Reformulation of Coal-Derived Transportation Fuels:
Selective Oxidation of Carbon Monoxide on Metal Foam Catalysts

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Abstract

Several different catalytic reactions must be carried out in order to convert hydrocarbons (or alcohols) into hydrogen for use as a fuel for polyelectrolyte membrane (PEM) fuel cells. Each reaction in the fuel-processing sequence has a different set of characteristics, which influences the type of catalyst support that should be used for that particular reaction. A wide range of supports are being evaluated for the various reactions in the fuel-processing scheme, including porous and non-porous particles, ceramic and metal straight-channel monoliths, and ceramic and metal monolithic foams. These different types of support have distinctly different transport characteristics. The best choice of support for a given reaction will depend on the design constraints for the system, e.g., allowable pressure drop, and on the characteristics of the reaction for which the catalyst is being designed. Three of the most important reaction characteristics are the intrinsic reaction rate, the exothermicity/endothermicity of the reaction, and the nature of the reaction network, e.g., whether more than one reaction takes place and, in the case of multiple reactions, the configuration of the network. Isotopic transient kinetic analysis was used to study the surface intermediates.

The preferential oxidation of low concentrations of carbon monoxide in the presence of high concentrations of hydrogen (PROX) is an important final step in most fuel processor designs. Data on the behavior of straight-channel monoliths and foam monolith supports will be presented to illustrate some of the factors involved in choosing a support for this reaction.
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1. Introduction
1.1 Preferential Oxidation
The development of practical fuel cell power for automotive transportation and for stationary applications will require the development of fuel processors that convert liquid fuels into hydrogen and carbon dioxide. These fuel processors will contain compact catalytic reactors that carry out a number of reactions between the fuel, oxygen, and steam: partial oxidation, steam reforming, water-gas shift, and selective oxidation of CO in the final hydrogen stream. Fuel processors must be compact, mechanically durable, quick-starting, responsive to transient demands, and inexpensive.

The gas stream that is fed to the fuel cell must have a very low (<10 ppm) concentration of CO to avoid poisoning the fuel cell electrode [11,12]. The final selective oxidation step requires a catalyst that is active for the oxidation of CO (Reaction 1) in order to reduce the concentration of CO from about 1% to less than 10 ppm in the presence of high concentrations of H₂, CO₂, steam, using a minimum volume of catalyst.

\[ CO + \frac{1}{2} O_2 \rightarrow CO_2 \]  
(1)

However, the catalyst must not oxidize a significant quantity of hydrogen (Reaction 2)

\[ H_2 + \frac{1}{2} O_2 \rightarrow H_2O \]  
(2)

\[ CO + H_2O \leftrightarrow H_2 + CO_2 \]  
(3)

since H₂ is the fuel used at the anode of the fuel cell, nor should it have a strong preference to the water-gas-shift reaction (Reaction 3). Hydrogen that is consumed by Reaction 2 during the selective oxidation step must be replaced by increasing the size of the fuel processor, and increasing the rate of feed to the fuel processor. Therefore, the catalyst not only must be highly active for the oxidation of CO, it also must be highly selective for Reaction 1 over Reaction 2. The process described above is known as “preferential oxidation” in the fuel cell community, and is often referred to using the acronym “PROX”.

Because of the exothermic nature of these two oxidation reactions, some commercial designs for this element of the fuel processor are based on two adiabatic reactors in series, with an intermediate cooling step [13].

