CATALYTIC REDUCTION OF NO AND N₂O WITH HYDROGEN IN WATER
BY POLYMER-PROTECTED PALLADIUM NANOPARTICLES

BY

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THESIS

Submitted in partial fulfillment of the requirements
for the degree of Master of Science in Chemistry
in the Graduate College of the
University of Illinois at Urbana-Champaign, 2010

Urbana, Illinois

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Abstract

Nitric oxide (NO) and nitrous oxide (N₂O) are important components of the global nitrogen cycle. They are intermediates or end products for natural bacterial processes such as nitrification and denitrification, and are formed in increasing amounts from anthropogenic sources such as increased bacterial denitrification of fertilizers. Both are contributors to ozone destruction, and N₂O is a potent greenhouse gas. Reduction of both gases to harmless dinitrogen by nanoparticulate palladium catalysts is a promising method for treating NO and N₂O formed in water. However, creating a better understanding of the method of catalytic activity and corresponding selectivity is critical for developing an optimal process.

We have synthesized a water-soluble Pd/PVP colloid (PVP= poly(N-vinyl-2-pyrrolidone) by an alcohol reduction method. Nitric oxide and nitrous oxide reduction activities were determined by monitoring the headspace composition in a reaction flask by GC-MS. NO reduction rates were considerably faster than N₂O reduction rates, and essentially no production of N₂ was observed until all of the NO had been reduced to N₂O. This is consistent with expectations that the binding constant of NO to the palladium nanoparticle surface is considerably larger than that of N₂O. Molar balances and post-experimental ammonia analysis confirmed that no side production of ammonia was occurring.

Further studies showed that no reaction occurred with an air-exposed catalyst until hydrogen added in a helium atmosphere was sufficient to remove oxygen from the surface. Hydrogen held by the Pd nanoparticles was modified by controlled heating under helium in order to confirm the need for hydrogen in N₂ production from N₂O.
Acknowledgements

I would like to thank my advisor, John R. Shapley, for helping me get to this point. This would not have been even remotely possible without him. Thanks also to Charlie Werth and Timothy Strauthman for their numerous suggestions, and for Mark Baker for help in data collection.

Thanks go to Shawn Qi in Newmark, who was always available when the instrument was having problems, Rudi Laufhutte for elemental analysis measurements under trying conditions, and Vera Mainz for her endless patience.

Throughout grad school there were many faculty members who provided opportunities for development, and I would be remiss if I did not thank Patricia Shapley, Alexander Scheeline, and Tom Rauchfuss for their help and encouragement during my time here.

Finally, thank you to my family, who stood by and encouraged me whenever I needed it.
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Introduction

1.1 NO and N\textsubscript{2}O in natural systems

Nitric oxide (NO) and nitrous oxide (N\textsubscript{2}O) are important components of the global nitrogen cycle as both intermediates and byproducts. Nitrogen is made available for use by organisms through the action of certain dinitrogen-fixing prokaryotes\textsuperscript{1,2,3}, which carry nitrogenase enzymes capable of catalyzing the reduction of nitrogen gas to the ammonium ion. Eukaryotes, and prokaryotes that are not capable of fixing N\textsubscript{2}, can either obtain nitrogen as NH\textsubscript{4}\textsuperscript{+} or as organic nitrogen directly from the environment, or they can reduce NO\textsubscript{3}\textsuperscript{−} to NH\textsubscript{4}\textsuperscript{+} through nitrate reduction pathways\textsuperscript{1,4,5}. After the ammonia is acquired or produced, it is oxidized by a series of enzymatic reactions to NO\textsubscript{3}\textsuperscript{−} in a process called nitrification. To close the cycle, NO\textsubscript{3}\textsuperscript{−} can be reduced to N\textsubscript{2} by a further series of stepwise denitrification reactions.

N\textsubscript{2}O can be a byproduct of nitrification, as already detailed above. Nitrification links the most reduced and the most oxidized forms of the nitrogen cycle. It occurs in at least two reactions\textsuperscript{1},

\[
\text{NH}_4^+ + 0.5 \text{O}_2 \rightarrow \text{NH}_2\text{OH} + \text{H}^+ \quad \Delta G = +17 \text{ kJ mol}^{-1} \quad (1) \\
\text{NH}_2\text{OH} + \text{O}_2 \rightarrow \text{NO}_2^- + \text{H}_2\text{O} + \text{H}^+ \quad \Delta G = -289 \text{ kJ mol}^{-1} \quad (2)
\]

The NH\textsubscript{2}OH in equation (2) is unstable in aqueous solutions and will rapidly degrade to N\textsubscript{2}, N\textsubscript{2}O, or NH\textsubscript{4}\textsuperscript{+}, and, although the first and second steps are closely coupled, some production of N\textsubscript{2}O is thought to occur from hydroxylamine released into the environment during this process\textsuperscript{6}. The bulk of N\textsubscript{2}O production during nitrification, however, occurs in the final reduction of nitrite under anaerobic conditions.

Bacteria such as those in the \textit{Nitrosomonas} genus can produce the enzyme nitrite reductase to reduce NO\textsubscript{2}\textsuperscript{−} to N\textsubscript{2}O under anaerobic conditions or aerobically with concurrent oxidation of ammonium to nitrite\textsuperscript{6-10}.

