac{\sqrt{\pi}}{d_{\text{metal-metal}}^3}. \]  
(D.20)  
(D.21)  
(D.22)  
(D.23)

\[ D_{\text{rod}} = \frac{\frac{T\alpha_{(100)}PLD_{(100)} + T\alpha_{(110)}PLD_{(110)} + TEL \times LD}{V \times PAD}}{\sqrt{2}kd_{\text{metal-metal}} + (2\sqrt{2} - 2)d_{\text{metal-metal}} + 2\sqrt{2}kd_{\text{metal-metal}} + (8 - 4\sqrt{2})h_{\text{metal-metal}}^2}. \]  
(D.24)

\[ F_{\text{rod}}^{(100)} = \frac{T\alpha_{(100)}PLD_{(100)}}{T\alpha_{(100)}PLD_{(100)} + T\alpha_{(110)}PLD_{(110)} + TEL \times LD} = \frac{(2\sqrt{2} - 2)kh + (2\sqrt{2} - 2)h^2}{\sqrt{2}kh + (2\sqrt{2} - 2)h^2 + 2\sqrt{2}kd_{\text{metal-metal}} + (8 - 4\sqrt{2})h_{\text{metal-metal}}^2}. \]  
(D.25)

\[ F_{\text{rod}}^{\text{low}} = \frac{TEL \times LD}{T\alpha_{(100)}PLD_{(100)} + T\alpha_{(110)}PLD_{(110)} + TEL \times LD} = \frac{2\sqrt{2}kd_{\text{metal-metal}} + (8 - 4\sqrt{2})h_{\text{metal-metal}}}{\sqrt{2}kh + (2\sqrt{2} - 2)h^2 + 2\sqrt{2}kd_{\text{metal-metal}} + (8 - 4\sqrt{2})h_{\text{metal-metal}}^2}. \]  
(D.26)

\[ F_{\text{rod}}^{\text{terrace}} = 1 - F_{\text{rod}}^{\text{low}} = \frac{\sqrt{2}kh + (2\sqrt{2} - 2)h^2}{\sqrt{2}kh + (2\sqrt{2} - 2)h^2 + 2\sqrt{2}kd_{\text{metal-metal}} + (8 - 4\sqrt{2})h_{\text{metal-metal}}^2}. \]  
(D.27)

All \( D, F_{\text{rod}}^{(100)}, F_{\text{rod}}^{\text{low}}, \) and \( F_{\text{rod}}^{\text{terrace}} \) were calculated for every Pd nanoparticle analyzed, and their mean values were statistically calculated from ca. 300 nanoparticles for each sample.

X-ray powder diffraction (XRD) was used to characterize the size and crystallinity of Pd nanoparticle catalysts. Powder XRD data were collected on a Bruker General Area Detector Diffraction System (GADDS) equipped with a four-circle diffractometer and HiStar multiwire area detector. A Bruker M18XHF\textsuperscript{22} rotating anode generator operating at 50 kV and 40 mA
supplied the graphite monochromated incident beam. The dried sample was mixed with paratone oil, and loaded into a 0.7 mm special glass capillary and exposed for 900 s for each of 5 frames. Scatter from the glass capillary was removed by coincidence correction before merging the five frames for integration from 30-100 degrees 2θ. The final spectrum was truncated to remove boundary anomalies, normalized to facilitate pattern matching, and the baseline or background was corrected using a fourth or fifth order Chebyshev polynomial. Full pattern refinement was performed in TOPAS (Bruker AXS, Inc., version 3) using a Pd CIF file (4), and the crystallite size was estimated based on the integral breadth, assuming the intermediate crystallite size broadening modeled by a Voigt function (5).