Packed catalyst beds, as well as ceramic monoliths, have been evaluated for the PROX reactor. Other potential supports include metal monoliths. The objective of this research is to demonstrate that effective PROX catalysts could be prepared on metallic foam supports, and to compare these catalysts with identical catalysts prepared on ceramic monoliths.
1.2 Literature Review

The selective oxidation of CO in the presence of hydrogen was first studied using a Pt/alumina catalyst in 1963. In 1997, Igarashi et al. investigated the effect of the support on the selectivity of Pt catalysts for CO oxidation and found that Pt supported on mordenite showed the highest selectivity, as well as high conversion of CO during oxidation at low oxygen concentration [13]. In the same year, Kahlich et al. [14] used the preferential oxidation process (PROX) to determine the optimum temperature, the reaction order, and the apparent activation energy of CO oxidation on Pt/Al₂O₃. It was found that the optimum temperature was 200°C at 1 bar and the reaction orders were -0.4 for CO and +0.8 for O₂ for temperatures between 150°C and 250°C.

Korotkikh and Farrauto [1] investigated the effect of a promoter oxide on the activity of 5 wt% Pt/alumina. With a base metal oxide promoter, the CO conversion was significantly increased from 13.2 to 68% at 90°C and a molar ratio of O₂/CO = 0.5 without affecting the selectivity. Recently, Manasilp and Gulari [9] studied the selectivity of a 2% Pt/alumina sol-gel catalyst in a mixed feed stream including CO₂ and water. This catalyst was found to have an activity and a selectivity high enough to oxidize CO in hydrogen down to a few ppm. Water vapor had a positive effect in reducing the activation energy, resulting in an increase in conversion without any significant change in selectivity. Carbon dioxide in the feed stream decreased the activity of the catalyst in the absence of water vapor. Other metal-based catalysts have also been found to be active for selective CO oxidation, including Ru [4], Rh [4], and Au [16-18].

Most of the previous studies of the selective oxidation of CO have been conducted under steady-state conditions. However, although Nibbelke et al. [19] commented in their paper that Pt/γ-Al₂O₃ exhibited a higher initial activity during startup compared to the activity measured after a few hours on stream, initial catalyst deactivation has not been investigated. This initial rapid deactivation can result in a loss of 90% of the initial activity of a Pt catalyst before steady state is reached.

In order to obtain surface kinetic information about CO oxidation, isotopic-transient kinetic analysis (ITKA) has been used in a portion of this study. Since it allows in-situ measurement of the concentration of surface intermediates and their intrinsic reactivities while the reaction is maintained at stable reaction conditions, SSITKA (steady-state isotopic-transient kinetic analysis) or ITKA (when not at steady state) is one of the most powerful techniques for the kinetic study of heterogeneous catalysis. Extensive details about the use of (SS)ITKA are given in references [20,21]. A conventional selective CO oxidation catalyst, 5% Pt/Al₂O₃ was employed, and the effect of time-on-stream on CO oxidation rate, selectivity, concentration of surface intermediates, and catalyst intrinsic activity was investigated. Since this catalyst possesses very high activity and selectivity during initial reaction, a better understanding of the deactivation phenomena could lead to strategies to prevent or slow down deactivation, resulting in a better catalyst design.
1.3 Metal Foam Catalyst Supports

Metal foam catalyst supports consist of irregular, open cells in a rigid matrix, as shown in Figure A1a in Appendix A. The active catalytic material is added to the foam via a washcoating process, which is described in more detail later. Foams have been used as catalyst supports in several applications, such as radiant burners and exhaust catalysts for small engines. Among the metals of interest, Fecralloy® was particularly suited for the present study. The composition of Fecralloy® is: 72.8% Fe/22% Cr/5% Al/0.1% Y/0.1% Zr.

Metal foams have several potential advantages for fuel processors:

(1) The porosity of the foam can be very high, which helps to minimize pressure drop and results in a low heat capacity, which provides a rapid response to transients and to changes in the operating conditions of the fuel processor;

(2) Metal foams can be formed in shapes other than right cylinders and square blocks, as shown in Figure A1b in Appendix A, allowing the fuel processor to fit the demanding space requirements of an automotive fuel processor, which may not have a straight flow path. These foams have already been shown to be useful in similar situations, e.g., exhaust catalysts for small engines such as lawn mowers and power saws, where straight-channel monoliths could not be used;