1
Denitrification is the removal of fixed nitrogen from the environment. Denitrifying microorganisms are generally aerobic bacteria that have the capacity to reduce nitrogen oxides when oxygen becomes limiting in the environment,\textsuperscript{5,6,11-13} which can be either soil, freshwater, or salt water depending on the species. Bacteria capable of performing denitrification contain a series of enzymes that catalyze successive reduction steps following the general pathway of

\[ \text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2 \]  \hspace{2cm} (3)

The first two steps of the sequence are catalyzed by nitrate reductase and nitrite reductase respectively. NO is highly reactive with O\textsubscript{2} and with transition metals and in excess is toxic to living organisms. It does not accumulate within cells; instead it is either excreted into the surroundings or rapidly reduced intracellularly to N\textsubscript{2}O by nitric oxide reductase. However, the final reaction, the reduction of N\textsubscript{2}O to N\textsubscript{2}, is inhibited by NO\textsubscript{3} and H\textsuperscript{+}, and at pH below 5 N\textsubscript{2}O builds up in the cell and is excreted into the surrounding environment.\textsuperscript{12}

### 1.2 NO and N\textsubscript{2}O Pollution

The effects of humans on the nitrogen cycle are growing. Anthropogenic production of NO is estimated to be roughly 80% of the total global production of NO,\textsuperscript{14} primarily from fossil fuel combustion (~50%), burning of biomass (~20%), and human influence on microbial activity (~10%), with the remainder of NO production from ordinary microbial activity and formation by lightning. Ice core data has been used to monitor historic levels of N\textsubscript{2}O stretching as far back as 2,000 years,\textsuperscript{15,16} and for the first 1,800 of those years, the N\textsubscript{2}O levels remained relatively stable. The amount of N\textsubscript{2}O, however, rose 18% from 1750, when the N\textsubscript{2}O level was 270 ppb, to 2005, when it was 319 ppb, at an approximately steady rate of 0.26% yr\textsuperscript{-1}.\textsuperscript{17} Roughly 30% of world N\textsubscript{2}O production is estimated to be from human influence,\textsuperscript{18,19}
with a number of sources (fertilizers, N-enriched groundwater, biomass burning, fossil fuels, nylon manufacture, etc.) all contributing. However, approximately 68% of N₂O production in the US comes from biological production stimulated by nitrogen-containing fertilizers and fertilizer runoff.²⁰

NO is a short-lived gas, and when it enters the troposphere it can react rapidly with ozone to form nitrogen dioxide. NO₂ can photodissociate back to NO and triplet oxygen, which further reacts with dioxygen to reform ozone, as shown in equations 4-6.²¹

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \quad (4) \\
\text{NO}_2 + \text{hv} & \rightarrow \text{O}(^3\text{P}) + \text{NO} \quad (5) \\
\text{O}(^3\text{P}) + \text{O}_2 & \rightarrow \text{O}_3 \quad (6)
\end{align*}
\]

NO, NO₂, and O₃ typically equilibrate in sunlight. Other compounds, however, can also oxidize NO to NO₂. The most important of these is the hydroperoxy radical, HO₂, which is principally formed by the oxidation of carbon monoxide.

\[
\begin{align*}
\text{OH} + \text{CO} & \rightarrow \text{H} + \text{CO}_2 \quad (7) \\
\text{H} + \text{O}_2 & \rightarrow \text{HO}_2 \quad (8) \\
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 \quad (9)
\end{align*}
\]

Summing up the simplified reaction cycle shown in equations 4-9 gives the net reaction of carbon monoxide and oxygen to form carbon dioxide and ozone.

Net: \[ \text{CO} + 2 \text{O}_2 \rightarrow \text{CO}_2 + \text{O}_3 \quad (10) \]

An increase in the amount of NO present in the troposphere will therefore increase the total amount of ozone in the lower levels of the atmosphere, leading to health problems and decreased crop growth.²²,²³
NO$_2$ formed from NO will also react readily with the hydroxyl radical to form nitric acid, HNO$_3$, which is expelled from the atmosphere as acid rain.

In recent years there has been a rising awareness of the environmental effects of N$_2$O. N$_2$O does not react nearly as readily in the atmosphere as NO; the current estimated lifetime of an N$_2$O molecule in the stratosphere is 114 years.$^{15}$ The principle destruction mechanism is by photolysis at wavelengths shorter than 240 nm$^{21}$ (eq. 11), which will only naturally occur in the stratosphere.

$$N_2O + \text{hv} \rightarrow N_2 + O(^1D)$$ (11)

N$_2$O can also decompose by reaction with excited oxygen atoms. The reaction has three possible channels:

$$N_2O + O(^1D) \rightarrow 2 \text{ NO}$$ (12)

$$N_2O + O(^1D) \rightarrow N_2 + O_2$$ (13)

$$N_2O + O(^1D) \rightarrow N_2O + O(^3P)$$ (14)

The NO produced in equation (12) will react with ozone to form NO$_2$, as shown in equation (4) above, and so N$_2$O in the stratosphere contributes to the destruction of the ozone layer. In fact, nitrous oxide is currently the most important ozone-depleting emission that is not severely limited by international agreements.$^{20, 24, 25}$ Because it will only decompose in the stratosphere, N$_2$O in the troposphere also acts as a potent greenhouse gas, with a global warming potential (GWP) of 310 equivalents of CO$_2$, $^{17, 25}$ and is the third-most-important contributor to global climate change, after CO$_2$ and methane.

Also of concern in any discussion of NO and N$_2$O pollution is the growing problem of nitrate contamination of water sources. In recent years, the concentration of nitrates in groundwater has increased worldwide,$^{26-30}$ particularly in agricultural areas using nitrogen-rich fertilizers. As explained in
section 1, both NO and N₂O are intermediates in the stepwise enzymatic denitrification of nitrate (equation 3), and at low pH and high concentrations of nitrate or oxygen, N₂O is the final product of denitrification.⁷,¹² Denitrification in freshwater (groundwater, lakes, and streams) accounts for roughly 20% of the total global denitrification,³¹ and nitrate runoff from fertilizer is rising.⁴,¹⁸,³² Contamination of freshwater by nitrate is not trivial even when denitrification is not taken into account; through in-vivo reduction to nitrite, excess nitrates have been linked to methemoglobinemia (blue baby syndrome)³³,³⁴ and elevated risks of the cancer non-Hodgkin’s lymphoma.³⁵-³⁷

1.3 Aqueous Catalytic Reduction of NO and N₂O

There has been a great deal of study on the catalytic reduction of NO and N₂O with transition metals and various reductants,³⁸-⁵⁰ but the vast majority of the work has been done with applications towards catalytic converters to clean fossil fuel emissions, and has therefore been primarily conducted at high temperatures in the gas phase. The majority of the research into the aqueous reduction of NO and N₂O to dinitrogen has been a subset of the search for an artificial denitrification catalyst for eventual application to the treatment of drinking water.