X-ray photoelectron spectroscopy (XPS) was used to characterize the impurities on Pd nanoparticle surface after extensive wash (e.g., PVP, Cl, Br). XPS spectra were collected using a Kratos Axis ULTRA X-ray photoelectron spectrometer with monochromatic Al Kα excitation, 120 W (12kV, 10 mA). Data were collected using the hybrid lens setting with the slot aperture (300 µm × 700 µm analysis area) and charge neutralizer settings of 1.8 A filament current, 2.54 V charge balance and 1 V filament bias. Survey spectra were collected at a pass energy of 160 eV and high resolution spectra were collected using a pass energy of 40 eV. The data were fitted with Gaussian-Lorentzian line shapes. The binding energy scale was referenced to the aliphatic C 1s line at 285.0 eV.

Pd catalyst loading for each catalytic run was calculated based on Pd content of stock suspension, which was analyzed by PerkinElmer SCIEX - ELAN DRCe inductively coupled plasma mass spectrometer (ICP-MS).
D.1.3 Control Experiments

For control experiments, nitrite reduction on large octahedral Pd catalysts was evaluated without hydrogen, with a range of catalyst loadings, and with mixing rates. To conservatively estimate hydrogen supply and mass transfer limitations, nitrite with greater reduction rates than NDMA or diatrizoate was chosen, and its initial concentration was selected at 2 mM. No reaction occurred without hydrogen, and it indicates that hydrogen is essential to initiate and sustain reduction. Catalyst loading varied from $1.25 \times 10^{-3}$ to $10^{-2}$ g L$^{-1}$, and nitrite reduction rate constant increased proportionally with increasing catalyst loading ($R^2=0.969$). In addition, the amount of hydrogen gas in headspace is 829 µmol (assuming 1 atm, 21 °C, 20 mL), and it is greater than the maximal amount of hydrogen for nitrite reduction (i.e., 240 µmol, assuming all nitrogen ends up to ammonia). Moreover, Pd catalyst also absorbs hydrogen in sparging and activation. Hence, all evidences indicate that hydrogen supply is sufficient to sustain contaminant reduction. Next mixing rate varied from 0 to 640 rpm, and nitrite reduction rate constant was constant within the uncertainties ($6.14 \times 10^{-4}$ to $1.82 \times 10^{-3}$ min$^{-1}$). It indicates that mass transfer does not limit nitrite reduction rate even without mixing. It is reasonable because the majority of PVP has been removed (92.2% removal based on XPS analysis) and nanoparticle catalyst was exposed to reagents in reduction. A criterion was used to evaluate the aqueous-solid mass transfer limitations. No aqueous/solid mass transfer limitations is expected if mass transfer rate constant $k_{aq/sa}$ is much greater than the largest measured reduction rate constant $k_{obs}$ values, whereas significant aqueous/solid mass transfer limitations is expected if $k_{aq/sa}$ is close to or exceed the measured $k_{obs}$ values. First slip velocity of Pd nanoparticles is calculated, and it is
used to conservatively estimate mass transfer rate between aqueous solution and solid. In a mixing system, Pd nanoparticle slip velocity is always larger than the one only considering gravity. The slip velocity with no agitation is calculated by Stokes law:

\[ u_t = \frac{g d_p^2 (\rho_p - \rho)}{18 \mu}; \tag{D.28} \]

in which \( g \) is standard gravity (9.8 m s\(^{-2}\)), \( \rho_p \) is Pd nanoparticle density (12.0 g cm\(^{-3}\)), \( \rho \) is water density (1.0 g cm\(^{-3}\) at 20 °C), \( \mu \) is dynamic viscosity of water (1.0 g m\(^{-1}\) s\(^{-1}\) at 20 °C), and \( d_p \) is the diameter of a circumscribed sphere (15.1 nm), which equals to \( \sqrt{2} \times \) edge length (10.7 nm). The calculated slip velocity is \( 1.4 \times 10^{-9} \) m s\(^{-1}\), and its corresponding Reynolds number (\( Re = \frac{d_p u_t}{\nu} = 2.1 \times 10^{-11} \)) is significantly smaller than 1, suggesting it is a laminar flow and Stokes law is applicable. Next Sherwood number (Sh) is calculated based on a model developed by S. K. Friedlander, by taking advantages from boundary-layer theory (6). It is applicable for Re no more than 5. In order to estimate Sh, Peclet number (Pe) is first calculated, and it is expressed as:

\[ Pe = \frac{d_p u_t}{\nu}; \tag{D.29} \]

in which, \( D \) is diffusivity of nitrite in solution. Residual PVP in Pd samples dissolves in aqueous solution during reaction, and it may hinder nitrite diffusion onto Pd surface. Nitrite diffusion coefficient in PVP solution is conservatively estimated based on previous study of Carlfors et al. for the diffusion coefficients of 1,4-dioxane, glucosamine-hydrochloride, glucose-6-phosphate disodium salt, N-acetyl-glucosamine, and sucrose in PVP solution (7). PVP concentration in nitrite reduction solution is only \( 5.2 \times 10^{-3} \) kg m\(^{-3}\), and its inhibition to nitrite diffusion is negligible (7). Hence, nitrite diffusion coefficient in PVP solution is identical as the one in water.
(1.9×10⁻⁹ m² s⁻¹). The calculated Pe is 7.8×10⁻⁹, and it is significantly smaller than 1. Sh is expressed as:

\[ Sh = \frac{4}{Pe} \ln \left( \frac{1}{1-Pe/2} \right); \]  

(D.30)

and aqueous/solid mass transfer coefficient for nitrite is calculated by the following expression:

\[ k_{aq/s} = \frac{D}{d_p} Sh = \frac{4D}{Pe \times d_p} \ln \left( \frac{1}{1-Pe/2} \right); \]  

(D.31)

and it is 3.6×10⁻¹ m s⁻¹. Finally, aqueous/solid mass transfer rate constant is calculated by multiplying mass transfer coefficient by geometric surface area of the catalyst per volume of reaction solution a. For octahedra in control experiments, a is calculated by the following expression:

\[ a = \frac{\text{mass of Pd}}{\rho_p} \times \frac{\text{surface area of a octahedron}}{\text{volume of a octahedron}} \times \frac{1}{V_R}; \]  

(D.32)

in which, mass of Pd for each reduction is 0.2 mg, surface area of a Pd octahedron is 2\sqrt{3}×(edge length)² (395.9 nm²), volume of a Pd octahedron is \( \frac{1}{3} \sqrt[3]{2} \times \text{edge length}^3 \) (575.9 nm³), and \( V_R \) is the volume of reaction solution (40 mL). Hence, geometric surface area of the catalyst per volume of reaction solution a is 285.3 m⁻¹. Mass transfer rate constant \( k_{aq/s} a \) is 101.9 s⁻¹ and it is significantly larger than observed nitrite reduction rate constant (1.7×10⁻⁵ s⁻¹), therefore, aqueous/solid mass transfer limitations were overcome in the experiments.

A nitrogen mass balance experiment was carried out for ^1⁵N-nitrite reduction in the same setup described above. Both liquid and gas samples were withdrawn at different time intervals, and nitrite, nitric oxide, nitrous oxide, dinitrogen, and ammonia were analyzed with time course. Nitric oxide was not detected in the reaction. Carbon and nitrogen mass balance experiments were performed for all NDMA reduction experiments. NDMA, DMA, UDMH, and ammonia
were measured at the end of reactions. An extra nitrogen mass balance experiment was carried out to evaluate formation of gaseous nitrogen compounds during NDMA reduction. $^{15}$N$_2$ labeled NDMA was used, and gaseous samples were withdrawn at different time intervals and measured. Diatrizoate mass balance was evaluated at the end of reaction until complete deiodination. Dia-H$_3$ and iodide concentrations were measured.

