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COLUMBUS STATE UNIVERSITY

OXIDATION OF CARBON MONOXIDE OVER CERIA AND
ALUMINA SUPPORTED PALLADIUM CATALYSTS

A THESIS SUBMITTED TO THE COLLEGE OF LETTERS AND
SCIENCES IN THE PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
DEPARTMENT OF CHEMISTRY

BY

JOHN DAVIS GARY

COLUMBUS, GEORGIA

DECEMBER 2018

OXIDATION OF CARBON MONOXIDE OVER CERIA AND
ALUMINA SUPPORTED PALLADIUM CATALYSTS

BY

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December 2018

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ABSTRACT

Palladium catalysts on both Al_2O_3 and CeO_2 supports were studied for efficacy in low temperature carbon monoxide oxidation. Calcination temperatures were varied between 500-900°C for alumina supported catalysts and shown to have no significant difference in activity. X-Ray Photoelectron Spectroscopy studies revealed structural changes associated with palladium states and reacted catalysts and displayed a change from palladium oxide (PdO) to native palladium oxide (PdO_x) and elemental palladium (Pd). Activity studies were conducted on all catalysts synthesized and indicated that Pd/ Al_2O_3 achieved 100% CO conversion at 150°C when calcined at 500°C and pretreated with reduction process. Pd/ CeO_2 showed higher activity and achieved 100% CO conversion at 80°C. Stoichiometric mixtures of CO and O_2 as well as excess oxygen resulted in higher conversion CO.

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I. INTRODUCTION

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A. INTRODUCTION

Major advancements have been made in recent years with respect to the oxidation of carbon monoxide. Combinations of classical catalytic techniques with modern instrumentation and availability of specialized materials have spawned multiple investigative avenues into the nature of catalysts and their uses in industrial processes to curb or utilize the production of carbon monoxide. Despite the abundance of research, there has been little definitive evidence into the specific mechanism of the reaction for oxidation of carbon monoxide. Instead, conflicting evidence tends to indicate that multiple mechanisms are possible under varying conditions. As a search for the preferred mechanism ensues, carbon monoxide oxidation also offers a model experiment for improvement among catalytic techniques, in general.

B. CARBON MONOXIDE

Carbon Monoxide is an odorless and noxious gas formed in combustion reactions and has both natural and anthropogenic sources including the burning of fossil fuels in automobiles or industrial processing and manufacturing. Natural sources include volcanic activity, forest fires, and biogenic hydrocarbon oxidation.¹ Chronic exposure to carbon monoxide, usually resulting in short-term illness, can cause death by inhibiting the absorbance of oxygen to hemoglobin in the blood.^{2,3} Carbon monoxide has a much stronger affinity for hemoglobin in the blood than oxygen. A low affinity is necessary for transfer of oxygen to various parts of the body. As carbon monoxide is coordinated with hemoglobin, it prevents binding of oxygen, which leads to suffocation. Although death can occur, the body produces CO naturally as a neurotransmitter, and thus is typically largely unnoticed or dismissed when encountered in the environment.

The United States and most western European countries have implemented regulatory measures to control the release of carbon monoxide. NASA reported in 2015 that worldwide carbon monoxide levels have dropped continually over the past fifteen years, but especially in the northern hemisphere and attributes the decline to these regulations as well as reductions in deforestation.⁴ Industrialization of the southern hemisphere still presents issues as carbon monoxide levels are increasing at certain times of the year, depending on weather and temperature. Long term effects are not of typical concern because carbon monoxide only lasts approximately one month in the atmosphere. Carbon monoxide is a highly reactive gas and may have negative secondary effects due to interactions with the environment.

The main concern for carbon monoxide pollution is short term exposure. Because the number one source of immediate exposure to carbon monoxide is automobiles, the bulk of the regulations have fell on car companies. Yet, many companies are still having difficulties with emission standards and pay large fines due to their inability to combat the issue.⁵ Large influxes of automobiles into heavily populated countries, such as China and Indonesia, have resulted in an increase in carbon monoxide exposure.⁶ Recent studies have shown positive correlations between carbon monoxide exposure from heavy traffic and short term hospitalizations.⁷ Road workers, street vendors, or pedestrians that spent large amounts of time around heavy automobile traffic are more likely to be hospitalized due to carbon monoxide poisoning.⁸

The most common measure to curb the release of carbon monoxide in automobiles is the catalytic converter. Catalytic converters use various catalysts to convert high energy compounds such as nitrogen oxides, hydrocarbons, and carbon monoxide. However, temperatures for effective conversion of these compounds must typically exceed 300 degree Celsius to be effective. The "cold start," or the time between the point where combustion begins and the point where temperature is high enough to catalyze the reaction, has continued to be a contributor to atmospheric carbon monoxide levels. Catalytic converters also have a limited lifetime, with the catalyst being saturated or exhausted over time, resulting in a steady increase in the amount of toxic exhaust.⁹ For this reason, new catalysts with the ability to catalyze the oxidation of carbon monoxide at low temperatures are being developed and studied. One such catalyst that is promising in current research is supported palladium metal and/or its oxides.

C. PALLADIUM

Palladium (Pd) is a precious metal belonging to the platinum group. In metallic form, it is face centered cubic, while palladium oxide (PdO) is tetragonally coordinated with palladium atoms being in a square planar configuration. Non-stoichiometric palladium species exist which are referred to as native palladium oxides (Pd_xO_y). Metallic palladium is similar in color and texture to platinum but possesses more hardness than its counterpart. Despite relative hardness, palladium is still reasonably malleable, lending to its ability to be widely used in various jewelry applications from the production of white gold alloys to the replacement of platinum for repairs. Another major usage for palladium is hydrogenation in chemical and industrial

processes due to its ability to absorb large amounts of hydrogen. Although it is a noble metal, which tends to be non-corrosive and less reactive, palladium is the most reactive of the platinum group. This reactivity combined with relative stability make palladium an ideal candidate for catalytic research.

One area of such research is in the automobile industry. Standard catalytic converters mostly utilize platinum or palladium coordinated with cobalt, manganese, zinc, or a combination to catalyze all the necessary reactions. Palladium is less studied, but has been proven to be an effective catalyst with regard to the oxidation of carbon monoxide.¹⁰ Previous studies on palladium catalysts have reported 100% carbon monoxide conversion of temperatures ranging from 60-150°C depending on the support used and the treatment provided.¹¹⁻¹³ One of the more widely used supports is alumina oxide, which provides a relatively inert system for the loading of palladium. Although alumina support may still provide useful information in kinetic and mechanistic studies for carbon monoxide oxidation, a more interactive support may be necessary to achieve low temperature oxidation. One promising support gaining recognition for its use in oxidation catalysis is cerium.

D. CERIUM

Cerium [Ce] is a part of the lanthanide series and is a commonly used substance for polishing glass surfaces. It is relatively abundant yet is not used in many applications outside of chemistry. Certain cerium characteristics are beneficial to catalytic studies. The electronic

configuration of Cerium is $[\text{Xe}]4f^15d^16s^2$, but easily gives up the 4f electron. This allows Ce to exist in both the Ce^{3+} and Ce^{4+} and is unique to the lanthanide series. Cerium (IV) Oxide, or ceria (CeO_2), expresses similar characteristics in its configurations as high temperature causes oxygen vacancies in the fluorite structure, resulting in non-stoichiometric configurations (CeO_{2-x}). This ability to readily participate in redox reactions, as well as its ability to give up oxygen makes ceria a useful compound in numerous reactions.

Past experiments have shown ceria's ability to catalyze the oxidation of hydrocarbons such as propane.¹⁴ Ceria has also been used in many studies which examine the oxidation of carbon monoxide.¹⁵⁻¹⁷ It is believed that ceria's ability to give up oxygen is fundamental in these reactions. However, there is some discrepancy in how oxidation reactions proceed with respect to carbon monoxide on ceria-supported catalysts. Some theories have suggested that supports may house hydroxyl ions which help to facilitate this reaction.¹⁸ Others have suggested that CeO_2 provides energetic alterations to the catalyst so that variable oxidation states are more easily achieved.¹⁹ The most commonly accepted mechanism involves the dissociative adsorption of oxygen on ceria in a bimolecular reaction with carbon monoxide adsorbed on the metal surface.

E. OBJECTIVES FOR THIS STUDY

This report will investigate the catalytic oxidation of carbon monoxide using palladium (Pd) catalysts with alumina oxide (Al_2O_3) and ceria (CeO_2) supports. To determine the effect of calcination temperature in alumina supported palladium catalysts, multiple temperatures will

be tested including 500°, 600°, 750°, and 900°C. Once reactivity has been determined and preparation methods have been analyzed and improved, then the same methods will be applied for the most promising calcination temperature for ceria supported palladium catalysts.

Differential gas mixtures will be used to indicate changes in order with respect to the gas mixtures used, particularly CO and O₂. A table showing the activity of these catalysts will be provided to show which catalysts were the most successful at oxidizing carbon monoxide and what conversions were achieved at various temperatures. This information will indicate the efficacy of palladium catalysts on ceria supports.

Characterization of the catalysts studied will also be conducted. It is critical for catalyst studies to determine both the elemental composition on the surface, which can be achieved through XPS, and the relative amount of dispersion of the elements on the surface. The latter can be determined through chemisorption techniques. Structural analysis will also be provided through XRD. A report detailing the results of these studies is provided as well.

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II. METHODOLOGY

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A. CATALYST PREPARATION

I. Palladium on Alumina Oxide

Incipient wetness method (IWM) was used to prepare 10 wt.% Pd/Al₂O₃. 1.0828 grams of Palladium (II) Nitrate Hydrate (Sigma Aldrich, 230.43 g/mol, anhydrous basis) was dissolved in 3mL of deionized water and added, dropwise, to 5.00 grams of aluminum oxide nanopowder (α -Al₂O₃, Sigma Aldrich, 101.96 g/mol, 13nm) and stirred vigorously for thirty minutes. To ensure the transfer of all palladium, a second wash containing between 2.5-3.0 mL deionized water was performed and added to the catalyst mixture.

The sample was dried overnight at 110°C for approximately 12 hours to remove excess water. Catalyst samples were then removed and placed in desiccator to be allowed to cool to room temperature while also aiding in the removal of moisture. Subsequently, the sample mixture was ground very finely using mortar and pestle. Resulting powder was divided into three crucibles to be calcined at varying temperatures, 600°, 750°, and 900°C in a Benchtop Muffle Furnace for six hours. This procedure was later repeated to provide samples calcined at 500°C as well as more 600° calcined catalysts for further testing. The samples were stored at room temperature in a desiccator until various tests for their efficacy on the oxidation of carbon monoxide at low temperatures could be performed.