Nitrate salts are difficult to remove from water due to their high solubility and chemical stability. The current treatment methods have used ion exchange, reverse osmosis, or biological removal,²⁷,⁵¹-⁵⁶ but all have economical or ecological disadvantages that encourage research into alternatives. Ion exchange and reverse osmosis both produce concentrated salt brines that must be disposed of, significantly increasing the treatment cost. Biological denitrification of water meant for human consumption must go through filtration and disinfection to remove the bacteria and organic byproducts. A catalytic method for nitrate removal, which would be low-energy and potentially waste-free,⁵⁷ is desirable because of the disadvantages of the traditional methods.
A promising alternative method for removal of nitrogen oxides is catalytic hydrogenation to nitrogen or ammonia using palladium or platinum catalysts. Palladium shows greater selectivity towards N\textsubscript{2} than platinum does\textsuperscript{58}, although the reaction pathway on the two metals is generally assumed to be the same. The proposed reaction pathway is shown in Figure 1.1\textsuperscript{59}. Metal cocatalysts, such as copper, tin, or indium\textsuperscript{55,58,60-62} are necessary to reduce nitrate to nitrite, but a second metal is not necessary for further reduction of nitrite, NO, or N\textsubscript{2}O\textsuperscript{53,64}. Our research has therefore focused solely on palladium for the reduction of NO and N\textsubscript{2}O.

![Figure 1.1: Stepwise reduction of nitrate to dinitrogen](image)

Although N\textsubscript{2}O has been detected as an intermediate in the complete reduction of nitrite to N\textsubscript{2}\textsuperscript{65}, the mechanism of NO\textsubscript{2}\textsuperscript{-} reduction is currently unknown. However, even though only NO\textsubscript{2}\textsuperscript{-} and N\textsubscript{2}O have been seen in the gas phase, the formation and further reaction of NO on the catalyst surface, without dissociation, has been suggested as the key step in determining the selectivity for dinitrogen vs. ammonia\textsuperscript{63,67-69}. Further investigation into the reduction of NO to N\textsubscript{2}O and of N\textsubscript{2}O to N\textsubscript{2} on palladium in order to better understand the controlling factors in the reduction is presented in this work.
In choosing the palladium system to investigate, we had to take into account both the structure of the metal catalyst and of the catalyst support. The choice of supporting material can have a significant effect on the nitrogen selectivity\textsuperscript{55} and the kinetics\textsuperscript{60} of the reaction. The distribution of the catalyst on the heterogenous support surface ranges from isolated phases to alloys depending on the preparation method. In order to minimize support contribution and particle variability during an experiment, we have chosen to examine NO and N\textsubscript{2}O reduction using palladium nanoparticles encapsulated in a water-soluble poly(N-vinyl-2-pyrrolidone) (PVP) polymer. The formation of nanoparticles through the reduction of palladium acetate forms palladium clusters with a narrow size distribution,\textsuperscript{60,70} and the polymer protecting agent is not expected to interfere in the reaction.

In the following chapters of this thesis, the kinetics of the reduction of NO and N\textsubscript{2}O on Pd nanoparticles protected with a soluble PVP polymer are examined. Chapter 2 gives the synthetic and experimental methodology of the investigation. Chapter 3 lists the experimental results and discusses the broader implications of the experiments, and chapter 4 provides a summary of the conclusions.
2. Materials and Methods

2.1 Chemicals and Instruments

Catalytic reduction experiments used 18.2 MΩ-cm water (TOC < 10 ppb) obtained from a Barnstead E-pure 4-cartridge 240V deionization system, Model D4642-33. Tanks of hydrogen, helium, and air (>99% purity) were supplied by Linde Gas. A lecture-bottle of $^{15}$NO (98%+ labeled) was acquired from Cambridge Isotope Laboratories and portions were transferred to a 25 or 50 mL bulb using standard high-vacuum techniques. All other chemicals and solvents were reagent grade or better as supplied by Sigma Aldrich or Fischer Scientific, and each was used as received.

Elemental analyses were performed in the Microanalysis Laboratory of the School of Chemical Sciences (UIUC). Ammonia analysis was performed using the Hach Low Range Ammonia Reagent test. Concentrations of nitric oxide, nitrous oxide, and dinitrogen were measured by headspace analysis of the reaction vessel on a Varian 4000 GC/MS equipped by a CP-Molsieve 5 Å column (Fig. 2.1) chosen for its ability to separate small gases. Helium carrier gas flowed through the column at 1 mL/min.

![Diagram](image)

Figure 2.1. A schematic of the GC unit used to separate gases in the headspace of NO and N$_2$O reduction experiments (adapted from 59).
The Pd-PVP catalyst was prepared by adding 0.90 g (4.0 mmol) of Pd(OAc)$_2$ and 1.70 g PVP (average MW ca. 55,000) to 50 mL 2-ethoxyethanol in a 100-mL round bottom Schlenk flask (equipped with a reflux condenser and a magnetic Teflon-coated stirring bar) and refluxing for 2 hours under nitrogen. After cooling under N$_2$, the solution was stored in a sealed container and portions of the 2-ethoxyethanol solution were withdrawn to be used as needed. No precautions were taken to keep air out of the system.

To prepare the palladium nanoparticles for a catalytic experiment, the 2-ethoxyethanol was removed under reduced pressure from a 10 mL portion of the catalyst and the Pd-PVP residue was dissolved in a minimum amount of nanopure water. The solution was filtered through Celite and rinsed with nanopure water until the Celite was clean. The water was removed under vacuum and the Pd-PVP residue was dissolved in 10 mL nanopure water to give a dispersion with nominally 80 mM Pd.

2.2. Reaction Vessel and Sampling

The catalyst, the reaction solution (total volume = 80 mL), and a stirbar were added to a 120-mL glass bottle. The bottle was then sealed by a 1.0cm-thick rubber stopper held in place by a metal crimp cap (Fig. 2.2) and sparged with hydrogen through syringe needles for an hour, sometimes followed by further sparging with specific gases.
Figure 2.2. A schematic of the closed system reactor developed for NO and N₂O reduction experiments (adapted from 59).