D.1.4 Analytical Methods

The nitrite and iodide anion was analyzed using ion chromatography (Dionex ICS-2000, 30 °C). For nitrite analysis, a 990 µL loop was used to inject sample, and a Dionex IonPac AS19 column was used to separate nitrite and phosphate buffer. KOH was used as eluent, and its flow rate was maintained at 1.2 mL min$^{-1}$. KOH concentration and suppressor current was maintained at 10 mM and 30 mA for 12 min, and next KOH concentration was elevated to 45 mM from 12 to 12.5 min, maintained at 45 mM to 16 min, and dropped back to 10 mM from 16 to 16.5 min. Then KOH concentration was maintained at 10 mM to the end of analysis, till 18 min. The suppressor current was maintained at 134 mA from 12 to 18 min. For iodide analysis, a Dionex IonPac AS18 column was used coupled with a 25 µL injection loop. Eluent KOH was maintained at 36 mM at 1 mL min$^{-1}$ to the end of analysis, till 12 min. The suppressor current was maintained at 90 mA. NDMA, DMA, UDMH, diatrizoate, and Dia-H$_3$ were analyzed by high performance liquid chromatography (Shimadzu Prominence LC-20AT). Separation was achieved by a Dionex Acclaim 120 C18 column (3 µm Analytical, 4.6 × 100 mm) maintained at 40 °C. For NDMA analysis, the eluent was an 80/20 (by vol) nanopure water/methanol mixture at 1 mL min$^{-1}$. For DMA and UDMH, samples were first derivatized by DNFB (8) and NBA (9), respectively.
DNFB or NBA stock solution was prepared by dissolving 11 µL DNAB or 7.6 mg NBA in 10 mL acetonitrile. For DMA derivatization, 225 µL of sample, 225 µL of fresh-prepared DNFB stock solution, and 50 µL of 0.1 M fresh-prepared NaOH solution was mixed thoroughly at room temperature; while for UDMH derivatization, 225 µL of sample, 225 µL of fresh-prepared NBA stock solution, and 50 µL of acetate buffer (pH=5.5) was mixed thoroughly and heated at 70 °C for 15 min. The derivatized samples were analyzed by HPLC with a 40/60 (by vol) 0.2% acetic acid (pH=4) and methanol mixture as eluent at 1 mL min\(^{-1}\) for DMA (8, 10), and with a 30/70 (by vol) nanopure water and acetonitrile mixture as eluent at 1 mL min\(^{-1}\) for UDMH (9, 10). For diatrizoate and Dia-H\(_3\) analysis, the eluent was a mixture of 20 mM phosphate buffer (pH=7), 5 mM triethylamine, and 5% (by vol) methanol at 1 mL min\(^{-1}\). NDMA, DMA, UDMH, diatrizoate, and Dia-H\(_3\) were detected at 226 nm (10), 380 nm (8, 10), 393 nm (9, 10), 237 nm (11), and 229 nm (11) respectively, with a photodiode array detector. Ammonia was measured by the Hach salicylate method (low range, 0.02 to 2.50 mg/L NH\(_3\)-N, method 10023) using a Hach DR/4000U UV-Vis spectrophotometer. Control experiment indicates that nitrite, NDMA, DMA, UDMH, and phosphate buffer do not interfere colormetric measurements for ammonia under the experimental conditions. Gas samples were analyzed by gas chromatography-mass spectroscopy (GC-MS) for \(^{15}\)N labeled nitric oxide, nitrous oxide, and dinitrogen. A Varian 4000 GC/MS equipped with a CP-Molsieve 5Å column was used to separate the gas products. The oven was maintained at 165 °C, and the flow rate of the helium carrier gas was 1 mL/min. Charge-to-mass ratios of 31, 46, and 30 were selected to represent and analyze ionized nitric oxide, nitrous oxide, and dinitrogen, respectively.
D.2 Matlab Codes