(3) The cell density is variable over a larger range than metallic monoliths. Specifically, metallic foams can be made with densities as low as 3% of the theoretical volume (i.e. void volume of 97%). This allows the inevitable trade-off between pressure drop and mass transfer rates to be optimized for the wide range of flow rates required in an automotive fuel processor;

(4) The foams can be metallurgically bonded to reactor shells, forming light-weight, durable, and rugged reactors;

(5) Metal tubes can be mechanically inserted into the foam structure during the manufacturing process, as shown in Figure A1c in Appendix A. These tubes can be used to transfer heat out of the PROX catalyst. This type of heat transfer could, in principle, eliminate the need for a two-stage CO oxidation unit, saving space and cost, and minimizing hydrogen oxidation.

(6) The cellular nature of the metallic foams permits radial and axial flow and mixing of fluid. This type of mixing can help to alleviate problems associated with misdistribution of the gas that is fed to the reactor.

During this research, a Pt/Al₂O₃ catalyst promoted with Fe was evaluated. This catalyst was supported on a series of metallic foams with varying porosity and pore size. As a control, the same catalyst, deposited on a conventional ceramic monolith, was evaluated. Finally, a metal monolith and a ceramic foam were evaluated briefly. These supports were compared at the same volumetric washcoat loading and catalyst composition.
2. Executive Summary

This project is a joint effort among NC State University, Clemson University, and Porvair Fuel Cell Technologies (PFCT, Hendersonville, NC).

Several different catalytic reactions must be carried out in order to convert hydrocarbon fuels or oxygenates into hydrogen for use as a fuel for proton exchange membrane (PEM) fuel cells. Typically three sequential reactions are used: autothermal reforming, water-gas-shift, and preferential oxidation (PROX). In this last reaction, CO is selectively oxidized in the presence of ~40% hydrogen to prevent poisoning of the fuel cell electrode.

This paper focuses on the use of metal foams as supports for PROX catalysts. Ceramic and metallic straight-channel monoliths, conventional packed beds, and ceramic foams are candidate supports for these catalysts. The high thermal conductivity, mechanical strength, and wide range of physical properties of metal foams suggest that they may be suitable for this application. Here, these foams are compared directly with straight-channel ceramic monoliths for the PROX reaction.

Metal foams with void volumes of 96% and 88% were prepared by PFCT from Fecralloy®, a ferric alloy with an empirical composition of Fe 72.8/Cr 22/Al 5/Y 0.1/Zr 0.1. These foams were washcoated and impregnated with 5%Pt-0.5% Fe. Ceramic straight-channel monoliths were prepared with nominally identical volumetric loadings of catalyst (1.6 g cat/in³) by similar washcoating techniques. The catalysts were calcined at 300°C for 2 h and tested in an adiabatic fixed bed reactor. Outlet CO and oxygen concentrations were measured continuously using an NDIR analyzer. CO selectivity is calculated as \[0.5 \times \frac{(CO_{\text{in}} - CO_{\text{out}})}{(O_2,\text{in} - O_2,\text{out})}\].

![Figure 1. Comparison of CO conversion and selectivity on metal foams and straight-channel ceramic monoliths](image)

Figure 1 shows that the CO conversion and CO selectivity (the proportion of CO oxidized to CO₂ to the ratio of H₂ oxidized) for catalysts on a metal foam and a ceramic monolith are comparable when tested under the same operating conditions: P = 2 atm (abs.); inlet...
gas composition = H₂ – 42%, CO₂ – 9%, H₂O – 12%, CO – 1.0%, O₂ – 0.25-1.0%, and N₂ – Balance; inlet temperature = 80-170°C; space velocity = 5,000-60,000 hr⁻¹, catalyst length = 2”-6”.

