

Exploration of Reduction Catalysis for the Elimination of Nitrogen Oxides from Engine
Exhaust
Undergraduate Honors Thesis

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Degree with Honors Research Distinction in Chemical Engineering in The Ohio State
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Abstract

In recent years there has been a push for more efficient lean-burn engines that operate with higher air-to-fuel ratios. In order to support this demand, the need has arisen for an effective catalytic system to control the emissions of nitrogen oxides (NO_x) from such engines. In this work, a study was performed on reduction catalysts prepared with 0.3% Pd by mass supported on sulfated zirconia (0.3% Pd/SZ) through a single-pot sol-gel process. The catalysts were prepared with varying alkoxide concentrations and $\text{Zr}:\text{SO}_4^{2-}$ ratios. Surface area and pore volume characterizations were performed on the samples and it was found that increasing the $\text{Zr}:\text{SO}_4^{2-}$ ratio decreased the surface area and pore volume of the catalysts. Catalyst activity testing was performed on the catalysts in a simulated exhaust stream and the catalyst prepared with the highest alkoxide concentration (1.3 M) and the highest $\text{Zr}:\text{SO}_4^{2-}$ (3:1) ratio was found to have the highest activity per surface area. This catalyst was found to be highly resistant to increases in gas hourly space velocity. Pd supported on sulfated ceria and zirconia mixtures were prepared through incipient wetness impregnation. The addition of 10% Co/Ceria in varying ratios to 0.3% Pd/SZ (1.3/3) was found to significantly increase NO_x conversion and fully oxidize CO species. The optimum ratio of 0.3% Pd/SZ (1.3/3) to 10% Co/Ceria was found to be 8:1 by mass.

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Chapter 1: Introduction

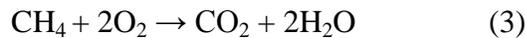
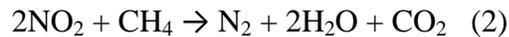
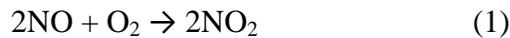
1A. Background

In recent years there has been a push for more efficient lean-burn engines that operate with higher air-to-fuel ratios. Standard three-way catalysts do not have the robustness to control the emissions of nitrogen oxides (NO_x) from such engines. The release of active nitrogen species, including NO_x , to the atmosphere has many negative impacts on the environment including soil and water acidification (which leads to destructive phenomena such as acid rain), coastal eutrophication (particularly more frequent occurrence of red tides and poisonous phytoplankton blooms), and reduced plant biodiversity¹. As a result, the need has arisen for an efficient and cost-effective catalytic system to control NO_x emissions created as a byproduct during fuel combustion to meet stringent regulatory requirements.

Currently, the most common method to control NO_x emissions from engines is through the selective catalytic reduction (SCR) of NO_x with ammonia to produce N_2 , H_2O , and CO_2 ². However, this process is costly and mostly restricted to stationary applications due to the likelihood of ammonia slip, the release of hazardous ammonia to the environment. Due to the complications associated with ammonia SCR, much emphasis has been placed on the development of catalytic systems for the reduction of NO_x by unused hydrocarbons from the combustion process²⁻⁹. This process eliminates the

introduction of a toxic reactant from outside of the system and eliminates unused hydrocarbons, reducing the overall output of volatile organic compounds from the engine.

In order to facilitate this NO_x reduction method, nitrogen monoxide (NO) should be first converted to nitrogen dioxide (NO₂) before being reduced to molecular nitrogen (N₂) by the hydrocarbon species. This is due to the fact that NO₂ is a stronger oxidizing agent than NO and can more readily react with the reducing agent (methane) to form N₂. The higher oxidation potential of NO₂ allows NO_x reduction to better compete with the methane combustion reaction. The brief reaction scheme can be described as follows:



Reaction 3 is an undesired side reaction as it uses up the methane available for NO_x reduction.

It is also important that the oxidation and reduction catalysts be intimately mixed rather than be contained in two separate reactors. A simple thought experiment can help demonstrate this point. Figure 1.1 shows a two reactor system for oxidation before reduction.

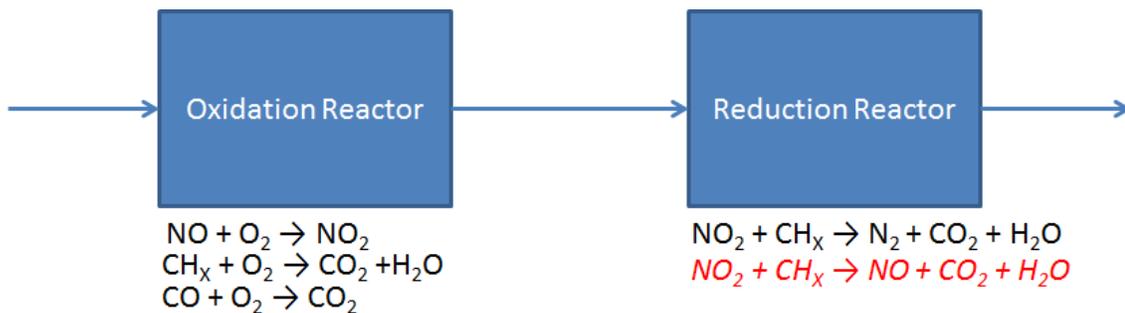


Figure 1.1. Two Reactor Oxidation-Reduction NO_x Reduction System

The italicized reaction shows that some of the NO_2 is partially reduced to NO . In order to obtain higher conversion, another oxidation reactor and reduction reactor would need to be placed after the first reduction reactor. By mixing the oxidation and reduction catalysts physically, this series of oxidation and reduction reactors can be achieved on an infinitesimal basis as shown in Figure 1.2.

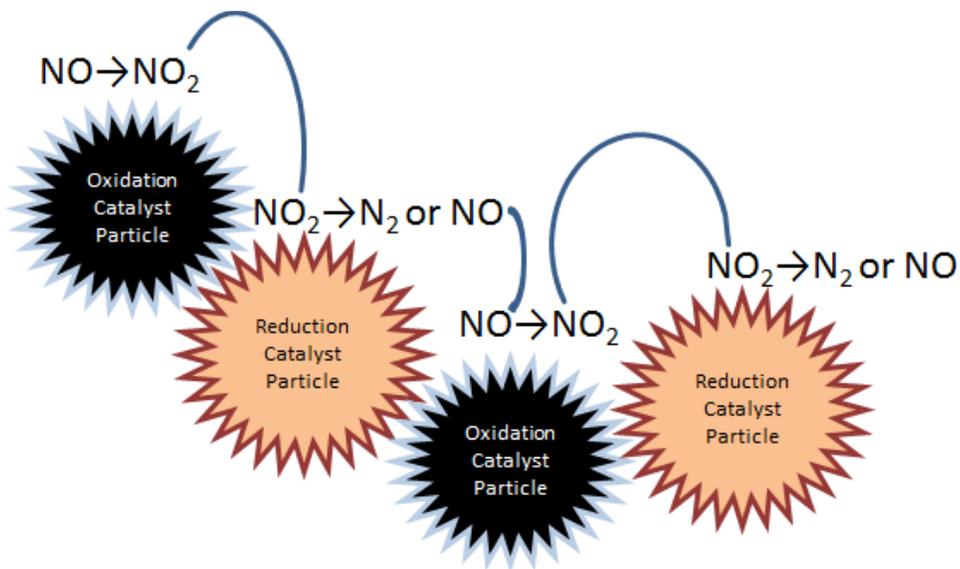


Figure 1.2. Catalyst Particles as an Infinitesimal Series of Reactors

By completing this process on an infinitesimal basis, very high conversions can be achieved.

The success of the catalytic pathway involving the oxidation of NO prior to NO_x reduction has previously been studied and found to yield favorable results. Previous work on highly active catalysts for the oxidation of NO has been performed by Dr. Ozkan's Heterogeneous Catalysis Research Group at the Ohio State University (HCRG). Catalysts comprised of cobalt supported on zirconia and titania nanoparticles have been found to be the most effective³⁻⁵. Further development of NO_x reduction catalysts is necessary for successful implementation of this catalytic process.

In this work, a reduction catalyst comprised of palladium supported on sulfated zirconia (Pd/SZ) prepared through a single vessel sol-gel process was examined for NO_x reduction activity. Surface area characterization and activity testing were performed on this catalyst. In addition, reduction catalysts comprised of palladium supported on sulfated zirconia and ceria were prepared through incipient wetness impregnation.

For optimum use of the oxidation-reduction catalyst path, an intimate mixture of the oxidation and reduction catalysts should be used. Previous work has been performed on the effect of the usage of an intimate mixture of an oxidation and reduction catalyst to achieve the selective catalytic reduction of NO_x species³⁻⁵. In this work, the effects of the catalyst ratio was examined for Pd/SZ and oxidation catalysts comprised of 2% and 10% cobalt supported on ceria nanoparticles.