odefcn.m

function du = odefcn(t, u, p, Q, sfPd, V)
    du = zeros(2,1);
    k11=Q(1); %nitrite reduction constant on sites 1
    k22=Q(2); %nitrite reduction constant on sites 2
    k31=Q(3); %nitric oxide reduction constant on sites 1
    k42=Q(4); %nitric oxide reduction constant on sites 2
    PN1=Q(5); %nitrite equilibrium adsorption constant on sites 1
    PNO1=Q(6); %nitric oxide adsorption constant on sites 1
    PN2=Q(7); %nitrite equilibrium adsorption constant on sites 2
    PNO2=Q(8); %nitric oxide equilibrium adsorption constant on sites 2

    r1=(k11*1E9)*p^2*sfPd^2/V^2*PN1*u(1)/(1+PN1*u(1)+PNO1*u(2))^2;
    r2=(k22*1E9)*(1-p)^2*sfPd^2/V^2*PN2*u(1)/(1+PN2*u(1)+PNO2*u(2))^2;
    r3=(k31*1E9)*p^2*sfPd^2/V^2*PNO1*u(2)/(1+PN1*u(1)+PNO1*u(2))^2;
    r4=(k42*1E9)*(1-p)^2*sfPd^2/V^2*PNO2*u(2)/(1+PN2*u(1)+PNO2*u(2))^2;

    %r1 and r2 are nitrite reduction rates on sites 1 and sites 2, r3 and r4 are nitric oxide reduction
    %rates on sites 1 and sites 2, p is the surface fraction of sites 1, and sfPd is the concentration of
    %total surface Pd sites.

    du(1) = -r1-r2;
    du(2) = r1+r2-r3-r4;

corefcn.m

function slope = corefcn(Q, m, tspan, pspan, sfPd, V)
    options = odeset('RelTol',1e-4,'AbsTol',[1e-4 1e-5]);
    IC = [m; 0]; %m is the initial nitrite concentration
    Y = zeros(length(tspan), 1);
    Z = zeros(length(tspan), 1);

    [T,Utemp] = ode45(@(t, u)odefcn(t, u, pspan, Q, sfPd, V), tspan,IC,options);
    Y = Utemp(:, 1);
    Z = Utemp(:, 2);

    [val, ind] = min(abs(Y-(0.5*max(Y)))); % find time point of half decay of initial nitrite
    T50 = tspan(ind);
    [T_ind, T_value] = find(T <= T50); % find the points before half decay of initial nitrite

    polypara = polyfit(T(T_ind), log(Y(T_ind)), 1); %linear regression

    slope = -polypara(1); %calculate the slopes, pseudo-first-order reduction rate constants for nitrite
**objcfcn.m**

```matlab
function F = objfcn(Q, t, p, sfPd)
  m_high = 2E-3;
  m_low = 100E-6;

  V_high = 40E-3;
  V_low = 20E-3;

  slope_low = zeros(size(p));
  slope_high = zeros(size(p));

  for i = 1 : length(p)
    slope_low(i) = corefcn(Q, m_low, t, p(i), sfPd(i), V_low);
    slope_high(i) = corefcn(Q, m_high, t, p(i), sfPd(i), V_high);
  end

  TOF_low_exp = [6.29E-02 4.65E-02 2.22E-02 2.65E-02 1.76E-02 2.30E-02 1.34E-02 2.40E-02 2.30E-02 3.93E-02];
  TOF_low_mod = V_low*m_low*slope_low./sfPd;

  TOF_high_mod = V_high*m_high*slope_high./sfPd;

  F = norm((TOF_low_exp - TOF_low_mod)./TOF_low_exp) + norm((TOF_high_exp - TOF_high_mod)./TOF_high_exp); %relative differences between experimental and model TOFs
```