Equilibrium calculations suggest that the decrease in CO conversion with increasing temperature is consistent with an increase in the equilibrium concentration of CO formed by the reverse water-gas-shift reaction. The decrease in CO selectivity is consistent with an increase in the rate of hydrogen oxidation compared to CO oxidation at higher temperatures on Pt-base metal catalysts [2]. Figure 2 shows that catalyst performance is very sensitive to iron loading. It has been suggested that Fe activates oxygen at the relatively low temperatures of this reaction in a dual-site mechanism [2]. Testing of 0%-1% wt. loadings of iron on a 5% Pt catalyst shows that this promoting effect is significant, and begins at an Fe loading of ~0.5 wt%.

The selective oxidation of CO in the presence of hydrogen using 5% Pt/γ-Al₂O₃ exhibited high initial partial deactivation before reaching steady state. The observed rate and CO₂ selectivity were very high during the initial reaction period, but decreased significantly with time-on-stream. By using isotopic transient analysis, the pseudo-first-order intrinsic rate constant was found to be relatively constant compared to the concentration of surface CO₂ reaction intermediates. It can be concluded that the deactivation of this Pt catalyst is mainly the result of a decrease in the concentration of surface intermediates, not the intrinsic activity. In addition, regeneration of the catalyst in the stream of hydrogen at temperatures higher than or equal to 300°C can completely recover the initial activity and selectivity of the deactivated catalyst. Approximately 12% of surface Pt was likely covered with carbonaceous species during initial deactivation. From this result, we suggest that the deactivation of Pt is due to carbon deposition on the Pt surface and that this carbon deposition also caused a significant decrease in CO₂ selectivity. Possibly CO₂ selectivity is decreased because CO adsorption is affected more than H₂ and O₂ adsorption.
3. Experimental

3.1 Catalyst Preparation (Metal Foams, Ceramic Monoliths, Provided by PFCT)

1” inner diameter (ID) and 2” length metallic foams and monolith supports were provided by Porvair Fuel Cell Technology (PFCT), in Hendersonville, NC. A series of Fe promoted Pt catalysts were synthesized and washcoated onto these supports, with a washcoat loading of approximately 1.6 g cat/in³.

The four different supports were included in our tests: four metal foams, which possessed 40 ppi ( pores per inch ), 4% density; 40 ppi, 12% density; 20 ppi, 4% density; and 20 ppi, 12% density structure; one 400 cpsi ( cells per square inch ) ceramic straight-channel monolith; one 20 ppi, 11% ceramic foam; one corrugated metal monolith. The metal monolith was made of a spiral-wound corrugated metal support with a repeating pattern of ~3 mm. This results in an open face are roughly equivalent to the 400 cpsi ceramic straight-channel monolith.

Pores per inch ( ppi ) can be described as the number of pores in the foam per given inch. For example, a 20 ppi foam will have larger channel sizes compared to a 40 ppi foam. A 40 ppi foam would give greater tortuosity compared to a 20 ppi foam. Secondly, percent density can be described as the actual volume of foam taken up divided by the total volume of the foam. For example, a 4% density foam has 96% void volume, while a 12% density foam has a 88% void volume. Finally, cells per square inch ( cpsi ) can be similarly characterized by the number of cells per given inch. For example, a 400 cpsi straight-channel monolith has smaller channels than a 200 cpsi straight-channel monolith. Figure A2 in Appendix A gives an example.

3.2 Catalyst Preparation (NCSU)

Kyle Bishop, a summer student from the University of Virginia, in the Green Processing research experience for undergraduates (REU) program, prepared powder samples to be used for washcoating of blank metal foams supplied by PFCT. These powders were not used in washcoating of the foam samples reported here, but will be used in later work. The technique is outlined below.

Pt catalyst:
1. Start with $\gamma$-Al₂O₃ powder with a particle size ranging from 63-200µm. Determine the pore volume to mass ratio by impregnating to incipient wetness with deionized water.

2. Calculate the appropriate concentration of hydrogen hexachloroplatinate ( IV ) hexahydrate ( H₂Cl₆Pt⋅6H₂O ) solution to achieve the desired platinum loading. Impregnate to incipient wetness ( i.e. the powder begins to look wet or shiny ).