For catalysis in general, the effects of residence time can be very significant in the overall performance of a catalyst. In order to examine this effect, the reduction catalyst was also examined under different gas hourly space velocity (GHSV) of reactant feed. This information can be used in developing the reactor in which the catalyst will be implemented.

The overall development and implementation of the catalysts examined in this work could have a significant impact on environmental conservation and sustainability. If exhaust aftertreatment of lean-burn engines is improved, they can replace some standard engines, increasing the efficiency of fossil fuel use. These engines also reduce the amount of unburned hydrocarbons that are released to the atmosphere. Through the further development of this technology, the health and environmental harms from the burning of fossil fuels can be greatly reduced.

1B. Literature Review

As mentioned above, there has been significant work done in the area of NO_x reduction using hydrocarbons present in the exhaust stream as the reducing agent. The following is a review of the literature pertaining to the use of catalysts containing palladium to this effect.

1B.1 Palladium Reduction Catalysts

It has been found that the catalytic reduction of NO_x over Pd catalysts supported on inert zeolitic supports occurs in a two-step mechanism. NO decomposition results in oxygen poisoning the active sites. Methane then reacts with the oxygen to combust, thus regenerating the active sites⁶. Therefore, catalysts comprised of Pd supported on inerts are poisoned in the presence of excess oxygen environments such as lean-burn engine exhaust. However, Pd supported on acidic materials, such as the zeolites H-ZSM-5 or H-Mordenite, has been shown to be selective for the reduction of NO over O₂. This selectivity is attributed to the improved dispersion of Pd on the surface of acidic supports leading to Pd²⁺ in the presence of oxygen rather than the methane-combustion-favoring PdO clusters that form on the surface of inert supports⁷. This makes Pd catalysts supported on acidic supports ideal candidates for study on the reduction of NO_x in lean-burn engine exhaust.

The benefit of the acidic catalyst supports is their ability to stabilize Pd²⁺ ions. Chin et al. examined the use of sulfated zirconia as a support for Pd in NO_x reduction catalysis and reported on its ability to stabilize the Pd²⁺ ions. Sulfated zirconia is preferred over the traditional zeolite supports due to its resistance to degradation in the presence of water vapor. Under high temperatures in the presence of water, zeolites are

known to collapse due to dealumination⁸. The effect of sulfate loading on sulfated zirconia supported palladium catalysts has also been studied. It has been shown that medium concentration of sulfate, approximately 4% by mass, yielded the highest activity and selectivity at the desired reaction temperature of 450°C. Variations in sulfate content had a significant effect on the catalytic activity as increased sulfate concentrations eventually had a negative effect on the palladium dispersion⁹. The effect of sulfate loading was studied further in this work.

The preparation of Pd supported on sulfated zirconia for these studies was a complicated process involving several incipient wetness impregnation steps⁸⁻⁹. Hamouda, et al. developed a simpler single-pot sol-gel process for the synthesis of sulfated zirconia for use in *n*-hexane isomerization. This process used acetic acid as an *in-situ* source of water for hydrolysis, greatly reducing the rate of gel formation which allowed a more consistent gel and improved acidity of catalyst¹⁰. This catalyst preparation method was further explored in this work as palladium was introduced to the sol-gel method to create a Pd supported on sulfated zirconia catalyst for NO_x reduction.

1B.2 Dual-Catalyst Mixed Bed

As discussed earlier, the introduction of oxidation catalyst to a NO_x reduction catalyst can be highly beneficial to overall NO_x conversion. Co catalysts supported on titania and zirconia prepared through incipient wetness impregnation as well as sol-gel methods have been shown to be highly active for NO and CO oxidation³. These recipes were adapted for the preparation of Co supported on ceria through a simple wetness impregnation. Pd supported over sulfated zirconia prepared through both incipient wetness impregnation and sol-gel techniques were tested with the Co supported on

zirconia catalysts and proved to have higher conversion in the presence of the oxidation catalyst⁴⁻⁵. This mixed-catalyst bed methodology was used in this work.

Chapter 2: Experimental Methodology

2A. Reaction Apparatus

In order to perform the desired activity testing on the catalysts, an experimental apparatus (NO_x reactor system) was assembled. The NO_x reactor system consisted of six mass flow controllers (MFCs) that allowed the simulation of different realistic exhaust compositions. The simulated exhaust is allowed to pass through a catalyst filled tube reactor in a custom-assembled temperature-controlled furnace. Samples of the reactor effluent stream were then analyzed by an Agilent Technologies Micro-Gas Chromatograph equipped with Molecular Sieve and Poraplot-Q columns (MicroGC) as well as a Thermo Electron Corporation Model 42i High Level Chemiluminescence NO-NO₂-NO_x analyzer (NO_x Analyzer). A schematic diagram of the NO_x reactor system is shown in Figure 2.1.

The NO_x Analyzer uses light generated from the reaction of ozone with NO. An ozonator takes oxygen from the air and creates ozone. A sample of the reactor effluent is split in two and sent either straight to the ozone reactor or through a stainless steel reactor to convert NO₂ to NO before being introduced to ozone. The NO in both the unreacted and NO₂ converted samples react with ozone in their respective reactors and a photomultiplier tube detects the amount of light given off by each reaction. From the

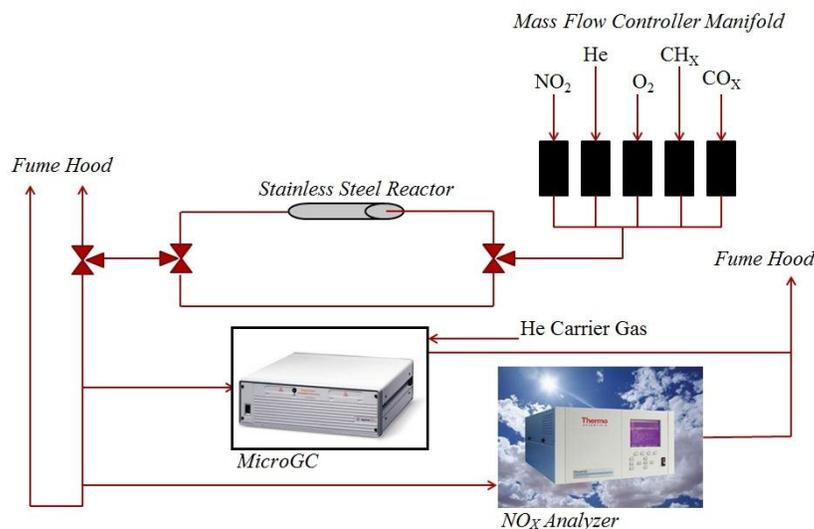


Figure 2.1 Schematic Diagram of NO_x Reactor System

light detected from the unconverted sample, the amount of NO in the effluent stream can be calculated. From the light detected in the NO₂-converted sample, the total amount of NO_x species in the effluent stream can be calculated. The difference in these two values gives the amount of NO₂ in the effluent stream¹¹.

The MicroGC uses gas chromatography to analyze the composition of an effluent stream. A sample of the effluent is fed to both columns. Depending on molecular interactions with the walls of the columns, different species pass through the columns at different rates. The flow rates leaving the column are measured and plotted versus time. Normalized peaks result from different species leaving the columns at different times. The areas under these peaks are converted to concentrations using calibrated response factors. The molecular sieve column was used to determine concentrations of O₂, N₂, CH₄, and CO. The plot Q column was used to determine concentrations of CO₂, N₂O, C₂H₆, and C₃H₈.

2B. Sol-Gel Catalyst

2B.1 Sol-Gel Catalyst Preparation

The Pd supported on sulfated zirconia reduction catalyst was prepared through a single vessel sol-gel process adapted from the work of Hamouda et al.¹⁰. A solution of palladium acetate in n-propanol was prepared with the appropriate amount of palladium to achieve a final catalyst of 0.3% Pd by weight. A portion of a solution of zirconium propoxide in n-propanol was added to the solution to achieve the desired alkoxide concentration. A portion of concentrated sulfuric acid was then added to the solution to achieve the desired $\text{Zr}:\text{SO}_4^{-2}$ ratio. Glacial acetic acid was added to the solution drop wise as a gelation agent while stirring to achieve a hydrolysis ratio of 4. See Appendix 1 for sample calculations. The solution was stirred until gelation occurred. The gels were then dried overnight at 110°C and then calcined at 700°C for 4 hours. Catalysts were prepared with the alkoxide concentrations and zirconium to sulfate ratios shown in Table 2.1.