A 1.0 mL Hamilton gas-tight syringe with a non-coring needle was used to remove 0.3 mL of the headspace gas for GC/MS sampling; when the experiment required more than 20 samples, the volume of the removed gas was periodically replaced by helium. After each addition of a gas to the headspace during the experiment, the reaction vessel was shaken for one minute to speed up equilibration between the headspace and the solution. Peak concentrations were compared to a calibration curve of 5 standards with NO, N₂O, and N₂ present in concentrations of 69 μM to 1.72 μM (Fig. 2.3).
Figure 2.3. (Continued on next page)
Figure 2.3. A representative calibration plot for A) $^{28}\text{N}_2$, B) $^{30}\text{NO}$, C) $^{14}\text{N}_2\text{O}$, where the different lines represent the base peak and the most common fragments of $\text{N}_2\text{O}$ in the mass spectrum.

2.3 Experiments using a 0.18 mM catalyst solution

2.3.1 Reduction of $^{15}\text{NO}$ under hydrogen atmosphere using a 0.18 mM catalyst solution

In a typical run, 0.18 mL of 80 mM catalyst solution, 0.66 mL of a 1.13 M phosphate buffer, 79 mL nanopure water, and a Teflon-coated stirbar were added to a 120-mL glass bottle, resulting in a solution containing (0.18 mL x 80 mM/ 80 mL ) 0.18 mM Pd. After being sealed as previously described, the bottle was sparged with hydrogen for an hour before the addition of $^{15}\text{NO}$. The reduction of $^{15}\text{NO}$
and the formation of $^{30}\text{N}_2\text{O}$ was monitored by GC/MS until all of the NO was reduced, and the slower reduction of N$_2$O to $^{30}\text{N}_2$ was monitored for at least one half-life. In all cases, standards made using $^{28}\text{N}_2$, $^{14}\text{NO}$, and $^{28}\text{N}_2\text{O}$ were used to calibrate the reaction curves, and it was assumed that the reaction of the mass spectrometer was the same for all isotopes of the same gas. After the completion of the reaction, 2 mL of the reaction solution were filtered through a 0.2 μm syringe filter to remove the Pd-PVP catalyst and kept for ammonia analysis.

### 2.3.2 Effect of buffer concentration on NO reduction using a 0.18 mM catalyst solution

In a typical run, 0.18 mL of 80 mM catalyst, 0, 1.32, or 2.64 mL of a 1.13 M phosphate buffer, enough nanopure water to make 80 mL total volume, and a Teflon-coated stirbar were added to a 120-mL glass bottle. After being sealed with a rubber stopper and a crimp cap, the bottle was sparged with hydrogen for an hour before the addition of $^{15}\text{NO}$. The reduction of $^{15}\text{NO}$ and the formation of $^{46}\text{N}_2\text{O}$ was monitored by GC/MS until all of the NO was reduced, and the slower reduction of N$_2$O to $^{30}\text{N}_2$ was monitored for at least one half-life. After the completion of the reaction, 2 mL of the reaction solution were filtered through an 0.2-micron filter and kept for ammonia analysis.

### 2.4 Experiments using a 1.8 mM catalyst solution without buffer

In a typical run, 1.8 mL of 80 mM catalyst, 78 mL nanopure water, and a Teflon-coated stirbar were added to a 120-mL glass bottle. The same catalyst solution was used for several experiments; in all cases, the composition of the gases in the headspace after sparging was measured to ensure that there was no reactant from the previous experiment present. Catalyst concentration was nominally 1.8 mM in Pd, but ICP/MS analysis of a catalytic solution showed that the actual value could vary by up to 20% less.
2.4.1 $^{15}$NO reduction under helium atmosphere with hydrogen pretreatment

1.8 mL of 80 mM catalyst, 78 mL nanopure water, and a Teflon-coated stirbar were added to a 120-mL glass bottle. The bottle was sealed with a rubber stopper and metal crimp cap as previously described and sparged with hydrogen for one hour, then with helium for one hour, and the gas concentrations in the reaction flask were measured before the addition of 2 mL $^{15}$NO. The initial reduction of NO to $^{46}$N$_2$O was monitored, and additional aliquots of 0.5 mL (~20 μmol) H$_2$ were added after it was observed that the ratios of gases in the reaction flask had remained constant for three samples. Complete reduction of $^{31}$NO to $^{46}$N$_2$O and of $^{46}$N$_2$O to $^{30}$N$_2$ was achieved over the course of two days. Before resuming the experiment on the second day, the concentrations of the gases in the reaction flask were measured to confirm that no further reaction had occurred overnight.

2.4.2 $^{44}$N$_2$O reduction under hydrogen atmosphere

A 1.8 mM catalyst solution prepared as described above was sparged by hydrogen for 1 hour and the gas concentrations in the reaction flask were measured before the addition of 4 mL N$_2$O. The reduction of N$_2$O to N$_2$ was monitored until the N$_2$O in the system dropped below the detection level and the N$_2$ level was stable.
2.4.3 \textsuperscript{44}N\textsubscript{2}O reduction under a helium atmosphere with H\textsubscript{2} pretreatment

A 1.8 mM catalyst solution prepared as described above was sparged by hydrogen for 1 hour, then by helium for 1 hour, before the addition of 4 mL N\textsubscript{2}O. The initial reduction of N\textsubscript{2}O and formation of N\textsubscript{2} was monitored, and additional aliquots of 0.5 mL (~20 μmol) H\textsubscript{2} were added after it was observed that the ratios of gases in the reaction flask had remained constant for three samples.

2.4.4 \textsuperscript{44}N\textsubscript{2}O reduction by excess H\textsubscript{2} in a helium atmosphere

A 1.8 mM catalyst solution prepared as described above was sparged by hydrogen for 1 hour, then by helium for 1 hour, and the initial gas concentrations in the reaction flask were measured before the addition of 4 mL N\textsubscript{2}O. The initial reduction of N\textsubscript{2}O and formation of N\textsubscript{2} was monitored until the N\textsubscript{2} levels had been steady for three consecutive samples, then 10 mL of H\textsubscript{2} was added to the flask and the reduction to N\textsubscript{2} was monitored. When the N\textsubscript{2}O reduction slowed at low concentrations of N\textsubscript{2}O, 1 mL of N\textsubscript{2}O was added to confirm that there was still H\textsubscript{2} present in the system.