**MainRoutine2.m**

```matlab
clear;
clc;

Q_init = [1 1 1 1 1 1 1 1]'; %reaction rate constants and equilibrium adsorption constants for nitrite and nitric oxide on sites 1 and 2

LB = 1E-5*ones(1, 8); %lower limit
UB = 1E5*ones(1, 8); %upper limit

tspan = linspace(0, 100000, 100000); %time span for solving differential equations
```
pspan = [9.53E-01 9.50E-01 1.40E-01 1.39E-01 1.57E-01 0.00E+00 0.00E+00 0.00E+00 0.00E+00 4.40E-01]; % pspan is the surface fraction of sites 1
sfPd = [2.39E-07 2.54E-07 4.77E-07 5.15E-07 3.40E-07 2.77E-07 2.79E-07 5.96E-07 6.27E-07 3.83E-07];

options = optimset('Display','iter','TolFun',1e-4);

A = [1 -100 0 0 0 0 0 0; -1 0.01 0 0 0 0 0 0; 0 0 1 -100 0 0 0 0; 0 0 -1 0.01 0 0 0 0; 0 0 0 1 0 -100 0; 0 0 0 0 1 0 -100; 0 0 0 0 -1 0.01 0; 0 0 0 0 0 -1 0 0.01];

b = [0 0 0 0 0 0 0 0]; % A and b set up the relative values of parameters, 0.01<k11/k22<100, 0.01<k31/k42<100, 0.01<PN1/PN2<100, 0.01<PNO1/PNO2<100

[Q_opt, fval] = fmincon(@(Q)objfcn(Q, tspan, pspan, sfPd, Q_init, A,b, [], [], LB, UB, [], options);
D.3 Supporting Figures

Figure D.1 (a) Nitrite reduction kinetics with various Pd catalyst loadings; (b) nitrite reduction kinetics with a range of mixing speeds; and (c) nitrogen mass balance during nitrite reduction. Large sized octahedra were used for reduction tests. Error bars represent standard deviations of replicates. In (a), purple solid line represents linear regression of reduction rate constant versus catalyst loading, and orange dash lines represent 95% confidence intervals of regression.
Figure D.2 Low magnification and high resolution transmission electron microscopic (TEM) images of Pd cubes (a, g), rods (b, h), cuboctahedra (c, d, and i), and octahedra (e, f, and j). c and d are cuboctahedra with small and large size, and e and f are octahedra with small and large size. Lattice spacing is indicated in high resolution images.
Figure D.2 (cont.)
Figure D.2 (cont.)
Figure D.2 (cont.)
Figure D.3 Effects of Pd nanoparticle size on (a) dispersion, (b) surface fraction of low coordination sites (edge and vertex sites), (c) surface fraction of high coordination sites (terrace sites), (d) surface fraction of (100) facet, (e) surface fraction of (110) facet, and (f) surface fraction of (111) facet. Green diamond •, red hexagon •, gray cross •, and blue cube • represent data of octahedral, cubocatahedral, rod, and cubic Pd nanoparticle catalysts. Purple solid lines — are linear regressions of dispersion, surface fraction of low coordination sites, and surface.
fraction of high coordination sites versus TEM sizes of Pd nanoparticle catalysts, and orange dash lines represent the 95% confidence intervals of linear regressions.
Figure D.4 TEM images of Pd nanoparticle catalysts after reduction. Only small octahedral Pd nanoparticles changed their shape to near-sphere after used in diatrizoate reduction (TEM image is highlighted in light green). No significant shape change was observed for other Pd nanoparticles for nitrite, NDMA, and diatrizoate reduction.
NDMA, 100 µM

cube, 5d  cuboctahedron small, 5d

octahedron small, 1d  octahedron small, 2d  octahedron small, 3d

octahedron small, 4d  octahedron small, 5d

Figure D.4 (cont.)
Diatrizoate, 100 µM

Figure D.4 (cont.)
Figure D.5 TEM images of Pd nanoparticle catalysts after reaction with the amendment of $\Gamma$. Small octahedral Pd nanoparticles were used, and $\Gamma$ concentration was 35 $\mu$M. The presence of $\Gamma$ changes Pd nanoparticle shape to near-sphere (TEM image is highlighted in light green), but the addition 100 $\mu$M NDMA or 2 mM nitrite prevents the shape change.
### D.4 Supporting Tables