Table 2.1 Sol-Gel Preparation Parameters

Alkoxide Concentration	$\text{SO}_4^{-2}:\text{Zr}$ Ratio
0.3 M	0.5
0.3 M	1
0.3 M	2
0.3 M	3
0.6 M	0.5
0.6 M	1
0.6 M	2
0.6 M	3
1 M	0.5
1 M	1
1 M	2
1 M	3
1.3 M	0.5
1.3 M	1
1.3 M	2
1.3 M	3

2B.2 Sol-Gel Catalyst Characterization

The sol-gel catalysts were characterized using a Micromeritics Accelerated Surface Area and Porosimetry Analyzer (ASAP 2020). The Brunauer, Emmett, and Teller (BET) surface area analysis technique was used to determine the surface area and pore volume of the samples. In this nondestructive technique, a sample of approximately 500mg of catalyst is placed in a glass sample tube with a rubber stopper and glass rod that eliminates much of the free volume in the tube. This vial is placed in the degasification port where a vacuum is introduced to remove impurities and air from the sample tube over the course of 12 hours. The sample tube is then placed in the analysis port above a reservoir of liquid nitrogen. A flow of nitrogen is introduced to the sample tube which is then lowered into the reservoir of liquid nitrogen. The adsorption isotherm is observed as nitrogen adsorbs onto the surface of the sample in monolayers. The sample tube is then removed from the liquid nitrogen reservoir and the desorption isotherm is observed. From these isotherms and sample mass, the surface area and pore volume are calculated¹².

2B.3 Sol-Gel Catalyst Activity Testing

The sol-gel catalysts were each tested in the NO_x reactor system for activity in the NO_x reduction reaction. A mass of catalyst that had surface area of 10 m² was combined with quartz powder to a total mass of 300 mg and placed into a stainless steel reactor tube supported with small plugs of quartz wool. Sample calculations can be seen in Appendix 1. By keeping the surface area of the catalyst constant and adding quartz powder to achieve constant catalyst bed mass, the activity per surface area of the catalyst can be examined while holding the GHSV constant. The reactor was then placed in the NO_x

reactor system and was pretreated with 10% oxygen in helium at 400°C for 30 minutes at a flow rate of 40 cm³/minute. This pretreatment oxidizes any of the metal active sites to improve activity. The reactor temperature was then reduced to 300°C and a simulated exhaust stream consisting of 400 ppm NO₂, 2100 ppm CH₄, 10% O₂, and balance helium at a flow rate of 40 cm³/minute. MicroGC and NO_x analyzer readings were recorded once the system reached steady-state. The temperature of the reactor was increased in 50°C increments to 500°C and the same readings were taken.

In order to examine the effects of GHSV, the catalyst that achieved the highest conversion per surface area was tested under three different flow rates. A 263 mg sample of Pd/SZ prepared with an alkoxide concentration of 1.3M and a Zr:SO₄⁻² ratio of 3 (Pd/SZ (1.3/3)), which had a total surface area of 10 m², was combined with quartz powder to a total mass of 300 mg and placed into a stainless steel reactor tube supported with small plugs of quartz wool. The reactor was then placed in the NO_x reactor system and was pretreated with 10% oxygen in helium at 400°C for 30 minutes at a flow rate of 40 cm³/minute. The reactor temperature was then reduced to 300°C and a simulated exhaust stream consisting of 400 ppm NO₂, 2100 ppm CH₄, 10% O₂, and balance helium at a flow rate of 40 cm³/minute. MicroGC and NO_x analyzer readings were recorded once the system reached steady-state. The temperature of the reactor was increased in 50°C increments to 500°C and the same readings were taken. This process was repeated with new catalyst using flow rates of 50 cm³/minute and 70 cm³/minute.

2C. Incipient Wetness Catalyst Preparation

The ceria-zirconia supports of the incipient wetness catalysts were prepared through a coprecipitation reaction in a sodium hydroxide solution with cerium nitrate and zirconyl nitrate as the precious metal precursors. First, a solution of sodium hydroxide in water was prepared at the desired concentration. Then a solution of cerium nitrate and zirconyl nitrate in water was prepared at the desired ratio. The solution of sodium hydroxide was added to the precursor solution and allowed to stir for 24 hours. The precipitate was filtered from the solution and washed to neutral pH with distilled water. This filtered precipitate was dried at 115°C overnight and then calcined at 500°C for 3 hours to complete the oxidation process and drive off any unwanted organics.

A BET surface analysis was performed on each of these supports as described in section 2B.2 to determine the pore volume. Using these pore volumes, an incipient wetness impregnation of sulfate groups was performed. A solution of ammonium sulfate in water was prepared with a volume equal to the pore volume of a mass of sample at a concentration necessary to deposit the desired amount of sulfate groups. This solution was added dropwise to the sample and spread evenly throughout the sample. The sample was mixed then placed in a drier at 115°C overnight for all of the water to evaporate from the surface. This method was repeated for higher concentrations of sulfate groups because the desired amount of ammonium sulfate could not be dissolved in one impregnation's volume of water. The samples were then calcined at 500°C for 3 hours to drive off all unwanted organics.

Another BET surface analysis was performed on each of these sulfated supports as described in section B.2 to determine the pore volume. Using these pore volumes, an

incipient wetness impregnation of palladium metal was performed. A solution of palladium chloride in water was prepared with a volume equal to the pore volume of a mass of sample at a concentration necessary to deposit 0.3% palladium by mass on the sample. This solution was added dropwise across the surface of the sample. The sample was mixed with a glass stirring rod then placed in a drier at 115°C overnight for all of the water to evaporate from the surface. This method was repeated because the necessary amount of palladium chloride could not be dissolved in one impregnation's volume of water. The samples were then calcined at 500°C for 3 hours to drive off all unwanted organics. Please see Appendix 1 for sample calculations. The catalysts formulations that were prepared are shown in Table 2.2.

Table 2.2. IWI Catalyst Formulations

Ce:Zr Ratio	[SO ₄ ⁻²] (% m/m)
1:0	5
1:0	10
1:0	15
1:1	5
1:1	10
1:1	15
1:3	5
1:3	10
1:3	15
3:1	5
3:1	10
3:1	15

Unfortunately, the project changed direction after the preparation of these catalysts and significant activity testing was never performed.

2D. Dual Catalyst Mixed Bed

2D.1 Oxidation Catalyst Preparation

The ceria nanoparticle support for the Co/CeO₂ oxidation catalyst was prepared through a coprecipitation reaction in a sodium hydroxide solution with cerium nitrate as the precious metal precursor. First, a solution of sodium hydroxide in water was prepared

at the desired concentration. Then a solution of cerium nitrate in water was prepared. The solution of sodium hydroxide was added to the precursor solution and allowed to stir for 24 hours. The precipitate was filtered from the solution and washed to neutral pH with distilled water. This filtered precipitate was dried at 115°C overnight and then calcined at 400°C for 3 hours to complete the oxidation process and drive off any unwanted organics.

The Co/CeO₂ oxidation catalyst was then prepared through a wetness impregnation of these ceria nanoparticles using a solution of cobalt nitrate. The wetness impregnation involved stirring the support powder in an aqueous solution of the cobalt nitrate precious metal precursor for twenty-four hours before evaporating off the water. The resulting solid was crushed into a powder and calcined at 400°C for three hours. The catalyst was prepared with 10% by weight cobalt (10% Co/CeO₂). Please see Appendix 1 for sample calculations.

2D.2 Mixed Bed Activity Testing

To test the activity of the mixed bed of oxidation and reduction catalyst, reaction experiments were performed on the NO_x reactor system. First, a 200 mg sample of Pd/SZ (1.3/3) was physically mixed with a sample of 10% Co/CeO₂ to achieve the desired mass ratio. In addition to pure reduction catalyst, physical catalyst mixtures with mass ratios of 2:1, 4:1, and 8:1 reduction to oxidation catalyst were tested in these experiments. The catalysts were mixed with quartz powder to achieve a total catalyst bed of 300 mg. This mixture was placed in a stainless steel reactor and held in place with quartz wool plugs. The reactor was then placed in the NO_x reactor system and was pretreated with 10% oxygen in helium at 400°C for 30 minutes at a flow rate of 50 cm³/minute. The reactor

temperature was then reduced to 300°C and a simulated exhaust stream consisting of 180 ppm NO₂, 1737 ppm CH₄, 208 ppm C₂H₆, 104 ppm C₃H₈, 10% O₂, 650 ppm CO, 6.5% CO₂, and balance helium at a flow rate of 50 cm³/minute. This composition represents a more realistic engine effluent from a lean-burn engine. MicroGC and NO_x analyzer readings were recorded once the system reached steady-state. The temperature of the reactor was increased in 50°C increments to 500°C and the same readings were taken.

Chapter 3: Results and Discussion

3A. Sol-Gel Catalyst

3A.1 Sol- Gel Catalyst Characterization

During the preparation of sol-gel reduction catalysts, samples with high alkoxide concentration and low $\text{Zr}:\text{SO}_4^{2-}$ ratios gelled too quickly before all of the acetic acid could be added to the solution. These catalysts were discarded as the preparation method was not effective for these samples. The surface area data for the catalysts that were successfully prepared is shown in Figure 3.1.