2.4.5 \textsuperscript{44}N\textsubscript{2}O interaction with an oxygen-pretreated surface

A 1.8 mM catalyst solution prepared and sealed as described above was sparged by hydrogen for one hour, by air for one hour, and then by helium for one hour, and the initial gas concentrations in the reaction flask were measured before the addition of 4 mL N\textsubscript{2}O. The initial GC/MS analysis did not show a significant amount of oxygen in the headspace. The reaction flask was monitored long enough to confirm that there was no increase in the N\textsubscript{2} concentration in the headspace. Hydrogen was then added in 0.5 mL (~20 μmol) aliquots until complete reduction to N\textsubscript{2} was achieved.
2.4.6 Effect of helium sparging time

A series of experiments on a 1.8 mM catalyst solution, prepared as described above, were conducted to investigate the effect of helium sparging time following H$_2$ exposure on the extent of N$_2$O reaction. The solution was sparged by hydrogen for 1 hour, then by helium for 2, 4, 6, 8, 10, or 12 hours. The amount of N$_2$ in the headspace was measured before the addition of 4 mL N$_2$O. The reduction of N$_2$O and formation of N$_2$ was monitored until the amount of dinitrogen in the headspace of the reaction vessel was constant.

2.4.7 Effect of elevated temperature during helium sparging.

A series of experiments on a 1.8 mM catalyst solution, prepared as described above, were conducted to investigate the effect of higher temperatures during the helium sparge on the extent of the N$_2$O reaction. The solution was sparged by hydrogen for 1 hour, then by helium for 1 or 2 hours in a fifty-degree water bath. The helium was bubbled through a water bubbler before addition to the reaction flask in order to avoid excess loss of water to evaporation. The amount of N$_2$ in the headspace was measured before the addition of 4 mL N$_2$O. The reduction of N$_2$O and formation of N$_2$ was monitored until the amount of dinitrogen in the headspace of the reaction vessel was constant.

2.4.8 Effect of temperature during reaction under H$_2$ atmosphere.

A series of experiments on a 1.8 mM catalyst solution, prepared as described above, were conducted to investigate the effect of higher temperatures during the reaction on the rate of the N$_2$O
reduction. The solution was sparged by hydrogen for 1 hour, then incubated in a water bath for half an hour. The bath temperatures were at 40° C, 30° C, or 0° C. The amount of N₂ in the headspace was measured before the addition of 4 mL N₂O, and the reaction flask was returned to the water bath between samples. The reduction of N₂O and formation of N₂ was monitored until the amount of dinitrogen in the headspace of the reaction vessel was constant.
3. Results and Discussion

3.1 Reduction of $^{15}$NO under hydrogen atmosphere using a 0.18 mM catalyst solution

The reduction of isotopically labeled $^{31}$NO using palladium nanoparticles protected by a soluble poly(N-vinyl-2-pyrrolidone) (PVP) polymer proceeded to completion, forming $^{46}$N$_2$O which was in turn reduced to $^{30}$N$_2$. In all cases of NO reduction, except for the experiments run without any buffer (discussed in the next section), the initial catalytic activity was only the reduction of NO to N$_2$O, without production of N$_2$ until the NO was almost completely gone.

The kinetics of the NO was pseudo-zero-order, with an average k-value of $0.39 \pm 0.07$ M/sec. The average k-value of N$_2$O reduction to N$_2$ was $0.047 \pm 0.009$ M/sec, an order of magnitude less than the slope of the NO reduction line (Fig. 3.1B, C) indicating that the reduction of N$_2$O on Pd-PVP is considerably slower than the reduction of NO. Previous runs using a separate suspension of catalyst with an experimental concentration of 0.18 mM also displayed a zero-order reduction profile, and the rate constants at different initial concentrations of NO were not statistically different from each other. The lack of dependence on the concentration of NO suggests that the rate-limiting step of the reaction is the reduction of NO on the palladium nanoparticles, rather than transport between the headspace and the catalyst solution, despite the relatively low solubility of NO in water.
Figure 3.1 (continued on next page)
The molar balance of the reduction of $^{31}$NO to $^{16}$N$_2$O is expected to be 2:1 from the reaction equation

$$2 \text{NO} + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \quad (15)$$

in the absence of ammonia production, and this is what was observed (Fig. 3.1 A, B.). When there was a discrepancy in the produced N$_2$O, the molar imbalance was consistently in favor of N$_2$O production (Fig. 3.2), suggesting a calibration difficulty rather than formation of ammonia. This was confirmed by the very low amount of NH$_3$ found in solution in post-experimental testing. Ammonia analysis by the HACH Low-range Ammonia test indicated that the produced ammonia was less than one ppm in all cases.
Figure 3.2. NO reduction with a greater-than-expected amount of N$_2$O production. The expected amount of N$_2$O production from t=1 min to t= 180 min, based on NO reduction, was 32.0 μmol. The actual ΔN$_2$O was 40.8 μmol. The difference is attributed to a calibration error; the NO calibration slope was significantly different than the calibration curves for other experiments run in that time period.

Ammonia production on Pd catalysts appears to vary greatly depending on the catalyst support, the phase of reaction, and any co-metals used. Production of NH$_3$ has been observed from NO on reactions of Pd-mixed metal catalysts in both the gas and the liquid phase. There are mixed results for ammonia production using pure Pd; IR studies of a Pd/Al$_2$O$_3$ catalyst observe no ammonia production from adsorbed NO, but previous experiments using the reaction setup explained in this work have observed up to 36% ammonia production. In no case was NH$_3$ production observed from N$_2$O. It is clear that the Pd/PVP catalysts have a potential application in the consistent production of N$_2$, rather than NH$_3$, from NO.