II. Palladium on Cerium Oxide

A modified slurry method was used to prepare 5 wt.% Pd/CeO₂ by dissolving Palladium (II) Nitrate Dihydrate in 2mL of deionized water. The slurry method is similar to wetness impregnation in that a solution of palladium was added to a dry support. However, oversaturation occurs more quickly due to ceria's high density. This led to a solution of both palladium and ceria most accurately described as a "slurry." A palladium solution was added dropwise to Cerium (IV) Oxide (Sigma Aldrich, 172.11 g/mol) while stirring. Another 2.0mL of deionized water was used to wash all palladium solution into mixing batch. A vortex mixer was employed to increase dispersion and consistency of catalyst preparation methods. The mixture was vortexed for 30 minutes and resulted in a wet, sticky substance similar in texture and color to melted chocolate. The catalyst mixture was collected and placed in a porcelain crucible to be dried overnight at 110°C. Once dried, the sample was ground in a mortar and pestle and calcined at 600°C for six hours. The catalyst samples were used in activity studies to test their ability to catalyze the oxidation of carbon monoxide at low temperatures.

20 wt.% Palladium on Ceria (IV) Oxide, Pd/CeO₂ was also prepared using a similar slurry method. However, the excess water needed to dilute the increased amount of palladium resulted in a much different consistency from the original sample. To remove excess water, the palladium and ceria solution was heated on a hot plate to 150°C and stirred for several hours until the consistency matched the original. The catalyst mixture was dried overnight at 110°C

and calcined at 600°C. The sample was then collected, ground, and stored in a desiccator at room temperature until testing.

III. Standards

Standard grade Palladium (II) Oxide, Cerium (IV) Oxide, and Aluminum Oxide was purchased from Sigma Aldrich to be used in comparative studies and characterization.

IV. Catalyst Reference

All catalysts with corresponding composition and treatment is provided in Table 2.1.

Table 2.1 Catalyst Reference

Catalyst Index				
Reference	Composition	Precursor	Calcination Temp.	Preparation Method
CSU-1	10 wt% Pd/Al ₂ O ₃	Pd(II) nitrate hydrate	900°C	Incipient Wetness
CSU-2	10 wt% Pd/Al ₂ O ₃	Pd(II) nitrate hydrate	750°C	Incipient Wetness
CSU-3	10 wt% Pd/Al ₂ O ₃	Pd(II) nitrate hydrate	600°C	Incipient Wetness
CSU-4	10 wt% Pd/Al ₂ O ₃	Pd(II) nitrate hydrate	500°C	Incipient Wetness
CSU-5	10 wt% Pd/Al ₂ O ₃ (Oxidized)	Pd(II) nitrate hydrate	600°C	Incipient Wetness
CSU-6	10 wt% Pd/Al ₂ O ₃ (Reduced)	Pd(II) nitrate hydrate	500°C	Incipient Wetness
CSU-7	PdO standard	PdO	n/a	n/a
CSU-8	5 wt % Pd/CeO ₂	Pd(II) nitrate dihydrate	600°	Slurry
CSU-9	5 wt % Pd/CeO ₂ (Reacted)	Pd(II) nitrate dihydrate	600°	Slurry
CSU-10	20 wt% Pd/CeO ₂	Pd(II) nitrate dihydrate	600°	Slurry
CSU-11	20 wt% Pd/CeO ₂ (Reacted)	Pd(II) nitrate dihydrate	600°	Slurry
CSU-12	CeO ₂ (Calcined)	n/a	600°	Slurry
CSU-13	CeO ₂	n/a	n/a	n/a
CSU-14	Al ₂ O ₃	n/a	n/a	n/a

B. CATALYTIC ACTIVITY STUDIES

I. Reaction Procedure

A fixed bed reactor was used to provide the catalytic environment needed for activity studies.

A layer of glass wool (Sigma Aldrich) was loaded into a quartz tubular reactor followed by

approximately 0.200g of the catalyst and a second layer of glass wool. Next, the reactor was layered with 3mm borosilicate glass beads and a subsequent layer of glass wool which allowed the reaction bed to be easily packed using a glass rod. The reactor was then placed within a horizontal reaction furnace where the reaction temperature can be controlled as the affluent gas is passed over the catalyst bed. Temperature was also monitored by an Omega thermocouple thermometer which could be inserted into the end of the reactor to monitor the actual temperature inside the reactor. Gas flow was controlled by a Mass Flow Controller (Aalborg, GFC17) and kept at 1.0L/min for all experiments. All gases used were standard gas mixtures purchased from Airgas. All experiments were conducted under a fume hood with carbon monoxide detectors present to ensure safety.

Helium was passed over reaction bed for fifteen minutes prior to experiments to ensure that no contaminants were contained in the gas lines as well as in the reaction bed. A series of coiled gas lines preceding the reactor ensured proper mixing of gasses. Gas mixtures were passed through the catalyst bed at fixed temperatures for fifteen minutes. A glass T-junction was fitted to the exiting end of the reactor via plastic tubing and sealed using a rubber septum and an exhaust line, which was submerged in water to ensure gas flow remains constant. An air-tight syringe was used to extract 1.0mL from the reactor exhaust following the reaction. The gas sample was transferred and analyzed for effluent gas mixture concentrations. Varying catalysts, reaction temperatures, and gas mixture composition provided data for kinetic studies and qualifying information on the efficacy of palladium catalysts with alumina and ceria supports.

II. Analyzing Gas Mixtures

Following extraction from the reactor, the sample is immediately injected into a gas chromatograph (Buck Scientific Model 310) coupled with a Thermal Conductivity Detector (GC-TCD), which utilized a 6-foot Restek shincarbon packed column. A GC-TCD operates by separating compounds based on the ability to elute from a column at differing speeds. Changes in thermal energy can be detected as the gas passes over a resistor. Temperature programming allowed for an initial temperature of 40°C upon injection. After five minutes, the temperature rises at 20°C/min to 180°C. This temperature is held for three minutes, then allowed to cool back to 40°C. Data obtained from experiments was analyzed using PeakSimple software. This software interprets GC-TCD data based on retention times and intensity. The intensity is integrated to produce an area, which is directly proportional to gas concentration. Retention times correspond to specific gases, thus each peak can be measured and identified, determining composition of the effluent gas mixture. A calibration curve describing the relationship between carbon monoxide concentration and PeakSimple area is provided in Figure 2.1.

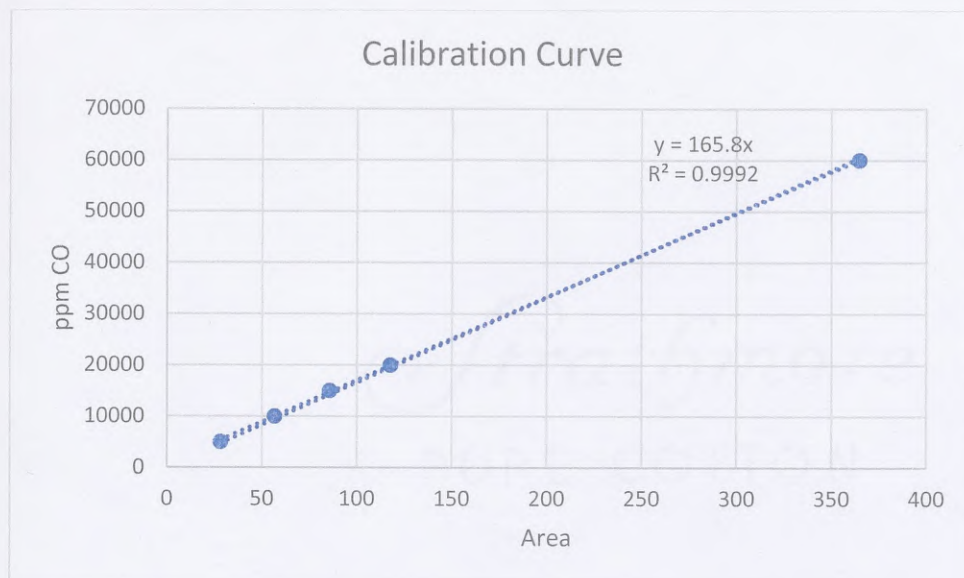


Figure 2.1 CO concentration vs. PeakSimple integration area.

The calibration curve was constructed by varying volumes of gas mixture (0.25mL, 0.5mL, 0.75mL, and 1.0 mL) with 2%CO, 2%O₂. Higher concentrations of CO were also correlated with the PeakSimple area using 1.0 mL of 6%CO, 2%O₂ gas mixture. The slope from the calibration curve was used to determine the concentrations of effluent gas mixtures based on PeakSimple area. The concentrations determined after reaction could then be compared to original gas concentrations to evaluate CO conversion.

C. CHARACTERIZATION

I. X-Ray Photoelectron Spectroscopy (XPS)

XPS utilizes x-ray photons to collide with surface elements and cause photoelectrons to be ejected. The energy reflected by these photoelectrons is used to calculate relative percentages

as well as bonding characteristics based on atomic binding energies previously studied. XPS provides chemical surface composition information useful in catalysts because reactions in these studies are presumed to occur on the surface. Procedures such as Energy-dispersive X-ray Spectroscopy (EDS) provide chemical composition of the bulk sample. However, many catalysts do not exhibit similar characteristics in the bulk as they do on the surface. XPS provides surface composition up to 10nm under normal conditions. However, 100-200nm depths can be achieved through a process called sputtering which uses Argon cations to remove layers of the catalyst, essentially drilling holes into the surface.

All palladium catalysts utilized in reaction studies, as well as a palladium standard for comparison, were sent to be studied using XPS at the NSF Center for Advanced Vehicle and Extreme Environment Electronics (CAVE3) at the University of Auburn. Procedures and parameters can be found in Appendix A.

II. X-Ray Powder Diffraction (XRD)

XRD is used to determine elements present in a crystalline structure. The instrument utilizes Bragg's law, which states that a crystalline lattice structure will reflect constructive interference when atomic spacings coincide with matching wavelengths and is expressed in the equation, $2d \sin\theta = n\lambda$. Because atomic spacings and orientations have been well studied, it is possible to compare samples tested with previous references to determine the constitution of the materials studied. XRD experiments were conducted at Auburn University.