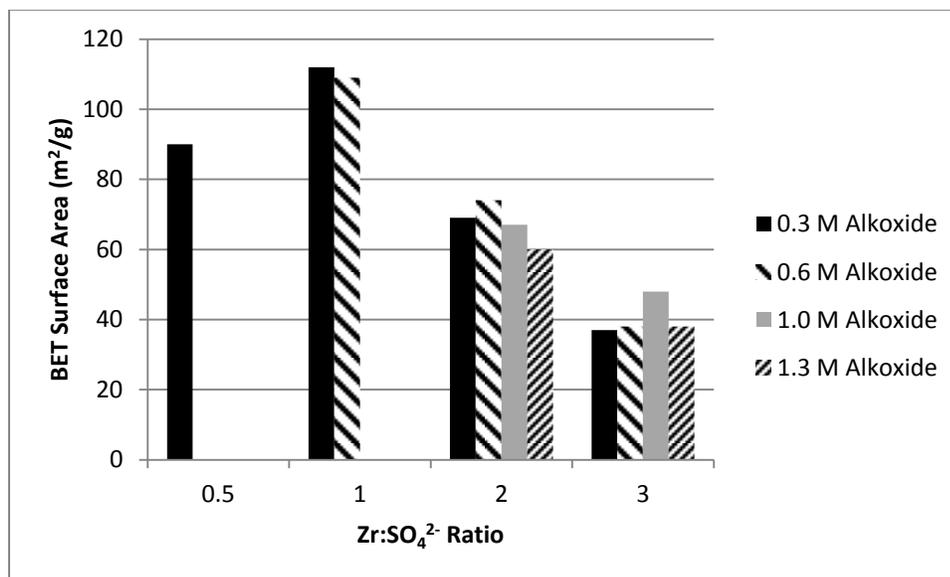


Figure 3.1. BET Surface Area of Pd/SZ Sol-Gel Catalysts

As can be seen from this figure, higher ratios of zirconium to sulfate during preparation resulted in a catalyst with lower surface area. However, a significant trend in

the relationship between alkoxide concentration and surface area does not appear in the data. The pore volume data for the catalysts is shown in Figure 3.2. This data follows a similar trend of decreasing pore volume with increasing $\text{Zr}:\text{SO}_4^{2-}$ ratio. There is also not a significant trend in the relationship between alkoxide concentration and pore volume in the data

Because the samples prepared with lower $\text{Zr}:\text{SO}_4^{2-}$ ratios gelled before all of the acetic acid could be added, it can be inferred that decreasing this ratio decreases the gelation time of the catalyst. When compared with the data in Figures 3.1 and 3.2, this suggests a possible inverse relationship between gelation time and surface area or pore volume.

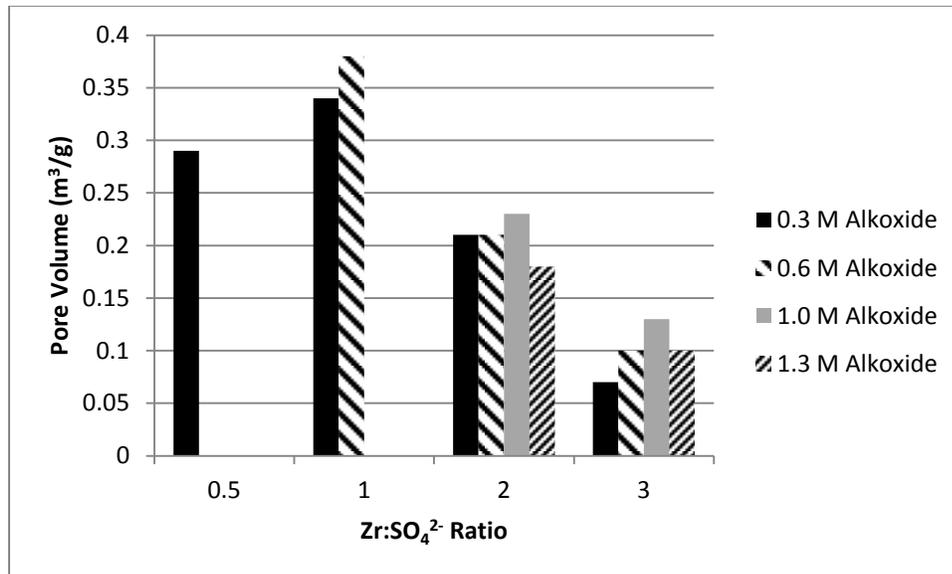


Figure 3.2. Pore Volume of Pd/SZ Sol-Gel Catalysts

3A.2 Sol-Gel Activity Testing

In order to examine the results of the sol-gel activity testing, the catalysts that were prepared under each alkoxide concentration were compared. It is important to note that the temperature of 450°C is of most significance because it is closest to the standard

operating temperature of natural gas engines. Figure 3.3 shows the NO_x conversion for the Pd/SZ reduction catalysts that were prepared using 0.3 M alkoxide.

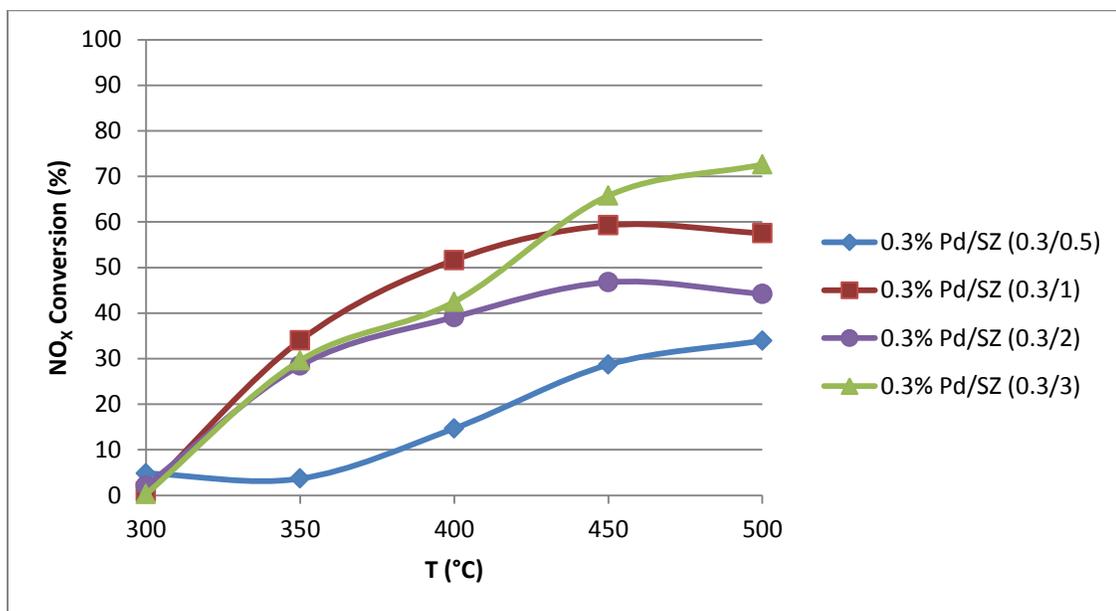


Figure 3.3. NO_x Conversion of Pd/SZ Catalysts Prepared with 0.3 M Alkoxide

From this data it can be seen that the catalysts prepared with a Zr:SO₄²⁻ ratio of 0.5 had significantly less conversion than the other catalysts. However, there is not a noticeable trend in activity as this ratio is increased. When the data from the catalysts prepared with an alkoxide concentration of 0.6M and 1M is analyzed (Figures 3.4 and 3.5), the conversions are even more similar between the different Zr:SO₄²⁻ ratios.

The most significant difference in activity can be seen in the activity testing of the Pd/SZ catalysts that were prepared with an alkoxide concentration of 1.3 M shown in Figure 3.6. The catalyst prepared with a Zr:SO₄²⁻ ratio of 3 had significantly higher activity than that with a ratio of 2. Two more trials with the better performing catalyst were done to test the repeatability. These repeated tests returned slightly lower NO_x conversion, but the conversion was still higher than the catalyst with a Zr:SO₄²⁻ ratio of 2.