3. Dry in a 110°C oven for 12 hr to remove all water.

4. Calcine in air at 450°C for 5 hr.
Fe-promoted Pt catalysts:
1. Start with Pt/\(\gamma\)-Al\(_2\)O\(_3\) powder. Determine the pore volume to mass ratio by impregnating to incipient wetness with deionized water. (Note: The ratio may or may not be less than the pure alumina depending on the platinum loading.)

2. Calculate the appropriate concentration of iron (III) nitrate nonahydrate (Fe(NO\(_3\))\(_3\)\(\cdot\)9H\(_2\)O) to achieve the desired iron loading. Impregnate the Pt/\(\gamma\)-Al\(_2\)O\(_3\) powder to incipient wetness.

3. Dry in a 110°C oven for 12 hr to remove all water.

4. Calcine in air at 300°C for 2-3 hr.

Ni-promoted Pt catalysts:
Prepare exactly as the iron-promoted catalysts using nickel (II) nitrate hexahydrate (Ni(NO\(_3\))\(_2\)\(\cdot\)6H\(_2\)O) as the nickel precursor.

3.3 Catalyst Preparation (Clemson)
A catalyst consisting of 5 wt% Pt on \(\gamma\)-Al\(_2\)O\(_3\) powder was prepared by incipient wetness impregnation. The support (Al\(_2\)O\(_3\), Vista B) was first calcined at 500°C for 10 h before being impregnated at room temperature with an aqueous solution of chloroplatinic acid hexahydrate. The catalyst was then dried overnight at 110°C and calcined at 500°C for 2 h under flowing dry air.

3.4 Reactor system (NCSU)
Figure A3 in Appendix A shows a schematic of the process design used for this study. Gases were fed from four cylinders, which contain 10% CO/balance N\(_2\), 10% O\(_2\)/balance N\(_2\), 17.6% CO\(_2\)/balance H\(_2\) and ultra high pure (UHP) N\(_2\), respectively. Four mass flow controllers were used to measure and control the gas flow rate from each cylinder. A carbonyl trap (activated carbon bed) was installed to remove any iron and/or nickel carbonyls that might be present in the 10% CO/N\(_2\) line. An oxygen trap was installed on the 17.6% CO/H\(_2\) line to remove any traces of O\(_2\). Liquid water, which was supplied to the system by a HPLC pump, was then added to the gas stream. This mixture then passed through a fluidized sand bath to generate steam and to heat up the gas stream to the desired temperature.

Foam and monolith support catalysts were wrapped with ceramic fiber insulation and fitted into a 1 1/8” ID stainless steel reactor. The reactor design is shown in Figure A4 in Appendix A. Trying to maintain an adiabatic operation, the reactor was first wrapped with a ceramic blanket as isolation layer, and secondly with heating tapes, providing a temperature close to the inner reactor temperature. Lastly, another insulation layer was placed around the reactor. This design minimized the heat loss through the reactor.

A control thermocouple was positioned at the inlet section of the catalyst support, and another thermocouple was positioned at the outlet section of the catalyst bed. With the two thermocouples, the temperature rise (\(\Delta T_{ad}\)) was recorded to monitor the reactor
operation. A back pressure regulator downstream of the reactor kept the pressure in the reactor at 2 atm (absolute).

After passing through the reactor tube, a certain amount of the gas outlet stream passed a gas sample conditioning system, or a gas chiller system, which was installed prior to the gas analyzers. The rest of the gas outlet stream branched off to a room-temperature partial condenser, where most of the water was removed before venting to the atmosphere. This gas conditioning system is a two channel, thermoelectric heat exchanger. It has a chill capacity to 5°C dew point moisture. After the gas conditioning system, this certain amount dry gases then was introduced into CO and O₂ analyzers. A wet test meter was installed prior to the analyzers to allow us to check the flow rate, and served as a vent.