XRD analysis was performed using a Bruker AXS D2 Phaser. Samples were tested at increments of 0.02 degrees between 2-theta angles of 15 and 90 degrees. Each increment, or step, was reflected for 0.500 seconds, which allows for more precision in analysis versus a shorter step time. The XRD used incorporates a copper tube with 1.54184\AA and a Lynxeye detector. X-ray generator parameters were as follows: 30kV voltage, 10mA current, 300W power.

Samples were ground to a fine powder that could be easily dispersed evenly. Test runs were conducted to determine the best method for analysis using the XRD. Two methods were employed for dispersion of materials on the XRD slide, a zero plate and double-sided tape. Catalysts applied to double-sided tape were especially adhesive in general and thus were easily applied evenly over the application tape and XRD slide. Tests employing the zero-plate method utilized more of the sample than the double-sided tape, providing pronounced peaks and resolution for certain samples. However, even distribution is more difficult to achieve on a zero-plate, but shouldn't impact analysis, other than slight differentials in peak intensity and sharpness. Palladium catalysts tend to exhibit more adhesion, thus were especially conducive to the double-sided tape method.

III. Chemisorption

Chemisorption techniques provide descriptive characteristics of materials such as metal surface area, CO uptake, particle size, and dispersion. It operates on principles of chemistry that state a change in energy will be exhibited as adsorbate bonds are formed and broken on a material surface. Relationships can be drawn from the amount of metal present and the availability of active sites, thus inferring particle size and dispersion, etc. Temperature programmed reduction and Pulse CO chemisorption was performed at the University of Georgia Tech. Methods and parameters are provided in Appendix B.

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III. RESULTS AND DISCUSSION

A. ACTIVITY

I. Pd/Al₂O₃

Palladium catalysts on alumina support were prepared via IWM and tested for efficacy in catalytic oxidation of carbon monoxide. Table 3.1 shows the results from testing of various calcination temperatures as well as the oxidation of Pd/Al₂O₃ calcined at 600°C and the reduction of Pd/Al₂O₃ at 500°C.

Pd/Al₂O₃ show conversion of carbon monoxide between 150°-200°C, depending on the preparation method and treatment. Calculations for carbon monoxide conversion were determined based on the following equations:

$$\%Conversion = \frac{(mol\ CO)_{in} - (mol\ CO)_{out}}{(mol\ CO)_{in}} \times 100\%$$

Conversion was determined for each reaction using the calibration curve and the relationship:

$$Area = \frac{ppm\ CO}{165.28}$$

And

$$\frac{(ppm\ CO)_{out}}{(ppm\ CO)_{in}} = \%Conversion$$

Table 3.1 Activity for Pd/Al₂O₃.

Reference	Calcination Temp.	Reaction Temp	O ₂ area	CO area	CO ₂ area	CO conversion	CO ppm
CSU-3	600	100	114.33	105.29	7.00	3%	600
	600	150	119.88	107.36	5.02	2%	400
	600	175	118.21	107.18	9.96	4%	800
	600	200	43.65	0.00	221.50	100%	0
CSU-1	900	100	528.99	390.62	0.00	0%	20000
	900	125	422.44	384.11	0.00	0%	20000
	900	150	420.89	396.03	15.10	2%	400
	900	175	244.30	0.00	746.60	100%	0
CSU-2	750	150	299.83	389.34	14.60	2%	400
	750	175	311.93	379.18	30.25	4%	800
	750	200	99.81	0.00	755.77	100%	0
CSU-5	600(Oxidized)	100	75.57	110.75	0.00	0%	20000
	600(Oxidized)	150	75.26	105.56	6.00	3%	600
	600(Oxidized)	175	41.16	0.00	217.71	99%	0
	600(Oxidized)	200	37.67	0.00	218.83	100%	0
CSU-4	500	100	50.13	68.34	0.00	0%	20000
	500	150	112.92	101.77	0.00	0%	20000
	500	175	110.34	0.00	7.62	100%	0
CSU-6	500 (Reduced)	100	223.51	107.08	0.00	0%	20000
	500 (Reduced)	125	45.43	7.15	198.58	93%	18700
	500 (Reduced)	150	68.60	0.00	212.71	100%	0
	500 (Reduced)	200	36.29	0.00	200.69	100%	0

Reactions were carried out in an oxygen rich environment of 2%O₂, 2%CO, and balanced with helium. There were marginal differences between calcination temperatures, with 500°C calcination being the most promising. Complete conversion was achieved at 175°C and reduction of the catalyst resulted in 93% CO conversion at 125°C. This is approximately equal or better than research of this type on Palladium catalysts on alumina supports.^{11,20} Alumina studies did offer improved preparation techniques, such as vortex assisted incipient wetness impregnation, leading to improved surface loading, as detailed in prior research.²¹

II. Pd/CeO₂

Palladium catalysts on ceria supports were tested after preparation using a modified slurry method and calcination at 500°C. Preliminary tests on carbon monoxide oxidation were carried out in the reactor using oxygen rich 2%CO, 2%O₂, and balance helium. Catalyst CSU-8 was tested and showed conversion of carbon monoxide as low as 50°C and achieved 100% conversion as low as 75°C. Following preliminary studies confirming increased activity, an experiment testing various gas mixtures was performed to reveal dependence of carbon monoxide and gaseous oxygen in the catalytic cycle. Table 3.2 lists detailed results from this study and Figure 3.1 shows how different gas mixtures affect the oxidation of carbon monoxide.

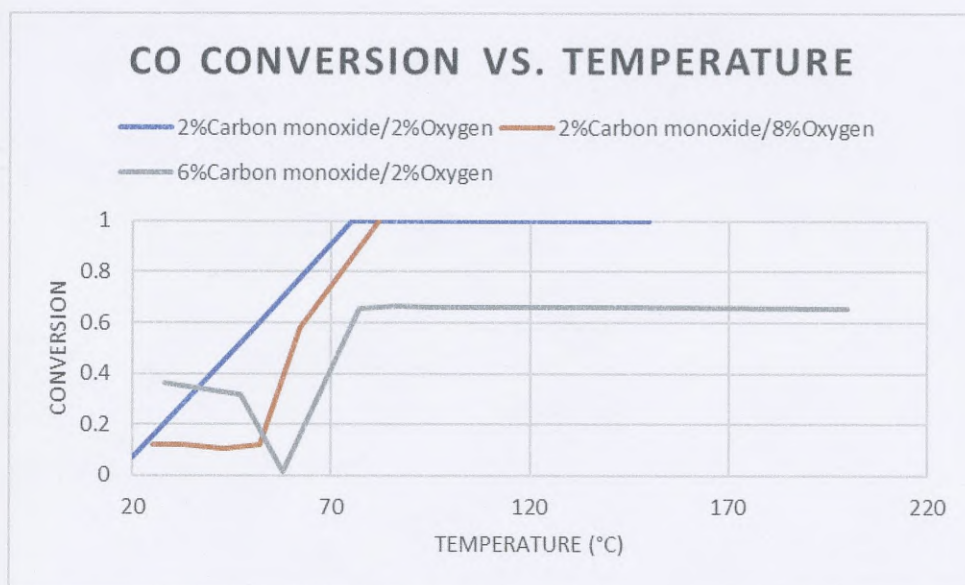


Figure 3.1 Various Gas Mixtures in CO Oxidation.

Table 3.2. CO Conversion Among Varying Gas Mixtures.

Gas Mixtures and Conversion for Activity Study on 5%Pd/CeO ₂				
Gas Mixture	Temperature(C°)	CO Area	CO Conversion	CO ₂ Area
2%O ₂ ,2%CO	20	112.41	7%	0.00
2%O ₂ ,2%CO	50	52.14	57%	125.43
2%O ₂ ,2%CO	75	0.00	100%	225.37
2%O ₂ ,2%CO	100	0.00	100%	224.79
2%O ₂ ,2%CO	150	0.00	100%	227.42
8%O ₂ ,2%CO	25	106.38	12%	15.58
8%O ₂ ,2%CO	33	106.64	12%	16.04
8%O ₂ ,2%CO	43	108.10	11%	18.66
8%O ₂ ,2%CO	52	106.49	12%	19.71
8%O ₂ ,2%CO	62	51.03	58%	11.95
8%O ₂ ,2%CO	82	0.00	100%	225.42
2%O ₂ ,6%CO	28	230.70	36%	0.00
2%O ₂ ,6%CO	47	248.26	32%	5.61
2%O ₂ ,6%CO	58	358.55	1%	3.67
2%O ₂ ,6%CO	77	124.96	66%	457.42
2%O ₂ ,6%CO	86	120.81	67%	452.22
2%O ₂ ,6%CO	96	122.32	66%	461.53
2%O ₂ ,6%CO	107	124.11	66%	464.55
2%O ₂ ,6%CO	130	122.42	66%	459.76
2%O ₂ ,6%CO	150	122.49	66%	462.29
2%O ₂ ,6%CO	200	124.54	66%	468.04

Analysis of the conversion among various gas mixtures shows that the reaction is dependent on the availability of oxygen. However, excess oxygen seemed to have inhibited the reaction momentarily, possibly due to the lack of available adsorption vacancies for CO to bind. All oxygen rich mixtures resulted in 100% CO conversion before 80°C, while CO rich gas resulted in

maximum conversion of CO at 67%. At low temperatures, CO rich gas mixture achieved conversion at room temperature, but fell to zero conversion around 60°C. Conversely, 8%O₂, 2%CO gas mixture showed very little conversion until the reaction temperature surpassed 60°C. This may suggest that 60°C, under these specific conditions, is an energy barrier represented by a change in dynamics among CO and O₂ affinity for the substrate. In fact, previous studies have concluded that CO binds very tightly at low temperatures and requires added energy to break bonding and undergo oxidation.²² Our results are in line with other catalytic studies on CO oxidation using palladium catalysts with ceria supports as most show 100% conversion before 100°C, depending on preparation techniques and co-catalysts.^{12,13}

Table 3.3 CO Conversion Over Time.