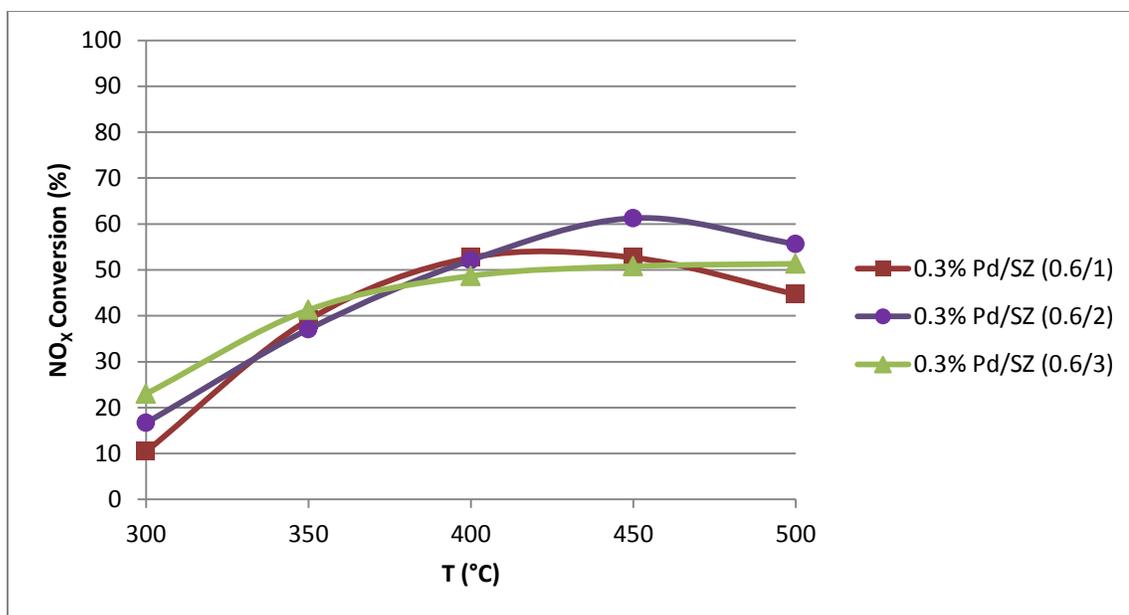


Figure 3.4. NO_x Conversion of Pd/SZ Catalysts Prepared with 0.6 M Alkoxide

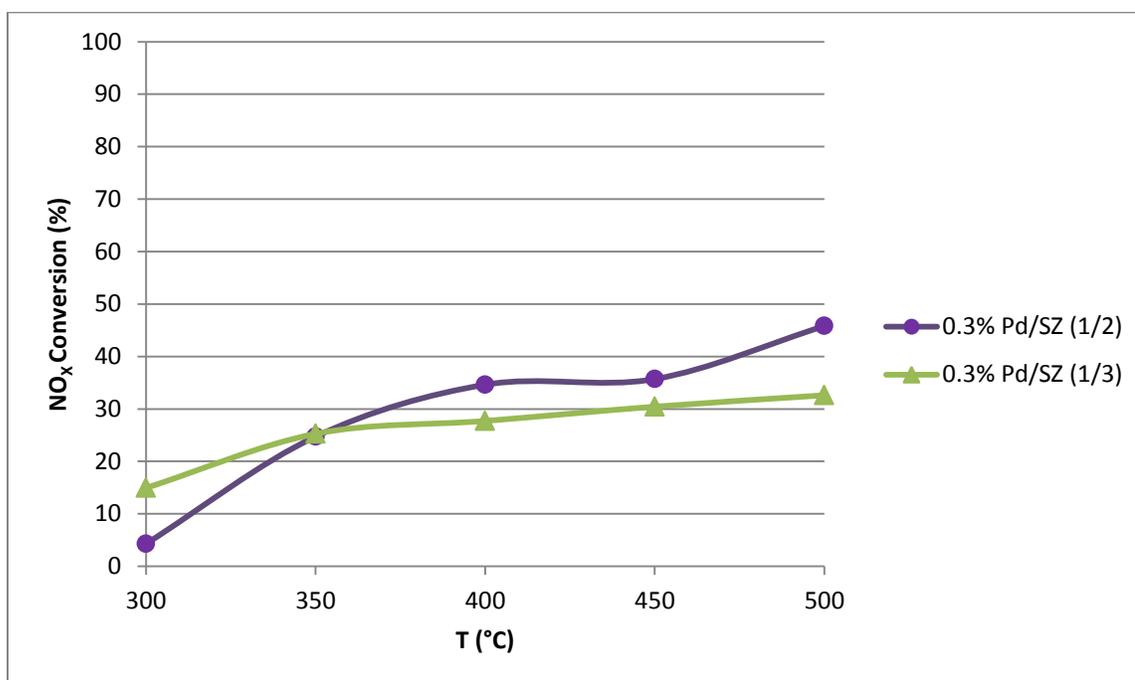


Figure 3.5. NO_x Conversion of Pd/SZ Catalysts Prepared with 1 M Alkoxide

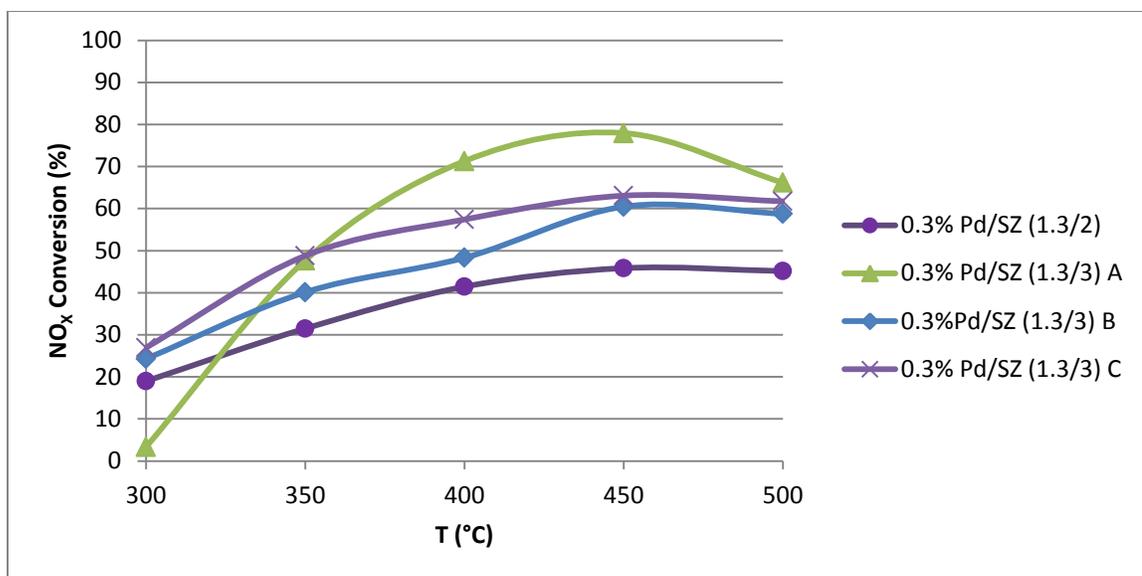


Figure 3.6. NO_x Conversion of Pd/SZ Catalysts Prepared with 1.3 M Alkoxide

From these data it can be seen that the catalyst 0.3% Pd/SZ (1.3/3) was able to achieve the highest NO_x conversion in the tests. This catalyst was able to achieve 60-78% NO_x conversion at 450°C. This catalyst was prepared with the highest alkoxide concentration and highest Zr:SO₄²⁻ ratio examined. This suggests that an interaction of high concentrations of zirconium propoxide and low concentrations of sulfuric acid create a catalyst with a high number of active sites per surface area of catalyst.

In addition to the main goal of NO_x reduction, another aspect of activity for the reduction catalysts that should be analyzed is the conversion of methane. As can be seen in Figures 3.7-3.10, there was not a large amount of variability in the methane conversion for these catalysts for the same activity testing shown above. However, it is obvious that the catalysts prepared with 1.3M alkoxide performed better with 50-70% methane conversion at 450°C while most other samples performed in the 30-60% range of methane conversion. The 0.3% Pd/SZ (1/2) performed significantly worse than the other samples. It is not clear why this occurred.