**Table D.1** Solved reaction rate constants and equilibrium adsorption constants for nitrite and nitric oxide on sites 1 and 2

<table>
<thead>
<tr>
<th>Kinetics</th>
<th>Values</th>
<th>Ratio of Values at Sites 1 to Values at sites 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrite reduction rate constant at sites 1</td>
<td>$k_{NO_2}^1$</td>
<td>$6.0 \times 10^7$</td>
</tr>
<tr>
<td>(L mol$^{-1}$ min$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrite reduction rate constant at sites 2</td>
<td>$k_{NO_2}^2$</td>
<td>$1.2 \times 10^8$</td>
</tr>
<tr>
<td>(L mol$^{-1}$ min$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitric oxide reduction rate constant at sites 1</td>
<td>$k_{NO}^1$</td>
<td>$2.1 \times 10^5$</td>
</tr>
<tr>
<td>(L mol$^{-1}$ min$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitric oxide reduction rate constant at sites 2</td>
<td>$k_{NO}^2$</td>
<td>$1.0 \times 10^6$</td>
</tr>
<tr>
<td>(L mol$^{-1}$ min$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>Values</td>
<td>Ratio of Values at Sites 1 to Values at sites 2</td>
</tr>
<tr>
<td>Nitrite equilibrium adsorption constant at sites 1</td>
<td>$K_{NO_2}^1$</td>
<td>0.9</td>
</tr>
<tr>
<td>(L mol$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrite equilibrium adsorption constant at sites 2</td>
<td>$K_{NO_2}^2$</td>
<td>0.1</td>
</tr>
<tr>
<td>(L mol$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitric oxide equilibrium adsorption constant at sites 1</td>
<td>$K_{NO}^1$</td>
<td>$1.7 \times 10^4$</td>
</tr>
<tr>
<td>(L mol$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitric oxide equilibrium adsorption constant at sites 2</td>
<td>$K_{NO}^2$</td>
<td>$1.7 \times 10^4$</td>
</tr>
</tbody>
</table>
Table D.2 Experimental and model TOFs for nitrite reduction with 100 µM and 2 mM as initial concentrations

<table>
<thead>
<tr>
<th>Shape and Size</th>
<th>Surface Fraction of (100) Facet</th>
<th>100 µM Nitrite Reduction</th>
<th>2 mM Nitrite Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Experimental TOFs (min⁻¹)</td>
<td>Model TOFs (min⁻¹)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>avg.</td>
<td>std.</td>
</tr>
<tr>
<td>Cubes</td>
<td>95.3%</td>
<td>6.3x10⁻²</td>
<td>4.9x10⁻³</td>
</tr>
<tr>
<td></td>
<td>95.0%</td>
<td>4.7x10⁻²</td>
<td>3.6x10⁻³</td>
</tr>
<tr>
<td>Small Cub-octahedra</td>
<td>14.0%</td>
<td>2.2x10⁻²</td>
<td>6.0x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>13.9%</td>
<td>2.7x10⁻²</td>
<td>4.6x10⁻³</td>
</tr>
<tr>
<td>Large Cub-octahedra</td>
<td>15.7%</td>
<td>1.8x10⁻²</td>
<td>4.7x10⁻⁴</td>
</tr>
<tr>
<td>Small Octahedra</td>
<td>0%</td>
<td>2.4x10⁻²</td>
<td>1.2x10⁻³</td>
</tr>
<tr>
<td></td>
<td>0%</td>
<td>2.3x10⁻²</td>
<td>4.7x10⁻⁴</td>
</tr>
<tr>
<td>Large Octahedra</td>
<td>0%</td>
<td>2.3x10⁻³</td>
<td>9.4x10⁻⁴</td>
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<tr>
<td>Rods</td>
<td>44.0%</td>
<td>3.9x10⁻²</td>
<td>6.6x10⁻⁴</td>
</tr>
</tbody>
</table>

D.5 References