In the complete reaction in buffered solution, there is no N$_2$ production until the NO is completely reduced. This suggests that, despite the greater solubility of N$_2$O, NO is preferentially occupying the reaction sites on the palladium nanoparticles, indicating that the binding constant of the NO to the palladium surface is considerably greater than the binding constant of the N$_2$O. DFT
calculations of the binding of NO to Pd indicate that NO adsorbs to a high coverage\textsuperscript{74}, and that N\textsubscript{2}O will adsorb weakly in a number of conformations on Pd(110).\textsuperscript{75} The calculated reaction binding constants of NO and N\textsubscript{2}O on Pd (111) surfaces are -2.6 eV and -0.2 eV, respectively,\textsuperscript{76} and so the experimental results agree well with the theoretical data.

The amount of buffer in solution did not have a significant effect on the rate of N\textsubscript{2}O reduction, but when no buffer was present the pattern of reduction was slightly changed (Fig. 3.3D). The production of NO from N\textsubscript{2}O began when NO was still present, suggesting that the pH or ionic concentration of the solution was affecting the reduction. Buffered solutions had a pH averaging 7 and the non-buffered reaction solutions had a pH averaging 6.1. In non-buffered solution there was a visible difference in the reaction profile, with N\textsubscript{2} being produced while there was still NO present, although the k-constants were not significantly different from the buffered experiments. Further investigation is needed to determine if the effect is statistically significant, and if so, if the cause is the pH difference, the difference in the ionic strength of the solution, or some other explanation.

A)

![Graph](image)

**Figure 3.3** (continued on next page)
Figure 3.3 (continued on next page)
3.2 Stepwise $^{15}$NO and $^{46}$N$_2$O reduction by a 1.8 mM catalyst solution under helium atmosphere with an oxidized surface

Addition of NO to the system under He atmosphere showed no production of N$_2$O. Addition of aliquots of H$_2$ to the reaction bottle induced the reaction, and the production of N$_2$O continued until all of the hydrogen in the system was used up (Fig. 3.4). In the absence of hydrogen, the NO, N$_2$O, and N$_2$ levels were stable at rest for the 12 hours between sample collection. The lack of any initial reduction indicates that, at a minimum, a reduced surface is needed for N2O production to begin.
Figure 3.4. A) NO reduction to N₂O. Lines represent addition of aliquots of H₂. The first two additions are of 0.2 mL (~4 μmol), and the remainder are of 0.5 mL (~20 μmol). B) Reduction of N₂O to N₂. Lines represent addition of 0.5 mL H₂.
3.3 \(^{15} \text{N}_2\text{O} \text{ reduction under hydrogen atmosphere}

Under H\(_2\) atmosphere, the reduction of N\(_2\text{O}\) in a 1.8 mM catalyst solution proceeded at a rate limited by the availability of N\(_2\text{O}\) (Fig. 3.5). The moles of N\(_2\text{O}\) present roughly equal the amount of dinitrogen reduced, suggesting that N\(_2\text{O}\) is primarily reduced to N\(_2\), without significant ammonia production, although this was not tested as the catalyst was meant to be re-used.

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**Figure 3.5.** The reduction of 4 mL N\(_2\text{O}\) to produce N\(_2\) under hydrogen atmosphere.

The reduction of 2 mL N\(_2\text{O}\) under hydrogen atmosphere using a 1.8 mM catalyst solution displayed pseudo-first-order reaction kinetics with a k-value of 0.054 sec\(^{-1}\) (Fig.3.6). The reduction of 4 mL N\(_2\text{O}\) under hydrogen atmosphere also displayed first-order reaction kinetics, but with a slower reduction rate (k=0.021 sec\(^{-1}\)) (Fig. 3.7). The difference in the reaction times may indicate that some catalyst degradation had taken place between the two experiments, or it may suggest that a lower coverage of N\(_2\text{O}\) on the catalyst surface is desirable for improved reaction kinetics.
Figure 3.6. The natural logarithms of N\textsubscript{2}O concentration vs. time when 2 mL N\textsubscript{2}O is added to a 1.8 mM catalyst solution under H\textsubscript{2} atmosphere.

Figure 3.7. The natural logarithms of N\textsubscript{2}O concentration vs. time when 4 mL N\textsubscript{2}O is added to a 1.8 mM catalyst solution under H\textsubscript{2} atmosphere.
3.4 Effect of temperature during reaction under H\textsubscript{2} atmosphere.

Increasing or decreasing the temperature of the reaction flask visibly increases or decreases the rate of reduction of N\textsubscript{2}O (Fig. 3.8). The half-life of the N\textsubscript{2}O when the reaction was conducted at 40\textdegree{} C was 22 minutes, at 30\textdegree{} C was 30 minutes, at 24\textdegree{} C was 45 minutes, and at 0\textdegree{} C was 85 minutes.

Figure 3.8 (continued on next page)
Figure 3.8. Reduction of 4 mL N₂O at varying temperatures. A) 0°C  B) 24°C  C) 31°C  D) 40°C
A comparison of the first-order rate constants of N$_2$O reduction at different temperatures (Table 1, Fig. 3.9, A-D) shows that the temperature of the reaction has an effect on the rate of the reaction. The first-order rate constants are shown in Table 3.1, and the Arrhenius plot is displayed in Fig. 3.10. The E$_a$ for N$_2$O on palladium nanoparticles is 41.4 kJ/mol while the A is 466 s$^{-1}$.

A) 

![Graph](image1)

\[ y = -0.0058x + 4.9685 \]

\[ R^2 = 0.9705 \]

B) 

![Graph](image2)

\[ y = -0.0275x + 5.2051 \]

\[ R^2 = 0.9893 \]

**Figure 3.9** (continued on next page)
Figure 3.9. Natural logarithms of the concentration of N$_2$O under H$_2$ at A) 0° C, B) 23° C, C) 31° C, D) 40° C.
<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>k-value (sec$^{-1}$)</th>
<th>1/T</th>
<th>ln(k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>0.0058</td>
<td>0.003663</td>
<td>-5.1499</td>
</tr>
<tr>
<td>296</td>
<td>0.0205</td>
<td>0.003378</td>
<td>-3.88733</td>
</tr>
<tr>
<td>304</td>
<td>0.0389</td>
<td>0.003289</td>
<td>-3.24676</td>
</tr>
<tr>
<td>313</td>
<td>0.0585</td>
<td>0.003195</td>
<td>-2.83873</td>
</tr>
</tbody>
</table>

Table 3.1. Summary of the first-order rate constants of the plots in Figure 5.