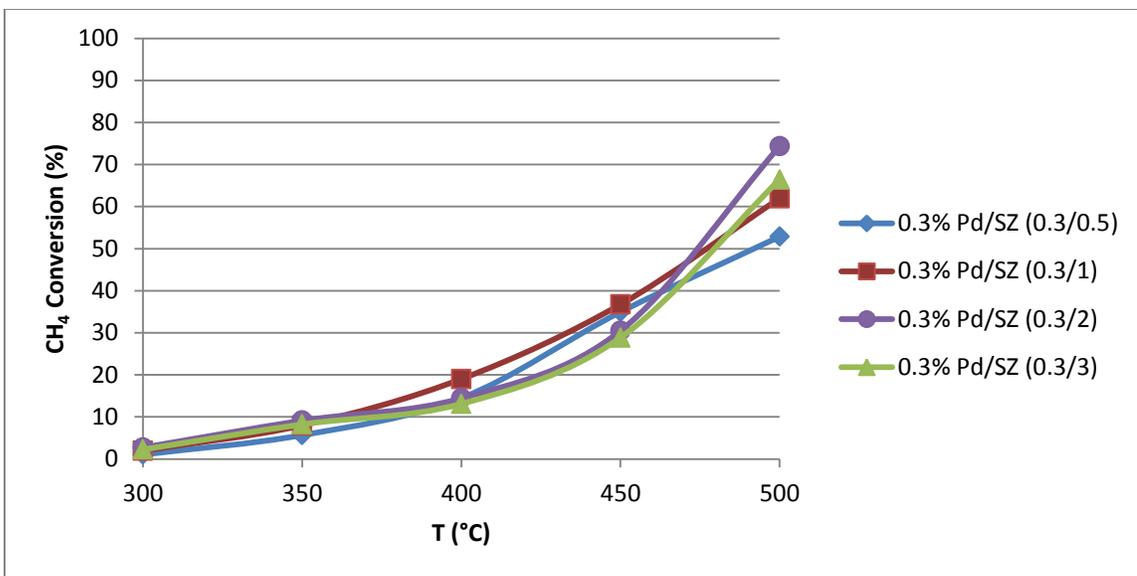


Figure 3.7. CH₄ Conversion of Pd/SZ Catalysts Prepared with 0.3 M Alkoxide

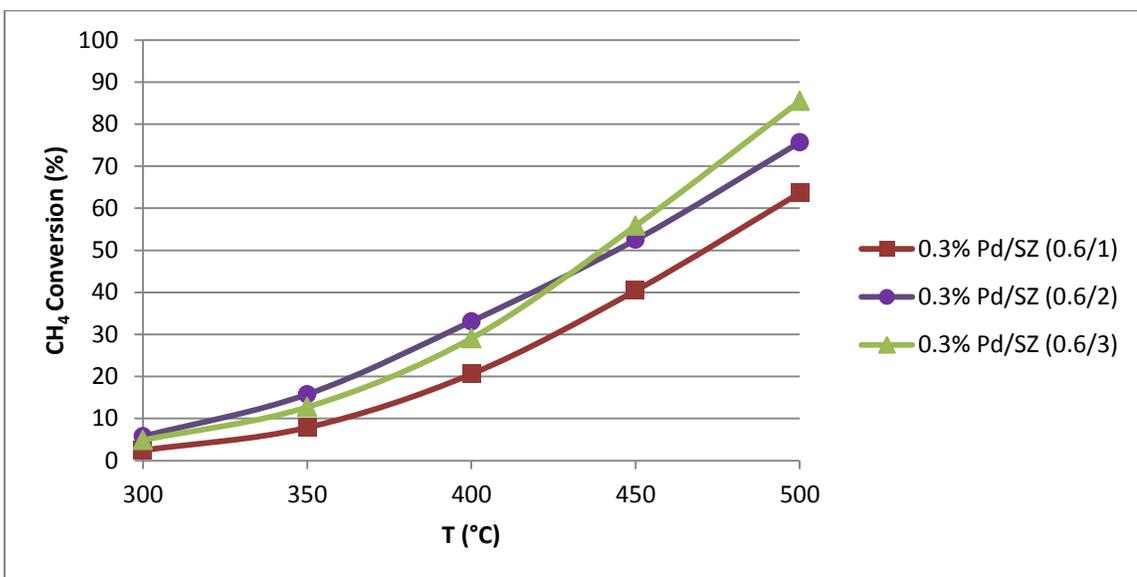


Figure 3.8. CH₄ Conversion of Pd/SZ Catalysts Prepared with 0.6 M Alkoxide

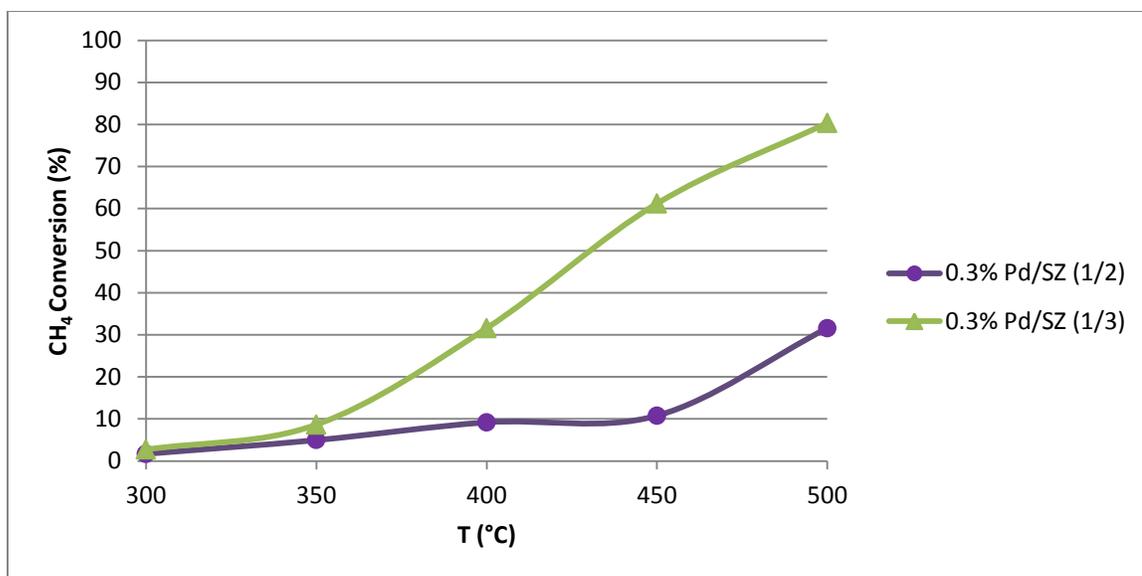


Figure 3.9. CH₄ Conversion of Pd/SZ Catalysts Prepared with 1 M Alkoxide

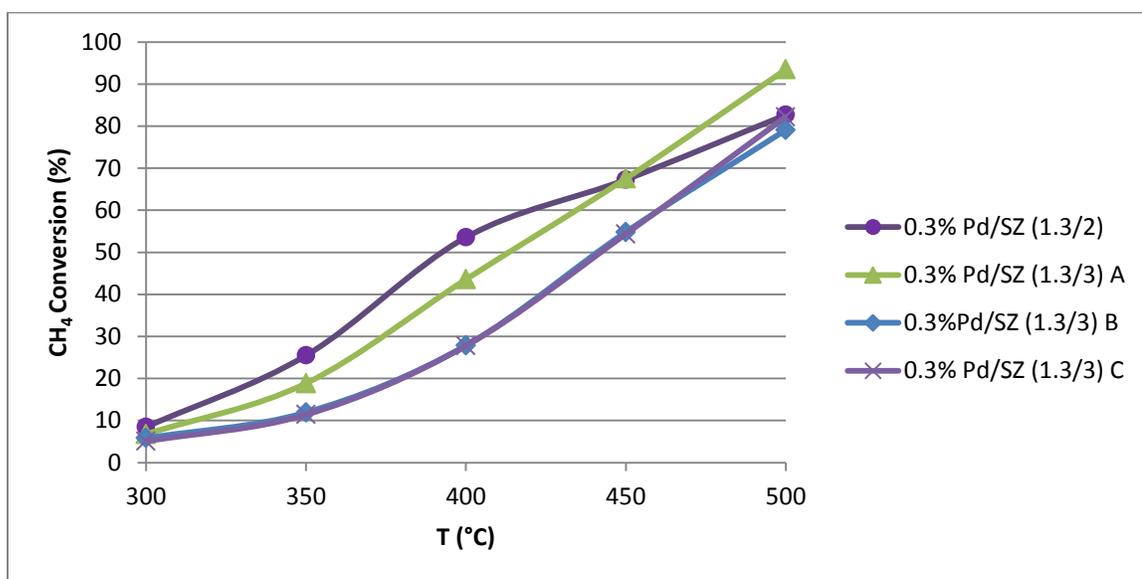


Figure 3.10. CH₄ Conversion of Pd/SZ Catalysts Prepared with 1.3 M Alkoxide

It is once again evident that the catalysts prepared with the highest alkoxide concentration and Zr:SO₄²⁻ ratio have the highest activity in methane conversion, making them good candidates for NO_x reduction catalysis. This is likely due to the fact that high concentrations of alkoxide and low concentrations of sulfuric acid create a catalyst with more active sites per surface area for the reduction of NO_x species by methane.

3.A3 Effects of GHSV on Activity

Because 0.3% Pd/SZ (1.3/3) had the best performance in NO_x reduction, the analysis of the effects of GHSV on catalyst performance was done using this catalyst.

Figure 3.11 shows the effects of GHSV on NO_x conversion.