For the gas product, CO was measured using an on-line NDIR (nondispersive infrared) gas analyzer, while O₂ was measured with a paramagnetic analyzer. Both analyzers were purchased by California Analytical Instruments, Inc. The specially designed CAI model 300 analyzer includes two CO analyzers and one O₂ analyzer. The high concentration CO analyzer had two ranges, which allowed it to measure CO concentrations from 0-3000 ppm or 0-1.5%. The low concentration CO analyzer contained two ranges as well, 0-200 ppm or 0 - 1000 ppm. The paramagnetic O₂ analyzer has 3 ranges, 0 – 1%, 0 – 15% or 0 – 25%. By choosing a suitable range, the CO/O₂ analyzer was able to provide an accurate reading.

3.5 Reaction System (Clemson)
The system consisted of a differential flow reactor connected to a gas chromatograph and mass spectrometer, as shown in Figure 1 in Appendix B. The catalyst was placed in a 0.3 in. (7.6 mm) I.D. stainless steel reactor. The pressure in the reactor was kept constant at 1.8 atm using a back pressure regulator. A thermocouple was placed at the bottom of the catalyst bed. A Valco two-position valve with an electric actuator was used to switch between the labeled CO (¹²CO vs. ¹³CO). The reactor outlet was connected to a gas chromatograph (Varian CP-3380) and a quadrupole mass spectrometer (Pfeiffer Vacuum). The reaction effluent was partially induced into the mass spectrometer via a 1/16 inch capillary tube and a differential pumping. A 6-port sampling valve was placed between the reactor outlet and the GC. In the GC, the products were separated by a 6-ft long 80/100 mesh carbosphere column (Alltech). Hydrogen, carbon monoxide, and oxygen were first separated at 35°C and then the GC was ramped to 150°C at 20°C/min to determine the concentration of CO₂.

3.6 Testing Conditions (NCSU)
The catalyst was evaluated at the following gas compositions: H₂ - 42%, CO₂ – 9%, H₂O – 12%, CO – X%, O₂ – Y%, and N₂ – balance gas. This composition simulated the reformulated gas stream exiting the WGS reactor. A wide range of testing conditions had been evaluated, with a fixed reactor pressure of 2 atm (abs.). The inlet temperature was varied from 80°C to 170°C. The O₂/CO ratios were tested from 0.25 – 1.0. Space velocity was studied in a range of 5,000 hr⁻¹ to 60, 000 hr⁻¹. Linear velocity was altered.
from 21.3 cm/sec to 64.0 cm/sec. The performance of the catalysts was studied with respect to the aforementioned testing conditions. The CO conversion, CO selectivity and O₂ conversion were examined as a measure of the catalyst performance.

The effect of reverse water-gas-shift (rWGS) reaction also was studied. This was achieved by cutting off the CO inlet while keeping all the other operating conditions the same. Under this circumstance, the CO measured by the NDIR in the product gas stream was formed only through the rWGS reaction. This rWGS reaction study revealed the actual limiting conditions for the CO conversion with our catalyst formula and testing conditions.

3.7 Reaction Measurements (Clemson)
The catalytic activity of the catalyst for the selective oxidation of CO in the presence of hydrogen was determined at 90°C and 1.8 atm. Prior to CO oxidation, approximately 50 mg of catalyst was diluted with α-alumina and reduced in a stream of hydrogen at 550°C for 1 h. After reduction, the temperature was gradually decreased over 4 h to the reaction temperature, at which time the flow was switched to a feed stream containing 45% H₂, 53% He, 1% CO and 1% O₂. A gas space velocity of ~190,000 h⁻¹ was used. The CO conversion and selectivity were determined periodically until the reaction reached steady state.