Time Elapsed (min)	CO Conversion (%)
15	100
30	100
45	100
60	100
75	100
90	100

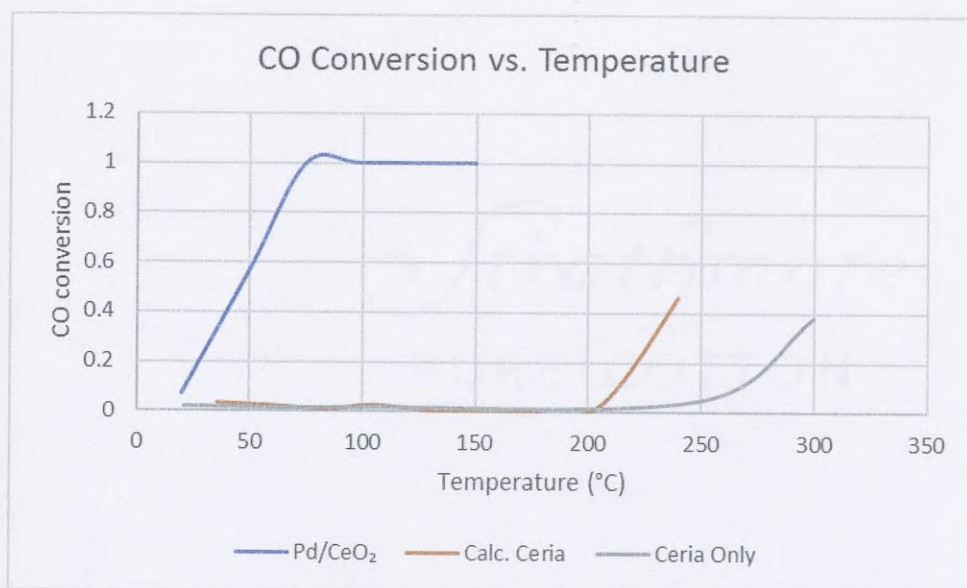


Figure 3.2 CO conversion vs Temperature over Ceria.

A sustained reaction lasting two hours shows that the ceria supported palladium catalysts maintain stability and activity. Results for this testing are provided in Table 3.3 and shows 100% conversion immediately at 100°C. To differentiate palladium catalytic performance from support contributions, several experiments were conducted on ceria only, including activity studies on both the support, untreated, as well as a CeO₂ catalyst that was prepared and treated with calcination similarly to the Pd/CeO₂ catalysts. Results for tests analyzing untreated ceria and 500°C calcined CeO₂ are shown in Figure 3.2 with the corresponding palladium catalysts using a ceria support.

B. CHARACTERIZATION

I. XRD Analysis

According to previous research, peaks for palladium can be differentiated based on the chemical state of palladium.²³ PdO shows peaks at, or around 2θ , 33° and 55° , while Pd native will exhibit peaks at 2θ , 40° . Ceria is less studied and more difficult to differentiate. However, previous research on similar catalysts show that peaks may be observable at 2θ , 30° , 49° , and 59° .²⁴ Figure 3.3 shows the XRD analysis of 5 wt. % Pd/CeO₂ (CSU-8).

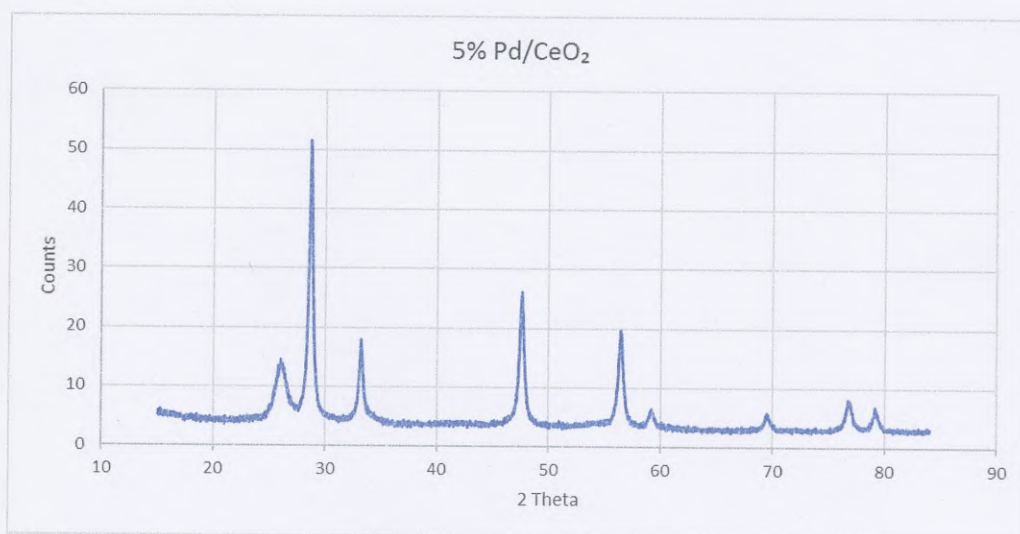


Figure 3.3 XRD analysis of 5 wt.% Pd/CeO₂ (CSU-8).

XRD Analysis of 5 wt.% Pd/CeO₂ (CSU-8) shows that PdO is present in much higher abundance than Pd native. The strong peak at 29° indicates the presence of CeO₂ and infers the configuration (111).²⁵ The peaks before 50° and 60° are also attributed to CeO₂. Some research

shows that different oxidation states of both palladium and ceria may be observed between 70° and 80° , thus we assume that peaks in this range represent those variable oxidation states.

Figure 3.4 shows the XRD analysis of reacted 5 wt.% Pd/CeO₂ (CSU-9).

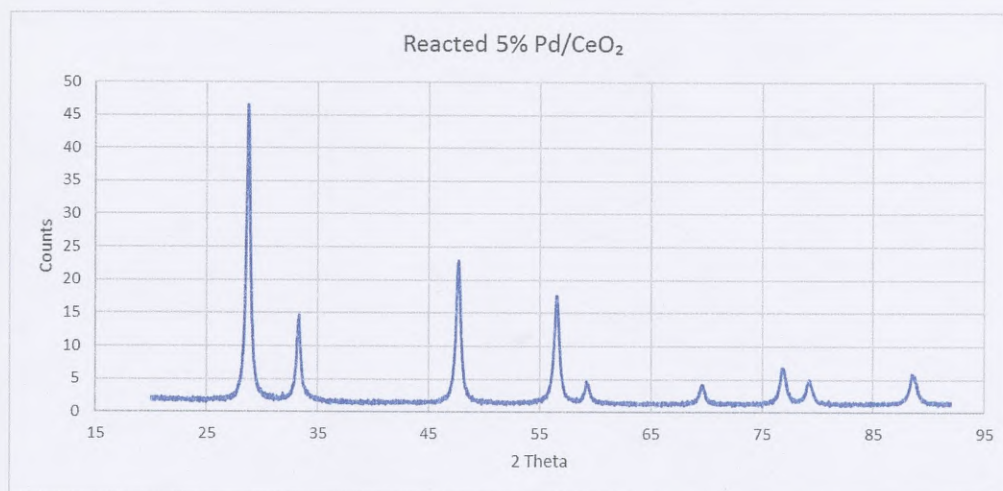


Figure 3.4 XRD analysis of reacted 5 wt. % Pd/CeO₂ (CSU-9).

20 wt.% Pd/CeO₂ (CSU-10) was analyzed using XRD and is displayed in Figure 3.5. A broadening of the peak concerned with PdO at $2\theta, 33^\circ$ may suggest larger particle size or larger complexes than the original specimen. A PdO standard (CSU-7) was also analyzed using XRD and is displayed in Figure 3.6. This confirms that peaks attributed to PdO do, in fact, belong to PdO. A peak around $2\theta, 25^\circ$ is believed to be a contaminant, perhaps the double-sided tape used for the procedure. Notice, also, that there are no clear peaks in the $75-85^\circ$ range, which lends credence to the fact that this region represents native palladium or ceria species. Interestingly, there is a peak at 40° which was not observed in other specimen and has been traditionally linked with Pd native species, although we should not expect any in this sample. XRD spectra for Pd/CeO₂ samples are in line with another study concerned with particle size of similar

catalyst and suggest broadness of peaks indicate particle sizes between 5-15nm, which is further confirmed by chemisorption results.²⁶

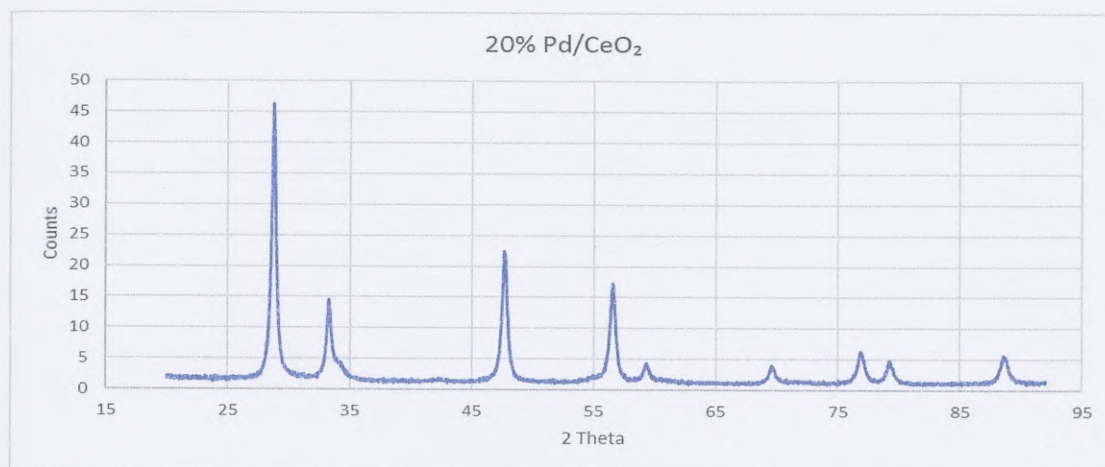


Figure 3.5 XRD analysis of 20 wt. % Pd/CeO₂ (CSU-10).