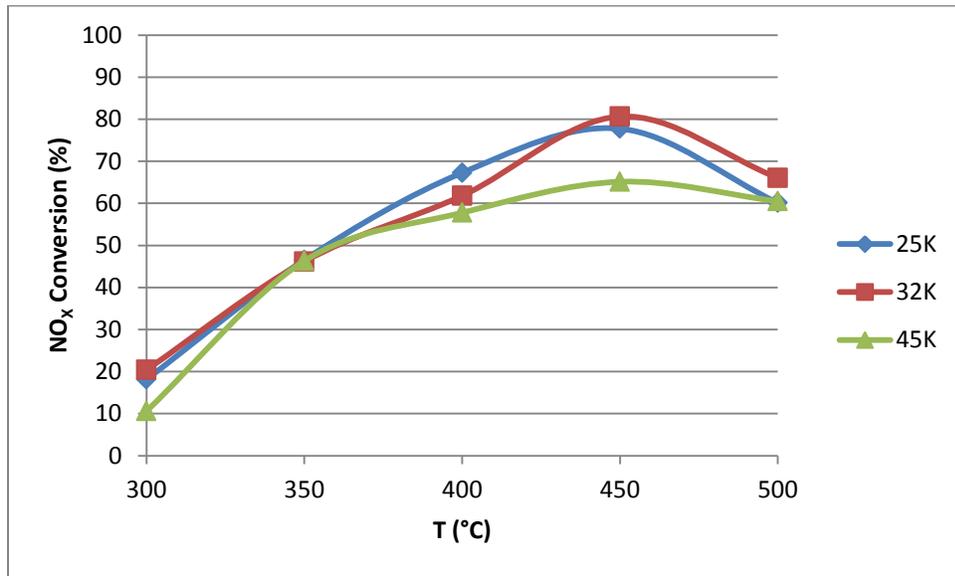


Figure 3.11. NO_x Conversion of Pd/SZ (1.3/3) Under Increasing GHSV (hr⁻¹)

As can be seen from this data, the catalyst is very resistant to increases in GHSV in terms of NO_x conversion. Figure 3.12 shows that this resistance also applies to CH₄ conversion.

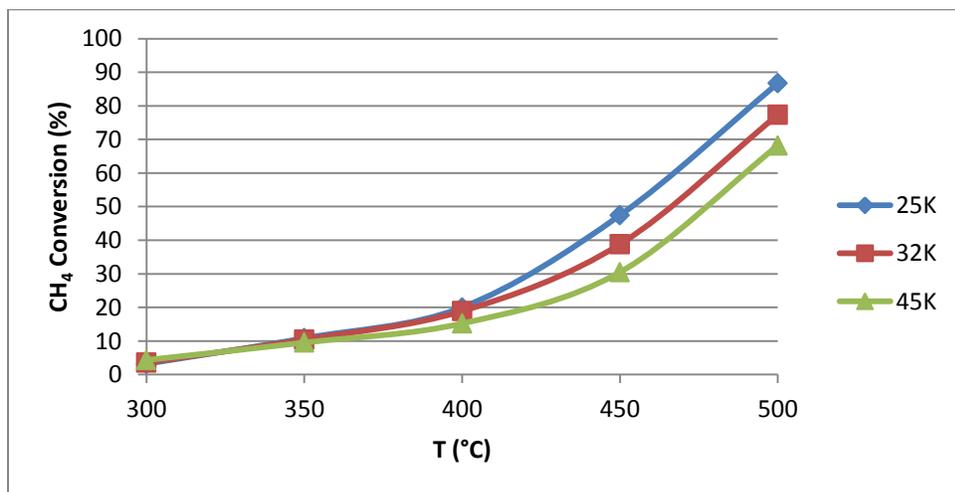


Figure 3.12. CH₄ Conversion of Pd/SZ (1.3/3) Under Increasing GHSV (hr⁻¹)

The fact this catalyst can achieve 65% NO_x conversion and 30% CH₄ conversion at a GHSV of 45,000 hr⁻¹ is encouraging for its overall performance in engine aftertreatment. The flow rates of exhaust can vary greatly depending on the power output of the engine at any given time, so the resistance to increased GHSV is important.

3.B Dual Catalyst Mixed Bed Activity Testing

In order to properly implement the dual catalyst methodology to NO_x reduction, the optimum ratio of oxidation to reduction catalyst must be found. Figure 3.13 shows the NO_x conversion for different ratios of oxidation to reduction catalyst.

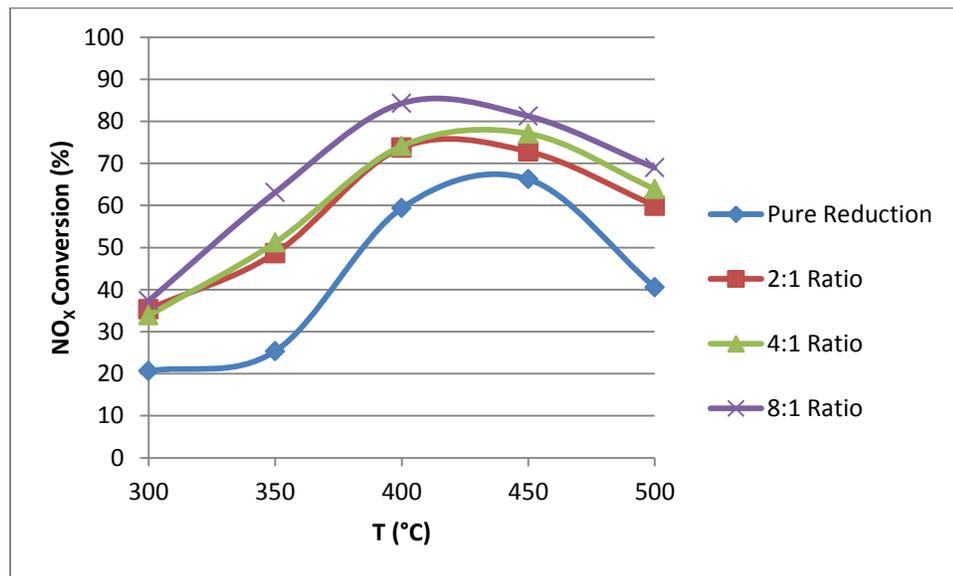


Figure 3.13. NO_x Conversion of Mixed Catalyst Bed

It can be seen from this data that the addition of oxidation catalyst causes an extreme improvement in NO_x conversion. From the different catalyst ratios that were examined, the highest NO_x conversion came from a sample with an 8:1 reduction to oxidation catalyst ratio. This shows that adding just a small amount of the oxidation increases the catalysts performance dramatically. Another important item to note is the fact that the addition of oxidation catalyst caused a higher impact at lower temperatures

(i.e. 350°C). For several of the ratios, including the best performing 8:1 ratio, this caused the catalyst to be more active at 400°C than 450°C. This information could be important for aftertreatment design using this catalyst.

Figure 3.14 shows a plot of the effect of mass fraction of oxidation catalyst on NO_x conversion at several temperatures.

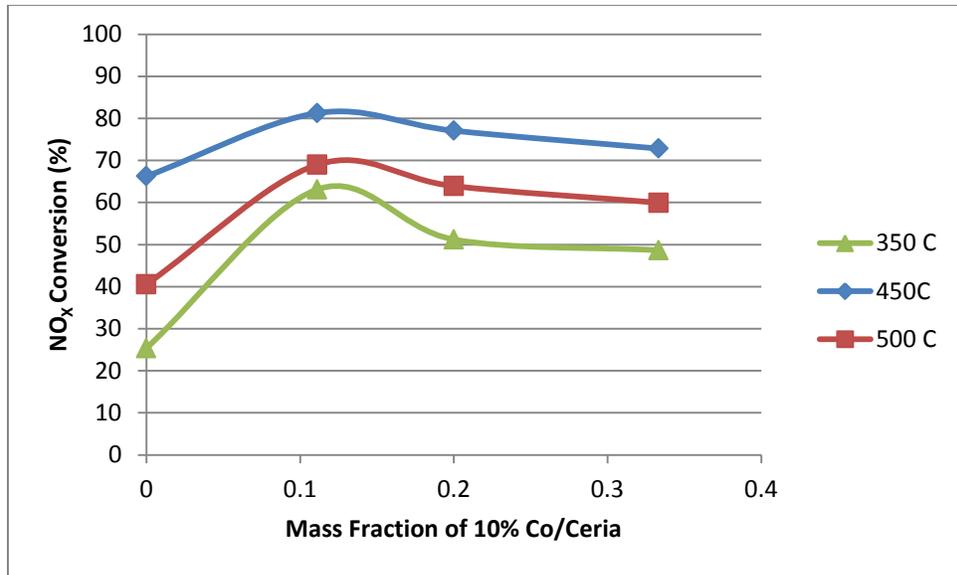


Figure 3.14. The Effects of Oxidation Catalyst Mass Fraction on NO_x Conversion

This data shows that the optimum mass fraction of oxidation catalyst is somewhere around 10-11%. More data points using smaller mass fraction of oxidation catalyst may have given a better optimum, but the amount of oxidation catalyst being used was so small that this information would not be particularly helpful as the 0.3% Pd/SZ (1.3/3) + 10% Co/Ceria (8:1) performed very well for NO_x reduction. It is also important to note that 100% conversion of CO to CO₂ was observed for all trials that involved the oxidation catalyst. This added side effect is a major bonus for emissions control.