Because of the detection limitation of the thermal conductivity detector (TCD) at low concentrations of CO₂, the amount of CO₂ produced during reaction was calculated from the amount of CO consumption. However, at high conversions of CO up to 50%, the conversions calculated based on CO₂ and CO concentrations were the same within experimental error. Since the change in total gas volumetric flow rate during reaction was relatively small, CO conversion, O₂ conversion, and selectivity were calculated using

\[
\%\text{CO conversion} = (1 - \frac{F_{CO}}{F_{CO_i}}) \times 100\% \approx (1 - \frac{C_{CO}}{C_{CO_i}}) \times 100\% \quad (4)
\]
\[
\%\text{O₂ conversion} = (1 - \frac{F_{O₂}}{F_{O₂_i}}) \times 100\% \approx (1 - \frac{C_{O₂}}{C_{O₂_i}}) \times 100\% \quad (5)
\]

and
\[
\%\text{CO₂ selectivity} = 0.5 \times \frac{(F_{CO_2} - F_{CO})}{(F_{O₂} - F_{O₂})} \times 100\%
\]
\[
\approx 0.5 \times \frac{(C_{CO_2} - C_{CO})}{(C_{O₂} - C_{O₂})} \times 100\% \quad (6)
\]

where \( F_i \) and \( F_{i0} \) are the molar flow rates of species \( i \) at the reactor outlet and inlet, respectively, and \( C_i \) and \( C_{i0} \) are the concentrations of species \( i \) at the reactor outlet and inlet, respectively.
3.8 Catalyst Characterization (Clemson)
The catalyst sample was characterized using the following techniques.

*BET Surface Area*
Measurement was performed to determine the total BET surface area of catalyst sample after calcination. Prior to the BET measurement, the catalyst sample was degassed at 300°C for 3 h. The sample was then analyzed using N₂ adsorption at 77 K in a Micromeritics ASAP 2010.

*X-ray Powder Diffraction*
X-ray diffraction (XRD) was used to determine the bulk crystalline phase of the platinum catalyst after calcination. The XRD patterns were collected with a Phillips X’pert X-Ray diffractometer with monochromatized CuKα radiation (λ =1.54439 Å). The sample was scanned at 1 degree/min in the range 2θ=2-90 degrees.

*Hydrogen Chemisorption*
Static hydrogen chemisorption at 35°C on the reduced platinum catalyst was used to determine the concentration of reduced surface platinum atoms. Prior to H₂-chemisorption, the calcined catalyst was evacuated to 10⁻⁶ mmHg at 100°C for 15 minutes and then reduced in flowing hydrogen at 550°C for 2 h after ramping up the temperature at 10°C/min. The catalyst was evacuated to 10⁻⁶ mmHg at 550°C for 30 min to desorb any hydrogen before the temperature was lowered to 35°C and evacuated for 30 min. The concentration of exposed metal atoms on the surface was calculated by extrapolating the irreversible adsorption isotherm to zero pressure and assuming the coverage of one H atom per Pt atom exposed on the surface. This measurement was performed in a Micromeritics ASAP 2010 using ASAP 2010C V 3.00 software.

3.9 Isotopic-Transient Kinetic Analysis (ITKA) (Clemson)
Isotopic transients were taken by switching between isotopically labeled CO (¹²CO vs. ¹³CO). A trace of argon was present in the ¹²CO stream to measure the gas phase holdup in the reaction system. The kinetic parameters, such as average surface residence time and concentration of surface intermediates, were calculated using the method described by Shannon and Goodwin [20]. By integrating the normalized step-decay of step input response, the overall mean surface residence time of all adsorbed surface intermediates can be determined. The decrease in the transient response of the old label and the increase in the transient response of the new label in the CO₂ and CO exiting the reactor were monitored by a mass spectrometer equipped with a high-speed data acquisition system interfaced to a personal computer using Balzers Quadstar 422 v 6.0 software.
4. Results and Discussion