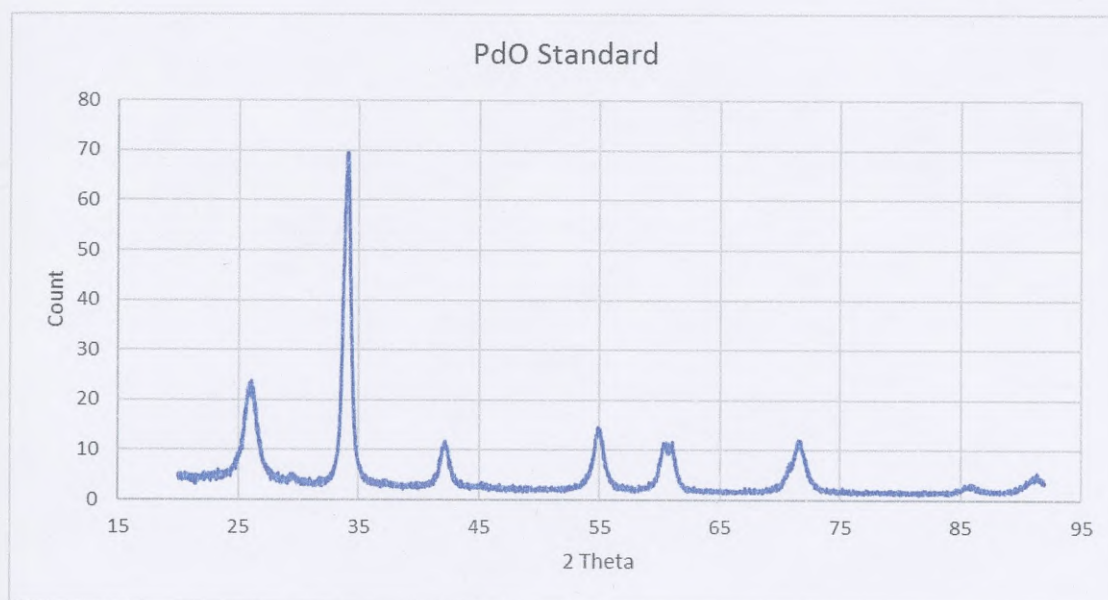


Figure 3.6 XRD analysis of PdO standard (CSU-7).

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PREFLECTION

II. XPS Analysis

Analysis of Palladium on alumina supports with XPS reveal the elemental surface composition of catalysts used in the conversion of carbon monoxide. Figure 3.6 illustrates the spectra for 10 wt.% Pd/Al₂O₃ (CSU-1), which was shown to only contain 0.2 at% at the surface. This translates to 0.77wt% palladium loading on the surface. Sputtering Argon ions allowed a depth of 200nm to be analyzed and revealed a slight increase to 1.42 wt.%, which again is lower than expected considering preparation called for 10 wt.% Palladium on alumina support. Figure 3.7 shows the spectra of sputtered CSU-1.

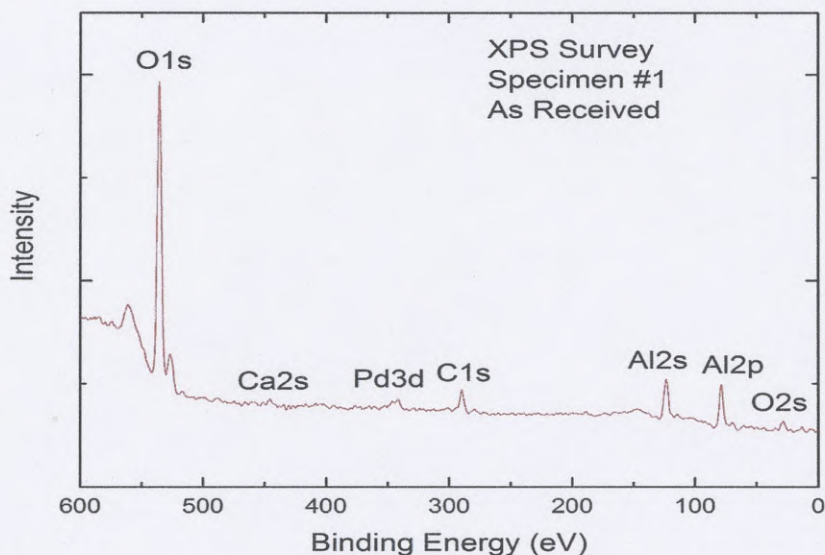


Figure 3.7 XPS spectra of 10 wt.% Pd/Al₂O₃ (CSU-1).

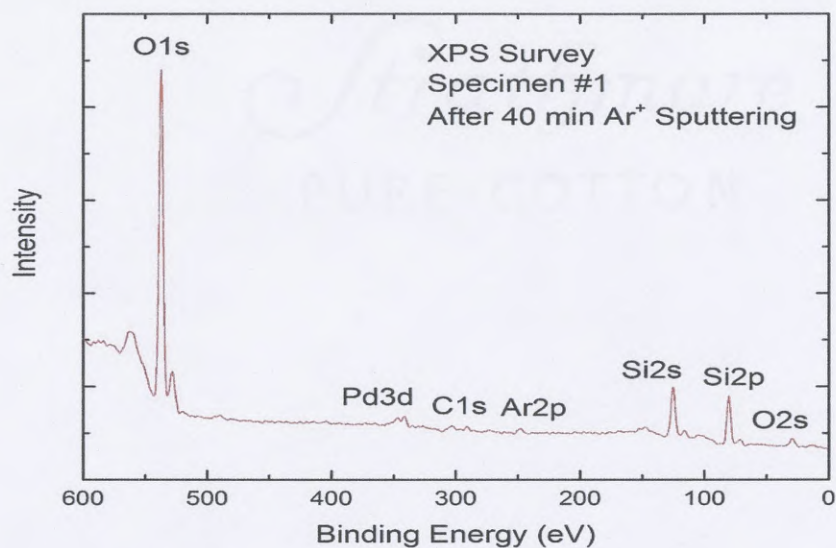


Figure 3.8 XPS spectra of 10 wt.% Pd/Al₂O₃ (CSU-1) after Sputtering.

Along with elemental surface composition, XPS also provides information concerning the chemical state of these elements. High resolution spectra and deconvolution provides comparative analysis of the relative percentage of each chemical state. Figure 3.9 shows the high-resolution spectra of 10 wt.% Pd/Al₂O₃ (CSU-1) at the surface, indicating that Palladium is present, mostly in the form of PdO. After sputtering for 40 min, at a depth of 200nm, a shift occurs indicating that the proportion of native palladium, or non-stoichiometric PdO_x, has increased. Figure 3.10 shows the high-resolution spectra of 10 wt.% Pd/Al₂O₃ (CSU-1) after sputtering. There was little difference between 10 wt.% Pd/Al₂O₃ catalysts with respect to palladium loading and surface chemistry. As a generalization, it can be concluded that PdO becomes less prevalent on the surface as calcination increases. PdO standard (CSU-7) was also

analyzed for comparison and indicates that all PdO appears in the region for PdO and contains no noticeable elemental palladium or native palladium oxides. The spectra for PdO standard are displayed in Figure 3.11.

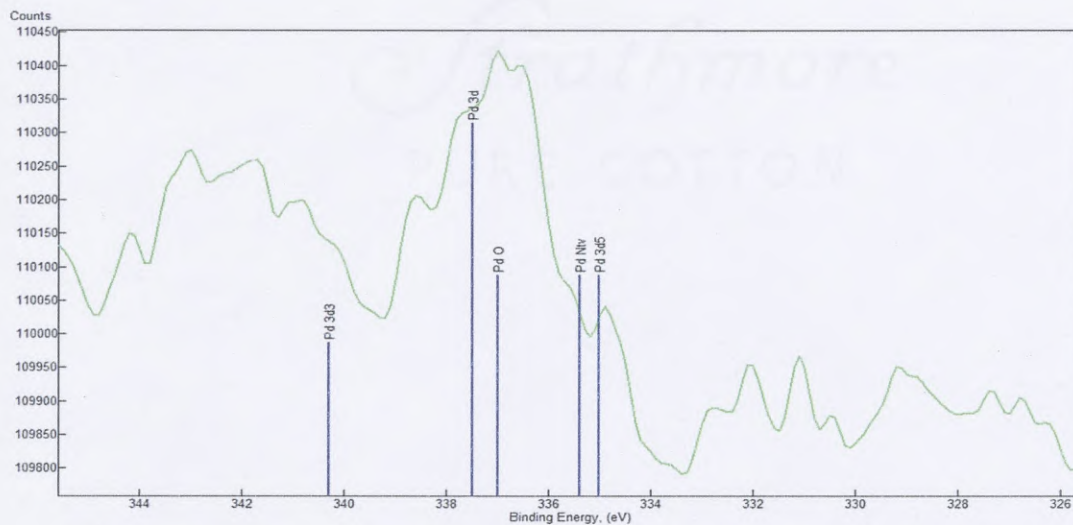


Figure 3.9 High Resolution Spectra over Pd3d on 10 wt.% Pd/Al₂O₃ (CSU-1).

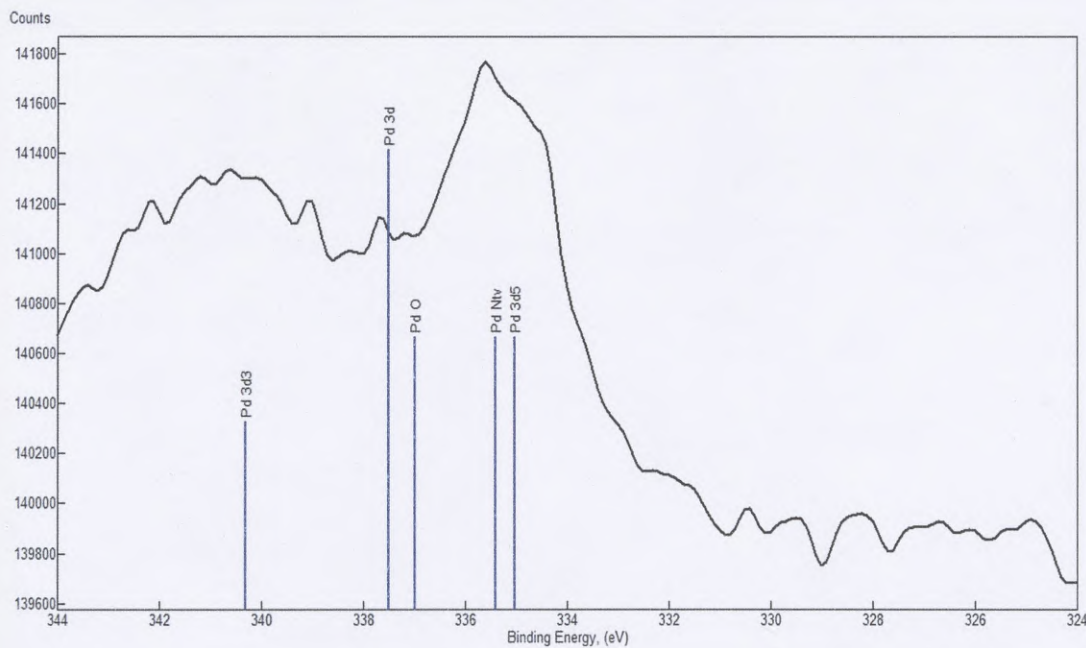


Figure 3.10 High Resolution Spectra over Pd3d of 10 wt.% Pd/Al₂O₃ (CSU-1) after Sputtering.