Chapter 4: Conclusions and Recommendations

The results of this work reveal the benefits of using Pd catalysts supported on sulfated zirconia prepared using a sol-gel method for NO_x catalysis. The characterization of the samples showed that increasing Zr:SO₄⁻² ratio significantly decreases surface area and pore volume of the catalyst. However, activity testing of the samples showed that catalysts prepared with the highest Zr:SO₄⁻² ratio and alkoxide concentration had the highest activity per surface area in terms of both NO_x reduction and methane oxidation. In order to decide which catalyst is most economically feasible, further activity testing on a per material basis should be performed.

Activity testing with increasing GHSV showed that 0.3% Pd/SZ (1.3/3) is highly resistant to decreases in residence time. Activity testing of catalyst beds comprised of differing ratios of reduction to oxidation catalyst showed that small amounts of oxidation catalyst can increase the overall NO_x conversion dramatically. Overall, a catalyst bed comprised of 0.3% Pd/SZ (1.3/3) and 10% Co/Ceria in an 8:1 ratio performs very well in NO_x reduction catalysis, achieving conversion higher than 80% conversion at 450°C.

If this catalyst is to be used on an industrial scale, further testing should be performed to determine the statistical significance of the data reported in this work. The next steps in determining the efficacy of this catalyst is to test resistance to common catalytic poisons that are present in exhaust streams, including water vapor and sulfur

species. The ability to coat a monolith with catalyst to be placed in the exhaust stream of the engine is also important to the feasibility of catalyst use. With these tests, it may be possible to successfully implement a catalyst to effectively reduce the NO_x and VOC output of lean-burn engines for more efficient use of our energy natural resources.

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Appendix 1 – Sample Calculations

A1.1 Sol-Gel Reduction Catalysts

For the sol-gel reduction catalysts prepared, the materials required to achieve the desired Pd concentration, alkoxide concentration, and Zr:SO₄²⁻ ratio, in solution were needed. Each recipe was calculated to make 4g of catalyst. From this mass, the mass of palladium acetate required was determined as shown in Equation I.

$$4 \text{ g catalyst} \times \frac{0.3 \text{ g Pd}}{100 \text{ g catalyst}} \times \frac{224.5 \frac{\text{g PdOAc}}{\text{mol PdOAc}}}{106.42 \frac{\text{g Pd}}{\text{mol Pd}}} = 0.025 \text{ g PdOAc} \quad (\text{I})$$

Since all samples were prepared with 0.3wt% Pd, 0.025 g of palladium acetate was used in each preparation.

Each catalyst preparation was performed using a 25 mL solution of zirconium propoxide in n-propanol. For the 0.3% Pd/SZ (1.3/3), a solution of 1.3 M zirconium propoxide was prepared. The zirconium propoxide used came in a solution of 70wt% zirconium propoxide in n-propanol with a density of 1.055 g/mL. The volume of this solution required was calculated as shown in Equation II.

$$0.025 \text{ L} \times 1.3 \text{ M Zr(OPr)}_4 \times \frac{327.57 \text{ g Zr(OPr)}_4}{1 \text{ mol Zr(OPr)}_4} \times \frac{1 \text{ g soln.}}{0.7 \text{ g Zr(OPr)}_4} \times \frac{1 \text{ ml soln.}}{1.055 \text{ g soln.}} = 14.4 \text{ ml soln.} \quad (\text{II})$$

Equation III shows that the sulfate to zirconia ratio in solution was equal to the ratio of sulfuric acid to zirconium propoxide in solution.

$$\text{SO}_4^{2-} : \text{Zr Ratio} = \frac{\text{Moles H}_2\text{SO}_4}{\text{Moles Zr(OPr)}_4} \quad (\text{III})$$

For the 0.3% Pd /SZ (1.3/3) catalyst, a ratio of 3:1 of H₂SO₄ to Zr(OPr)₄ by mole was used as calculated in Equation IV.

$$0.025 \text{ L} \times 1.3 \text{ M Zr(OPr)}_4 \times \frac{1 \text{ mol H}_2\text{SO}_4}{3 \text{ mol Zr(OPr)}_4} \times \frac{98 \text{ g H}_2\text{SO}_4}{1 \text{ mol H}_2\text{SO}_4} \times \frac{1 \text{ mL H}_2\text{SO}_4}{1.84 \text{ g H}_2\text{SO}_4} = 0.58 \text{ mL} \quad (\text{IV})$$

When the sol-gel reduction catalysts were tested with equal surface area of 10 m^2 , the mass required was calculated as shown in Equation V for 0.3% Pd/SZ (1.3/3).

$$10 \text{ m}^2 \times \frac{1 \text{ g}}{38 \text{ m}^2} = 0.263 \text{ g catalyst} \quad (\text{V})$$

This mass of catalyst was mixed with inert quartz powder to achieve a total mass of 500 mg to achieve constant bed height between trials.

A1.2 Incipient Wetness Impregnation Reduction Catalysts

The supports for the IWI reduction catalysts were prepared with varying ratios of ceria:zirconia. To calculate the mass of cerium and zirconium precursors, a basis of 10 g of support was used. An average molecular weight was calculated as shown in Equation VI for the 1:3 ratio of ceria to zirconia.

$$MW_{Avg} = 0.25MW_{CeO_2} + 0.75MW_{ZrO_2} = 0.25(172.116) + 0.75(123.244) = 135.462 \quad (\text{VI})$$

From this average molecular weight, the total number of moles of support was calculated as shown in Equation VII.

$$10 \text{ g Support} \times \frac{1 \text{ mol support}}{135.462 \text{ g}} = 0.0738 \text{ mol Support} \quad (\text{VII})$$

The moles of each precursor were calculated using the ratio as shown in Equations VIII and IX.

$$0.0738 \text{ mol Support} \times \frac{1 \text{ mol Ceria}}{4 \text{ mol Support}} \times \frac{1 \text{ mol Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O}}{1 \text{ mol Ceria}} \times \frac{434.22 \text{ g Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O}}{1 \text{ mol Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O}} =$$

$$8.01 \text{ g Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O} \quad (\text{VIII})$$

$$0.0738 \text{ mol Support} \times \frac{3 \text{ mol Zirconia}}{4 \text{ mol Support}} \times \frac{1 \text{ mol ZrOCl}_2 \cdot 8\text{H}_2\text{O}}{1 \text{ mol Zirconia}} \times \frac{322.124 \text{ g ZrOCl}_2 \cdot 8\text{H}_2\text{O}}{1 \text{ mol ZrOCl}_2 \cdot 8\text{H}_2\text{O}} =$$

$$17.83 \text{ g ZrOCl}_2 \cdot 8\text{H}_2\text{O} \quad (\text{IX})$$

After the supports were prepared, their pore volumes were used to determine what solutions should be used for the incipient wetness impregnations. Equations X-XII show

the calculations for the 5% sulfate impregnation of the support prepared with the 1:3 ratio of ceria to zirconia (pore volume = 0.146 mL/g) assuming a basis of 2g of sulfated support.

$$2 \text{ g Sulfated Support} \times \frac{0.95 \text{ g support}}{1 \text{ g sulfated support}} \times \frac{0.146 \text{ mL}}{1 \text{ g support}} = 0.2774 \text{ mL} \quad (\text{X})$$

$$2 \text{ g Sulfated Support} \times \frac{0.05 \text{ g SO}_4}{1 \text{ g sulfated support}} \times \frac{132.14 \frac{\text{g (NH}_4)_2\text{SO}_4}{\text{mol}}}{90.065 \frac{\text{SO}_4}{\text{mol}}} = 0.147 \text{ g (NH}_4)_2\text{SO}_4 \quad (\text{XI})$$

$$\frac{0.147 \text{ g (NH}_4)_2\text{SO}_4}{0.2774 \text{ mL}} = 0.53 \frac{\text{g (NH}_4)_2\text{SO}_4}{\text{mL}} \quad (\text{XII})$$

From these calculations, a solution of 0.53 g (NH₄)₂SO₄/mL was prepared and 0.2774 mL of this solution was added to 1.9 g of support.

A1.3 Cobalt over Ceria Wet Impregnation

The ceria support was prepared using calculations similar to Equation VI-IX. A wet impregnation was performed on this catalyst to achieve 10wt% Co loading. Assuming a basis of 1.5 g of catalyst, the amount of Co precursor required was calculated as shown in Equation XIII.

$$1.5 \text{ g catalyst} \times \frac{0.1 \text{ g Co}}{1 \text{ g catalyst}} \times \frac{291.04 \frac{\text{g Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}}{\text{mol}}}{58.93 \frac{\text{g Co}}{\text{mol}}} = 0.7407 \text{ g Co(NO}_3)_2 \cdot 6\text{H}_2\text{O} \quad (\text{XIII})$$

This amount of the cobalt precursor was dissolved in 40 mL of deionized water and 1.35 g of ceria support was added to the solution to achieve a total mass of Co plus support of 1.5 g.