Figure 3.10. Arrhenius plot for N$_2$O reduction on Pd-PVP catalysts
3.5 \( \text{N}_2\text{O} \) reduction by excess \( \text{H}_2 \) in a helium atmosphere

\( \text{N}_2\text{O} \) was reduced initially by the hydrogen associated with the palladium catalyst, and reduction ceased when the hydrogen was used up. \( \text{N}_2\text{O} \) reduction began again after the addition of an excess of hydrogen and continued until almost complete reduction. A further addition of \( \text{N}_2\text{O} \) demonstrated that there was still hydrogen present in the reaction flask and available for reaction (Fig. 3.11). The reaction displayed first-order reaction kinetics (Fig 3.12) with a \( k \)-value of only 0.012 \( \text{sec}^{-1} \), considerably lower than the \( k \)-values of reaction under pure hydrogen atmosphere. The difference in the reaction times may indicate that under circumstances of lowered hydrogen concentration, the reduction rate of \( \text{N}_2\text{O} \) is not dependent on the same rate-limiting step as when the solution is under hydrogen atmosphere. If the solution is saturated with hydrogen, any step in which hydrogen is involved will proceed at the maximum rate possible, and the rate of reaction may be controlled by the rate of a different step such as \( \text{N}_2\text{O} \) dissociation. If hydrogen is not as easily available, the reactions in which it is involved may be slowed, and the rate-limiting step may change.

![Graph](image)

**Figure 3.11.** Reduction of \( \text{N}_2\text{O} \) to \( \text{N}_2 \) starting from a hydrogen-treated, helium-flushed catalyst. 10 mL of hydrogen was injected into the headspace at \( t=86 \) minutes. An additional 1 mL of \( \text{N}_2\text{O} \) was added to the system at \( t=400 \) min
Figure 3.12. The natural logarithms of N$_2$O concentration vs. time when 4 mL N$_2$O is added to a 1.8 mM catalyst solution under He atmosphere with 10 mL added H$_2$.

3.6 $^{15}$N$_2$O interaction with oxygen or hydrogen-pretreated surfaces under helium atmosphere

Initial addition of N$_2$O to the reaction flask containing a catalyst solution that had been pretreated with oxygen before the helium sparge showed a decrease in the total N$_2$O found in the headspace but no corresponding increase in the dinitrogen amount. This implies that the total decrease in the N$_2$O can be attributed to the N$_2$O in the headspace, in solution, and adsorbed onto the palladium nanoparticles coming to equilibrium rather than to N$_2$O reduction to form N$_2$. Addition of hydrogen aliquots to the reaction vessel started the production of N$_2$, which ceased after the added hydrogen was completely reacted (Fig. 3.13A, 3.14A). In contrast, when N$_2$O was added to solutions that had been pre-treated with only hydrogen before the helium sparge, the production of N$_2$ showed that the hydrogen-pretreated surface in a helium atmosphere was capable of reducing N$_2$O for a brief period (Fig. 3.13B, 3.14B).

After the initial additions of hydrogen, the profiles for the reduction of N$_2$O on the oxygen- or hydrogen-pretreated catalyst were similar. The addition of an aliquot of 0.5 mL of hydrogen initiated the formation of dinitrogen, which continued until all of the available hydrogen had reacted.
Figure 3.13. A) Full reduction of N₂O to N₂ in a catalyst bottle sequentially treated with hydrogen, air, and helium. B) Full reduction of N₂O to N₂ starting from a surface only treated with hydrogen and helium. Lines represent the addition of 0.5 mL (~20 mmol) H₂.
3.7 Effects of the length and temperature of helium sparging on the hydrogen absorption into Pd nanoparticles

By investigating the reduction of nitrogen on hydrogen-pretreated surfaces under helium atmosphere, we wished to determine whether hydrogen was necessary for the initial dissociation of $N_2O$
into N₂ (g) and O(ads). If N₂O spontaneously dissociates on the Pd nanoparticles, and hydrogen is only necessary to remove the O(ads) from the palladium and clear the reaction side to allow another reaction to occur, then a clean palladium surface is all that is needed to observe the initial formation of N₂. If on the other hand, hydrogen is necessary for the initiation of the reaction, then N₂O dissociation can only occur if there is still Pd-H within or on the surface of the Pd nanoparticles. In order to investigate whether there was hydrogen present, the catalyst solutions were sparged with helium for extended lengths of time and at elevated temperatures to attempt to eliminate the hydrogen.

The changes in the amount of dinitrogen present before and after N₂O addition for different lengths of sparging time with helium at room temperature are shown in Table 3.2.

<table>
<thead>
<tr>
<th>Hours He sparge</th>
<th>N₂ produced (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>13.0</td>
</tr>
<tr>
<td>4</td>
<td>12.0</td>
</tr>
<tr>
<td>6</td>
<td>10.1</td>
</tr>
<tr>
<td>8</td>
<td>14.3</td>
</tr>
<tr>
<td>10</td>
<td>14.8</td>
</tr>
<tr>
<td>12</td>
<td>13.1</td>
</tr>
</tbody>
</table>

Table 3.2. Dinitrogen produced after differing lengths of helium sparge following H₂ pretreatment.

The variation between the amounts of N₂ produced for the different sparging times is within the range of variation for instrumental calibration, and there is no correlation between the sparging time
and the amount of dinitrogen produced. The amount of available hydrogen can therefore be considered to be unaffected by the He in the system after a stable state has been reached.

In the PVP-supported palladium nanoparticle studies, hydrogen can be absorbed on the surface of the palladium clusters and within the nanoparticle structure, but the poly(N-vinyl-2-pyrrolidone) support does not contribute hydrogen or accept spillover from the nanoparticles. Since the total nitrogen reduction on a pre-treated surface under helium atmosphere is reproducible within a margin of error, it can be assumed that the surface structures of the nanoparticles are not significantly altered over the course of the experiments. Because sparging the hydrogen-treated nanoparticles with helium for extended amounts of time did not affect the initial production of nitrogen on the particles, it is also clear that any Pd-H(ads) remaining on the particles is not in equilibrium with H₂(g) in the sample solution as is expected for hydrogen on solvated Pd nanoparticles at room temperature.