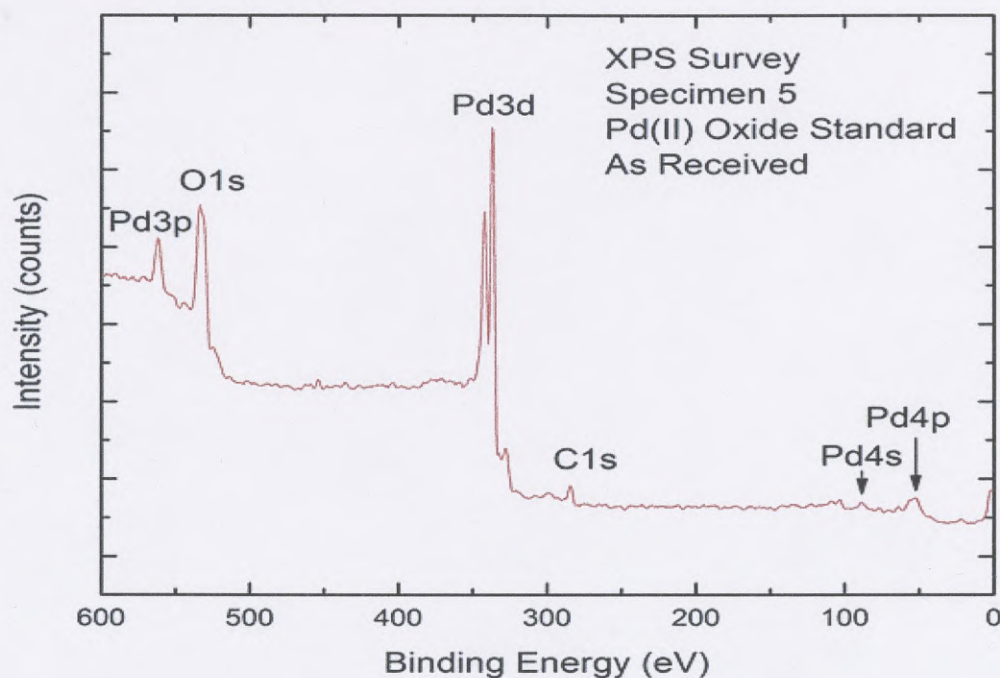


Figure 3.11 XPS spectra for PdO standard (CSU-7).

XPS analysis was also conducted on 5 wt.% Pd/CeO₂ (CSU-8), reacted 5 wt.% Pd/CeO₂ (CSU-9), and 20 wt.% Pd/CeO₂ (CSU-10) samples. Surface composition in relative percentages could not be determined because ceria is so little studied that quantification factors to accurately interpret spectra are not known. However, information on palladium and oxygen species provide insight into chemical changes occurring throughout the reaction. Figure 3.12 illustrates the spectra for 5 wt.% Pd/CeO₂ (CSU-8) and indicates the presence of Ceria, and accounting for chemical shifts due to interference with carbon, matches previous research which shows binding energies existing between 880-885eV. Figure 3.13 shows the deconvolution of the Ce3d area and shows that no variation exists with respect to the chemical states of ceria.

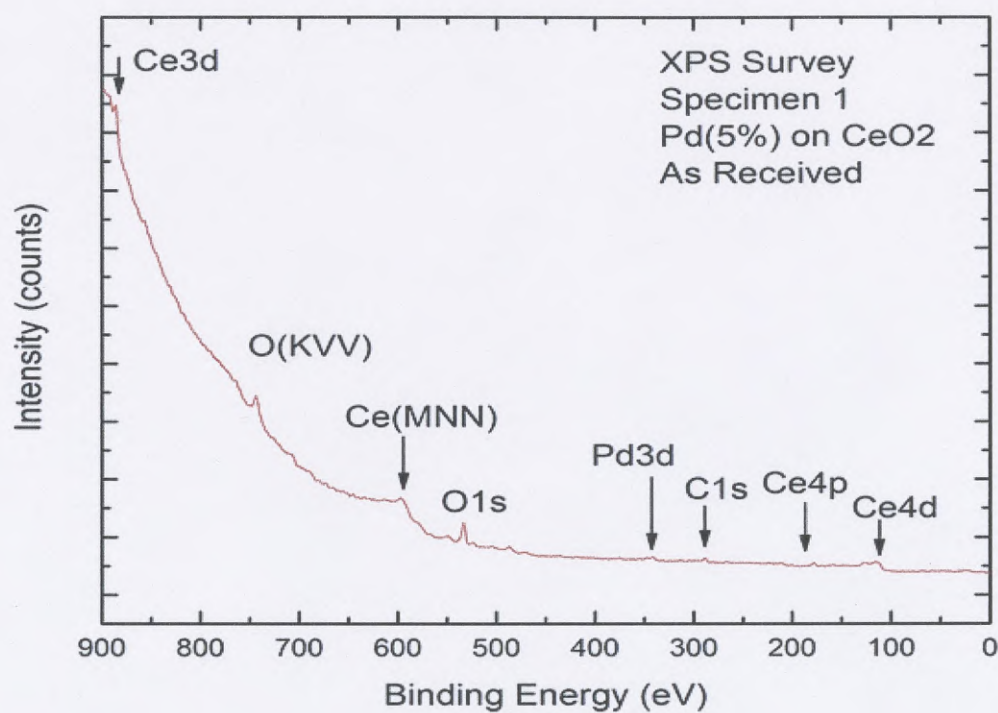


Figure 3.12 XPS Spectra of 5 wt.% Pd/CeO₂ (CSU-8).

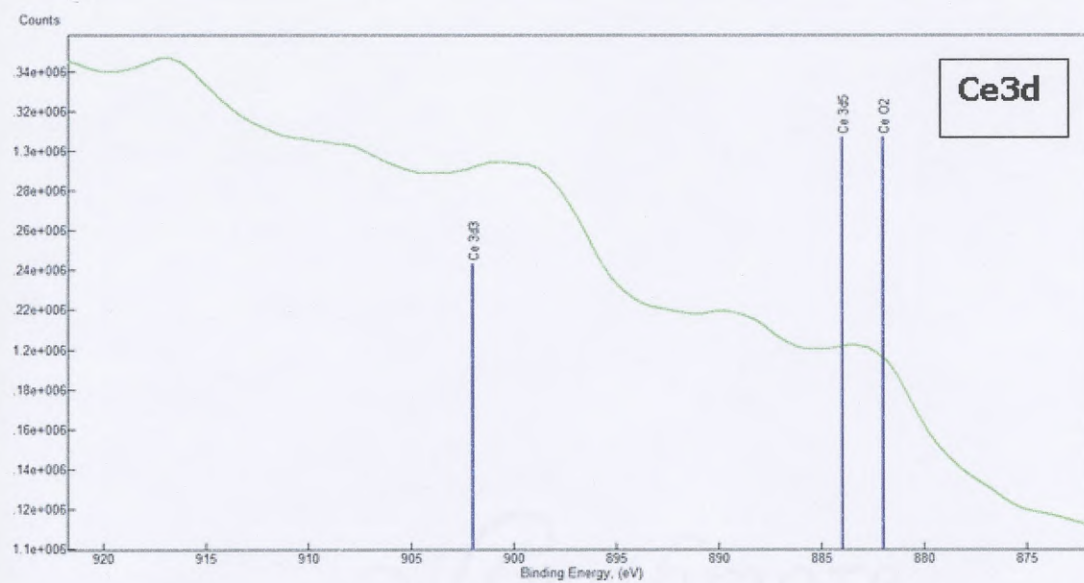


Figure 3.13 High Resolution Spectra over Ce3d, Sample 5 wt.% Pd/CeO₂ (CSU-8).

Figure 3.14 and Figure 3.15 show the high-resolution spectra of 5 wt.% Pd/CeO₂ (CSU-8) for oxygen and palladium species, respectively. Note that the oxygen in O1s deconvolution exists in one state for 5 wt.% Pd/CeO₂. After reaction, oxygen exhibits multiple chemical states, as evident from the high-resolution spectra displayed in Figure 3.16. Palladium was shown to be predominantly PdO in 5 wt.% Pd/CeO₂ (CSU-8). However, PdO undergoes a chemical change after reaction. Figure 3.17 shows that Pd native oxides and elemental Pd become more prevalent, accounting for the disappearance of PdO state. This has been seen in previous experiments and accounts for the notion that CO oxidation occurs mainly on elemental Pd species on the surface, and oxygen is transferred from both existing PdO as well as the support to facilitate reactions.^{27, 28}

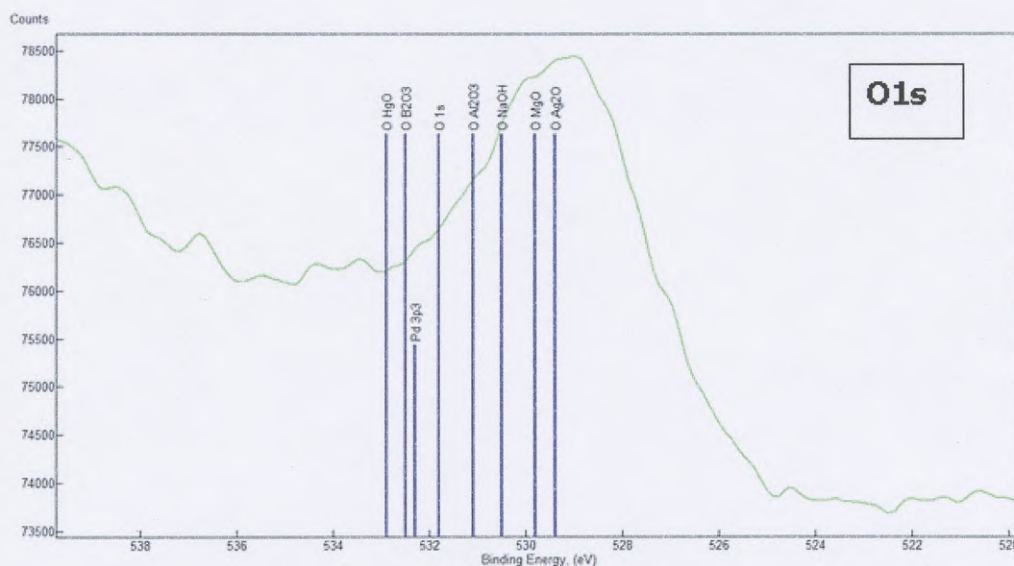


Figure 3.14 XPS High Resolution Spectra of 5 wt.% Pd/CeO₂ (CSU-8) over O1s.