The question of whether there was any hydrogen available at all, or if the helium sparge had swept all of the hydrogen off was answered by the reduction of N₂O on surfaces pretreated with hydrogen, then sparged with helium at differing temperatures. The production of N₂ and reduction of N₂O after sparging the reaction bottle with helium at room temperature, for 1 hour at 50°C, or for 2 hours at 50°C are summarized below (Table 3.3), and a representative experiment is shown in Figure 3.15. There was no significant difference in nitrogen production between the room temperature helium sparge and a one hour sparge at 50°C, but the sparge at two hours produced significantly less nitrogen, and the reduction of N₂O was not significantly different from zero. Each experiment with a sparge at elevated temperature was followed by an experiment with a sparge at room temperature to ensure that no permanent change in the Pd-PVP catalyst was causing the changes in the reduction pattern. These results suggest that surface or subsurface hydrogen on the nanoparticles is at least partially contributing
to the N₂O reduction; when there is a lessened amount of hydrogen on or in the nanoparticles, the initial N₂O reduction decreases.

<table>
<thead>
<tr>
<th></th>
<th>ΔN₂</th>
<th>ΔN₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temperature:</td>
<td>16.7 ± 3.0</td>
<td>14.5 ± 5.0</td>
</tr>
<tr>
<td>1 Hour 50°C sparge</td>
<td>16.0 ± 3.1</td>
<td>18.3 ± 5.0</td>
</tr>
<tr>
<td>2 Hours 50°C sparge</td>
<td>7.6 ± 2.1</td>
<td>-1.3 ± 3.64</td>
</tr>
</tbody>
</table>

**Table 3.3.** Average production of dinitrogen and reduction of nitrous oxide after helium sparge at room temperature or 50°C for 1 or 2 hours.

![Graph](image)

**Figure 3.15.** Measurement of N₂ production after a helium sparge at room temperature.

Attempts to determine whether the hydrogen is adsorbed on the nanoparticle surface or adsorbed into the palladium nanoparticles through the initial production of dinitrogen were
unsuccessful due to a coincidental similarity between the dispersion of Pd on the nanoparticle surface and the amount of hydrogen expected to be absorbed in the nanoparticle. The diameter of the palladium nanoparticles produced using our synthetic method is 5 nm and a good approximation of the dispersion of surface Pd is the reciprocal of the diameter in nanometers; that is, $(5 \text{ nm})^{-1}$, or 0.2. In other words, for a nanoparticle of 5 nm in diameter, 20% of the palladium is expected to be on the surface. The ratio of hydride to surface palladium (H:Pd$_s$) is expected to be 1:1, so the amount of hydride expected from the total palladium is also 0.2 H : 1 Pd. Yamauchi et al. have shown, however, that for adsorbed hydride in Pd/PVP nanoparticles, the expected amount of adsorbed hydride is also 0.2 H’s per Pd. Because the predicted amounts of absorbed and adsorbed hydride are equivalent, a definite assignment of the location of the hydrogen responsible for initial N$_2$O reduction is not possible with these experiments.
4. Conclusions

As was discussed in Section 1, the ability to catalytically reduce NO and N$_2$O will become increasingly important in coming years, both because of the health and environmental risks from increased production of the two gases and as a subset of research into the total catalytic reduction of nitrate to dinitrogen. Preliminary investigations showed that the catalytic system of palladium nanoparticles encapsulated in a water-soluble poly(N-vinyl-2-pyrrolidone) (PVP) polymer would reduce both gases completely to N$_2$ using hydrogen as the electron donor, and further study of the reduction mechanism was warranted.

Our investigations of NO reduction have shown that the transformation of NO to N$_2$O on the nanoparticle surface is rapid and that little or no dinitrogen is formed until the NO is completely reduced. Although IR investigations of NO$_2$ reduction to dinitrogen have seen NO formed on surface particles, NO has not been observed in the gas phase in nitrate reduction experiments. Also, DFT calculations indicate that the binding constant of N$_2$O to the palladium surface is considerably less than that of NO. Our results confirm that the NO is not seen in the gas phase of nitrite reduction because it binds to the palladium surface too strongly and reacts too quickly.

The stepwise reductions of NO and N$_2$O by hydrogen aliquots under a helium atmosphere confirm that hydrogen is necessary for continuous reaction, and that the ratios of the gases present are stable in the absence of hydrogen. No reaction occurs when the catalyst solution has been pretreated with air, but N$_2$ is formed from N$_2$O when the catalyst solution has been pretreated with only hydrogen. It is likely that in the air-sparged experiments oxygen adatoms occupy the reaction sites on the Pd nanoparticles, preventing further binding and reaction of NO and N$_2$O.
It was uncertain whether hydrogen was necessary for the reaction of $\text{N}_2\text{O}$ to $\text{N}_2$, or if it was simply needed to reduce the nanoparticle surface after the initial reaction in order to allow for further $\text{N}_2$ production. In order to determine this, the solutions were heated in order to drive off any hydrogen still present in or on the palladium. Significantly less dinitrogen production was observed when $\text{N}_2\text{O}$ was added to a catalyst solution that had been sparged by helium at 50 C for 2 hours, indicating that hydrogen is necessary for $\text{N}_2$ to be formed at all. Although the location of the hydrogen has not been experimentally determined, we have observed that there is no relationship between length of a helium sparge at room temperature and the amount of dinitrogen produced, indicating that Pd-H is not in equilibrium with the surrounding solution.

We have investigated the reduction of NO and $\text{N}_2\text{O}$ and have found that palladium nanoparticles supported on PVP are an effective catalyst for the complete reduction of these gases to dinitrogen without undesirable side reactions. Mechanistic investigations indicate that a reduced surface with hydrogen present is necessary for the reaction to proceed, and further research is needed to determine the exact role the hydrogen plays in the mechanism.
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