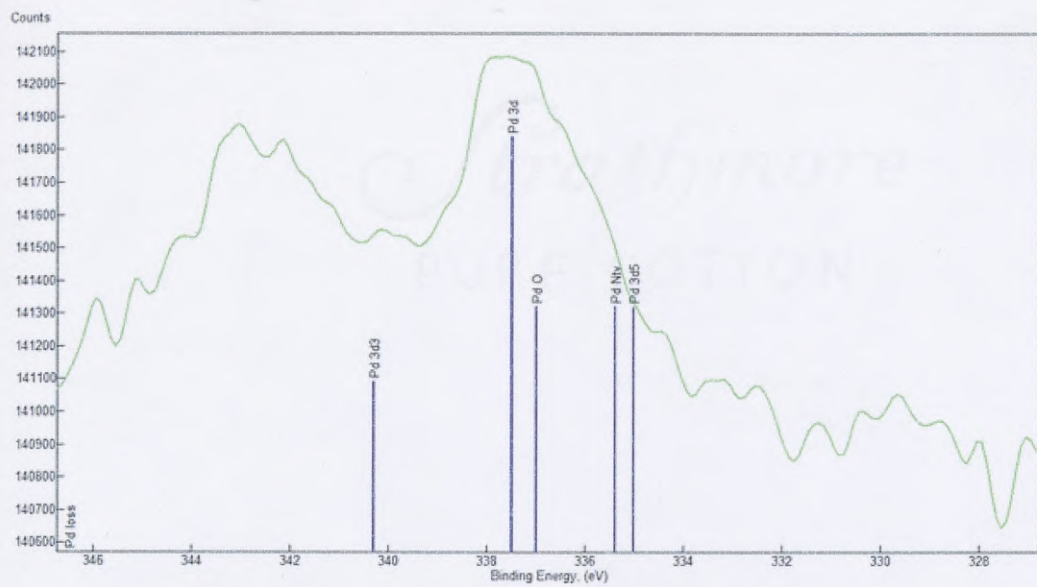


Figure 3.15 XPS High Resolution Spectra of 5 wt.% Pd/CeO₂ (CSU-8) over Pd3d.

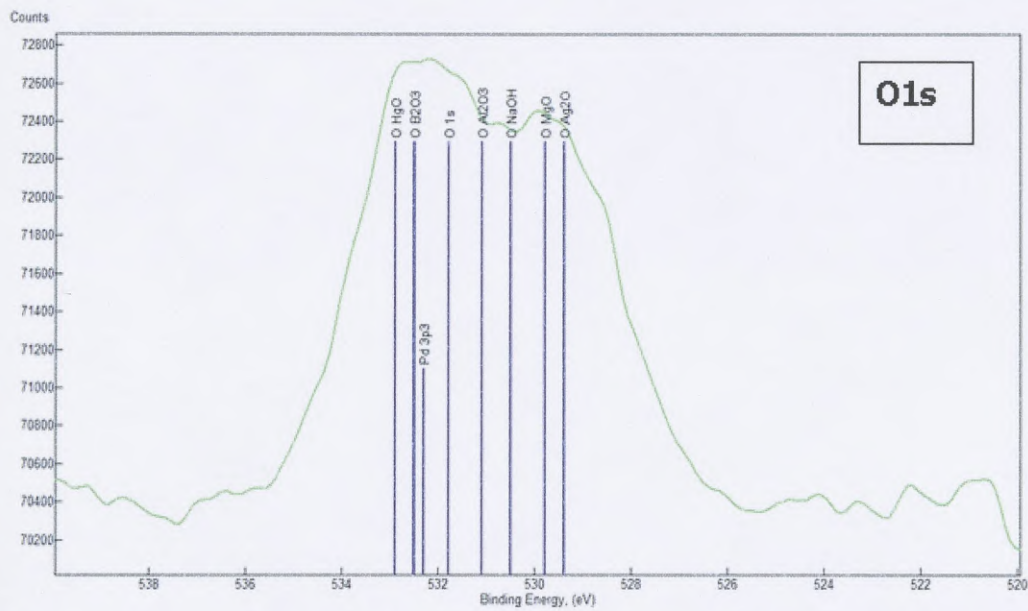


Figure 3.16 XPS High Resolution Spectra of Reacted 5 wt.% Pd/CeO₂ (CSU-9) over O1s.

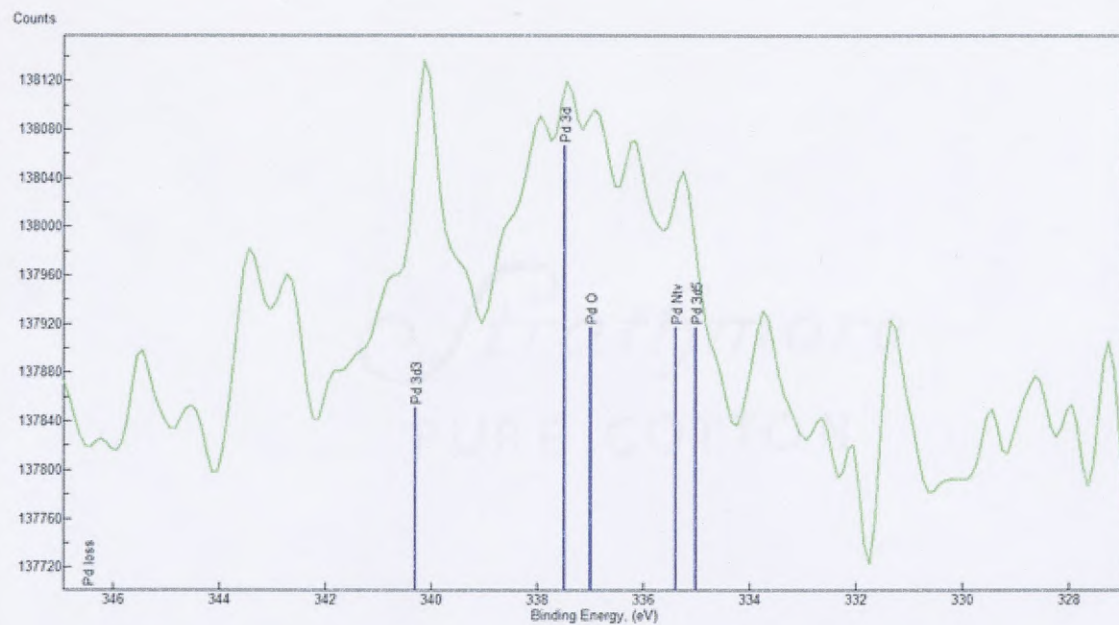


Figure 3.17 XPS High Resolution Spectra of reacted 5 wt.% Pd/CeO₂ (CSU-9) over Pd_{3d}.

XPS analysis was also conducted on 20 wt.% Pd/CeO₂ (CSU-10) and the spectra is provided in Figure 3.18. The increased weight percentage did not provide increased resolution between ceria chemical states as hoped. Therefore, this analysis is only useful in providing a comparison to earlier catalyst samples. 20 wt.% Pd/CeO₂ (CSU-10) shows relatively similar proportions to 5 wt.% Pd/CeO₂ with respect to PdO and native Pd.

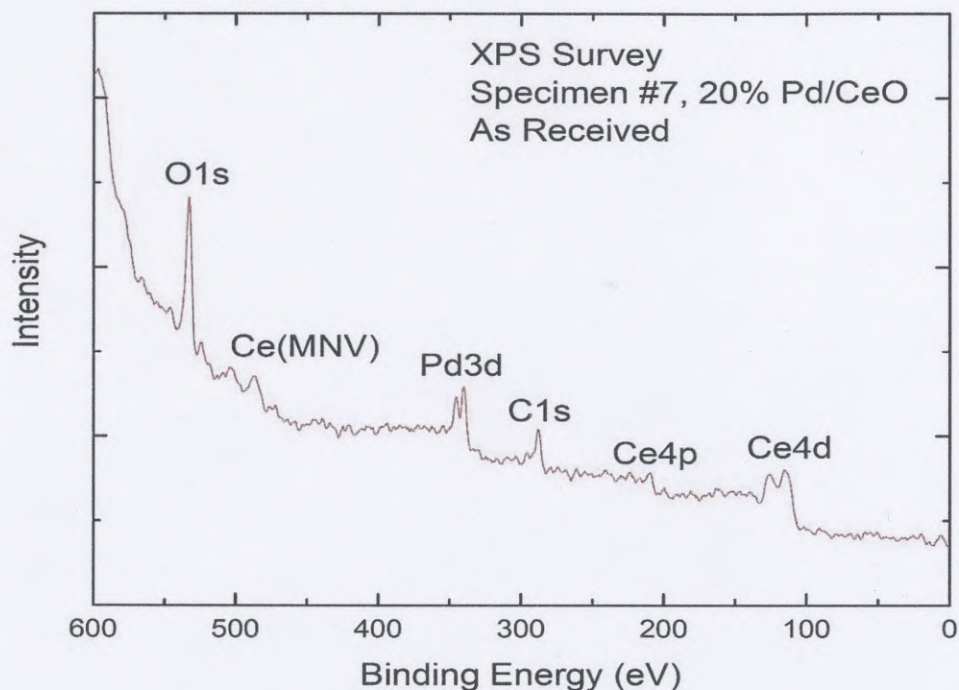


Figure 3.18 XPS Spectra of 20 wt.% Pd/CeO₂ (CSU-10).

III. Chemisorption

Chemisorption on 5 wt.% Pd/CeO₂ (CSU-8) was carried out by Dr. Kristina Golub at the Georgia Institute of Technology and Table 3.4 provides catalyst characteristics based on 5% Palladium loading. Comparisons to Pd/Al₂O₃ samples show a modest improvement in uptake from 56.1 to 57.8 μmol/g and increased dispersion from 11.95% to 12.28%.²¹ However, due to the actual palladium loading being less than expected, we can infer that the actual catalyst characteristics are even better than calculated. 9nm particle size is roughly similar in size to experiments using

similar preparation methods.²⁹ Although it is commonly accepted that lower particle size increases activity for carbon monoxide oxidation, our results show that activity for Pd/CeO₂ is competitive in performance with the smallest particle sizes. Appendix B lists the operating procedure for all chemisorption experiments.

Table 3.4 Chemisorption Results for 5% Pd/CeO₂

Pd/CeO₂ Chemisorption	
CO Uptake	57.72μg/mol
Dispersion	12.28%
Metal Surface Area	2.72m ² /g
Particle Size	9.12 nm

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IV. CONCLUSIONS AND FUTURE WORK

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A. CONCLUSION

Preliminary studies in the oxidation of carbon monoxide were conducted using palladium catalysts with alumina oxide supports. The calcination temperature was varied between 500°, 600°, 750°, and 900°C. Despite varying palladium oxidation states, revealed by XPS, catalytic activity remained relatively unchanged. It is believed that the lack in variability among results is due to the relatively inert nature of alumina oxide support. Both oxidized and reduced treatments showed increased activity, indicating that both PdO and elemental Pd_x can catalyze the oxidation of carbon monoxide.

Pd/CeO₂ catalysts synthesized and studies showed particle sizes between 5-15 nm, which was confirmed by both XRD and chemisorption techniques. Smaller particle size is achievable, but not believed to be as impactful as originally proposed. Maybe more important than particle size is the configuration at which palladium is loaded. Other studies conducted investigated the different configurations assumed by palladium on ceria supports and concluded that nanocubes (100) showed the highest catalytic activity.^{30,31} The Pd/CeO₂ synthesized in this experiment was shown by XRD to be mostly in nanoparticle (111) shape, although no definitive determination can be made as to the composition overall.

After optimal preparations techniques were determined based on preliminary studies, an experiment testing the catalytic activity of ceria-supported palladium catalysts was conducted. Pd/CeO₂ showed a major increase in activity compared with alumina-supported catalysts. This

is caused by the increased ability of ceria to change oxidation states and supply oxygen storage capabilities. Improvements are also attributed to vortex assisted incipient wetness impregnation, which is believed to increase surface loading of palladium and prevent agglomeration. However, achieving high palladium content by weight percentage proved to be unsuccessful because of either agglomeration, or the change in preparation method needed to coprecipitate palladium and ceria.

Overall, improved activity was achieved in both stoichiometric and oxygen rich conditions. At 60°C in a 6%CO, 2%O₂, balance helium mixture, CO conversion dropped to zero. This may be due to change in affinity at this temperature, causing saturation of active sites by CO. These results infer that the adsorption of oxygen is necessary for oxidation of carbon monoxide. Excess CO concentrations may provide the energy needed to overcome oxidation energy barriers at low temperatures. Excess oxygen shows decreased catalytic performance at low temperatures compared to CO rich environment at similar temperatures below 60°C, either due to the inability to dissociate or inhibition of CO adsorption. This finding confirms previous studies that show low temperature regimes are limited by dissociation of O₂, and perhaps the lack of high energy CO does not provide enough energy for oxidation at low temperature.³²

Although low temperature oxidation of carbon monoxide was achieved, the most recent literature indicates that room temperature conversion is possible by prefabricating structural components of the support to maximize palladium loading and proximity.^{33,34} It is notable, however, that the simplistic methods and relatively harmless compounds used may be utilized

more practically for experiments of this type than complex instrumentation and preparation techniques. For industrial purposes, a focus on inexpensive and clean methods is becoming more practical as regulations continue to increase. For this reason, it is believed that Pd/CeO₂ could be a highly utilized catalyst in the future for many various reactions.

B. FUTURE WORK

Despite improved catalytic activity in Pd/CeO₂, it is necessary to consider other factors that may influence the oxidation of carbon monoxide at low temperatures. Many catalytic converters operate in wet air conditions at temperatures that can far exceed 150°C. Some studies have shown improvements in catalytic performance under moisture conditions.^{35,36} Examination of CO oxidation in the presence of water over palladium catalysts at varying temperatures should be explored to provide similar kinetic data to those conducted in this experiment.

Studies concerning the long-term efficacy of these catalysts may also need to be explored.

Long term oxidation conditions lead to deactivation of many catalysts. Therefore, experiments testing activity after exposure to high oxidative stress would be indicative of sustainability. If Pd/CeO₂ cannot maintain relatively similar stability and longevity to currently used catalysts, then its efficacy may be questionable for high volume industrial processes.

Experimentation may also be needed to determine how Pd/CeO₂ catalysts react in the presence of multiple competitors such as nitrogen containing compounds, alcohols, and hydrocarbons typically found in complex reaction chambers. Although Pd/CeO₂ has shown an ability to catalyze numerous reactions, a study detailing how these mixtures compete for reaction sites would be useful in determining catalyst versatility.

Characterization of Pd/CeO₂ and activity studies on the oxidation of carbon monoxide suggest that improvements in palladium loading and stoichiometric balancing may further increase the rate of reaction and lower the energy barrier. In depth kinetic studies of these dynamics will be required to optimize conditions for oxidation of carbon monoxide over Pd/CeO₂. These studies should include various gas mixture studies at and around stoichiometric quantities to maximize conversion at low temperatures. Also, progression of reaction rates over time will help to supply more data for thermodynamic studies.

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APPENDIX A

Parameters for XPS provided by personal communication with Dr. Michael Bozack at the University of Auburn.

"Photoemission measurements were performed in a load-locked Kratos XSAM 800 surface analysis system equipped with a hemispherical energy analyzer. The base pressure of this ion- and turbo-pumped system was 8×10^{-9} torr as read on a nude ion gauge. The XPS analyzer was a 127 mm radius double-focusing concentric hemispherical energy analyzer (CHA) equipped with an aberration compensated input lens (ACIL). XPS spectra were recorded in the fixed analyzer transmission (FAT) mode with a pass energy of 80 eV, appropriate for acquisition of medium resolution, high signal-to-noise spectra. The magnification of the analyzer in the FAT mode was selected to collect electrons from the smallest allowable (5mm^2) area on the specimen. The resolution of the instrument at the operating parameters was measured from FWHM of the $\text{Ag}3d_{5/2}$ peak to be 1.0 eV. The XPS energy scale was calibrated by setting the $\text{Ag}3d_{5/2}$ line on clean silver to exactly 368.3 eV referenced to the Fermi level. Due to specimen charging during X-ray irradiation, the energy axis of each XPS spectra has been shifted to make the C1s binding energy line equal to 285.0 eV, which is a standard hydrocarbon energy (C-H and C-C bonds) used to reference charge affected materials. The potential measured on a typical sample was 0.5 V. The photoelectrons were excited by a water-cooled, conventional (i.e., non-monochromatic) dual anode X-ray gun equipped with an Al window. The angle of the incidence of the x-ray beam with the specimen normal was 51.5° . $\text{MgK}\alpha$ (1253.6 eV) radiation was used exclusively. In cases when the peaks were low in amplitude, the Savitsky-Golay smoothing routine was used in order to help determine the peak binding energies. The XPS surface composition was calculated based on the Scofield cross-sectional values accounting for the

instrumental transmission function in the FAT mode of operation. The specimen was pressed into double-sided carbon tape to a thickness which insured that the emitted photoelectrons would originate only from the specimen."

APPENDIX B.

Communication with Todd Sulmonetti at Georgia Tech describing parameters of Chemisorption.

“Chemisorption experiments including temperature programmed reduction (TPR) and pulse CO chemisorption were conducted in Micromeritics AutoChem II 2920. For each TPR experiment, approximately 30 mg of sample was placed on top of a small bed of quartz wool in a quartz U-tube. In regard to the TPR experiment, the material was pretreated in 30 mL/min of He (Airgas, UHP) at 110°C for 1 hours to remove preadsorbed species. The sample was then cooled to 30°C and 20 mL/min of 10% H₂ balance Ar was flown over the sample. The furnace was heated to 500 °C at 5 °C/min while under the flow of 10% H₂/Ar. The outlet gas passed through a liquid acetone/nitrogen trap, and then passed through a Thermal Conductivity Detector (TCD).

For each TPO experiment, approximately 30 mg of sample was placed on top of a small bed of quartz wool in a quartz U-tube. In regard to the TPO experiment, the material was pretreated in 30 mL/min of He (Airgas, UHP) at 110°C for 1 hours to remove pre-adsorbed species. The sample was then cooled to 30°C and 20 mL/min of 10% O₂ balance He was flown over the sample. The furnace was heated to 500°C at 5°C/min while under the flow of 10% O₂/He. The outlet gas passed through a Thermal Conductivity Detector (TCD).

CO with Reduction:

Approximately 30 mg catalyst sample was placed in the quartz tube held in place by quartz wool. The material was pretreated in 30 mL/min of He (Airgas, UHP) at 110°C for 1 hour to remove pre-adsorbed species. During the reduction step (see TPR for gas flow rates) the sample was heated to 450°C at 5°C/min and held for

30 min. The sample was then cooled to 400°C where He began to flow for 30 min to remove all adsorbed species. Afterwards the sample was cooled down to 30°C to begin pulse CO testing. Doses of 10% CO/He (Airgas) were passed over the sample and analyzed in the TCD. Once saturation was reached, He was flowed over the sample for 30 min to remove physisorbed species (50 mL/min). Finally, a second round of pulses was conducted to verify if there were any physisorbed species adsorbed, which was taken into consideration when calculating the active metallic surface area.

CO without reduction:

Approximately 30 mg catalyst sample was placed in the quartz tube held in place by quartz wool. The material was pretreated in 30 mL/min of He (Airgas, UHP) at 110°C for 1 hour to remove pre-adsorbed species. Afterwards the sample was cooled down to 30°C to begin pulse CO testing. Doses of 10% CO/He (Airgas) were passed over the sample and analyzed in the TCD. Once saturation was reached, He was flowed over the sample for 30 min to remove physisorbed species (50 mL/min). Finally, a second round of pulses was conducted to verify if there were any physisorbed species adsorbed, which was taken into consideration when calculating the active metallic surface area."

I have submitted this thesis in partial fulfillment of the requirements for the degree of Master of

Science

Nov. 26, 2018

Date

John Davis Gary

John Davis Gary

We approve the thesis of John Davis Gary as presented here.

11/26/2018

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