4.1 Catalyst Screening

It is well known that Pt based supported catalysts are active oxidation catalysts. On the other hand, CO also adsorbs very strongly on Pt [1-3,8,9]. The Pt surface must be covered with CO until the de-adsorption temperature of CO is reached, or the gas phase CO concentration approaches zero. CO oxidation is unlikely to happen with fully CO covered Pt surface since there is no active oxygen on the Pt surface. Kinetically, the reaction with CO and O₂ occurs with a Langmiur-Hinshelwood type of mechanism [1,5,6]. Making this mechanistic behavior assumption, it is necessary for both the O₂ and the CO to be adsorbed onto the Pt surface for a reaction to occur between the two gases. In order to use Pt as a catalyst, there must be another way for the O₂ to absorb and react.

Previous research has found that promotion with a base metal, such as Fe, Mn, Ni [3] as well as Sn [10], would minimize the inhibition and deactivation caused by the strong adsorption of CO on the Pt surface. Among all these promoters, Liu et al. [2] found that for Fe-oxide promoted Pt/alumina catalyst, Fe oxide provides the active oxygen for the CO oxidation. In their research, they believed that the only reaction possible for Pt/alumina is when adsorbed CO reacts with adsorbed O on adjacent Pt sites. Fe oxide in the promoted catalyst is located on or immediately adjacent to the surface of the Pt metal, therefore creating a non-competitive dual site adsorption pathway enhancing the CO activity for the promoted catalyst.

Because of this phenomenon, we initiated our research with 0.5 wt% Pt catalyst promoted with 0.005 wt% Fe. This catalyst formula was the most active of a series of materials studied by Straschil and Egbert [3]. The catalyst was washcoated onto a 1” ID and 2” length ceramic monolith.

This catalyst was placed on both metal foam and ceramic monolith. For an inlet CO concentration of 1.0%, both catalysts showed an O₂ conversion of less than 10%, which leads to a low CO conversion. In addition, there was no significant adiabatic temperature rise, even at an inlet temperature of 170°C. The low overall O₂ conversion also indicated that the competitive hydrogen oxidation reaction was inhibiting the reaction. In order to test this point, the CO inlet gas was shut off, to allow only hydrogen oxidation. At inlet temperatures of 100°C and 170°C, O₂ conversion was close to 100%, and there was a ΔTad between 65-90°C, significantly increasing the reactor outlet temperature. When the CO inlet line was reopened, the O₂ conversion dropped and the outlet concentration increased, while the outlet temperature quickly dropped back to the inlet temperature.

This strong CO poisoning phenomena suggested that the 0.005% Fe promoted on the 0.5% Pt catalyst acted as a pure Pt catalyst. Such a low Fe concentration did not provide enough active sites for the O₂ adsorption, and hence the CO oxidation reaction was stifled. A similar CO poison phenomenon has been observed [1,4].

Subsequently, a series of 5 wt% Pt coupled with a series of different Fe loadings, ranging from 0 wt% to 1.0 wt%, were synthesized onto ceramic monolith supports with 1” ID, 2”
length, and 400 cpsi. The CO conversion, CO selectivity, and O₂ conversion were measured on these catalysts:

\[
\text{CO Conversion} = \frac{\text{CO}_{\text{outlet}} - \text{CO}_{\text{inlet}}}{\text{CO}_{\text{inlet}}} \tag{7}
\]
\[
\text{CO Selectivity} = \frac{1}{2} \left[ \frac{\text{CO}_{\text{outlet}} - \text{CO}_{\text{inlet}}}{\text{O}_2,\text{outlet} - \text{O}_2,\text{inlet}} \right] \tag{8}
\]
\[
\text{O}_2 \text{ Conversion} = \frac{\text{O}_2,\text{outlet} - \text{O}_2,\text{inlet}}{\text{O}_2,\text{inlet}} \tag{9}
\]

where CO is the CO concentration, and O₂ is the O₂ concentration.

At \( T_{\text{in}} = 170°C \), all catalysts exhibited similar results. Figure 3, showed that the CO conversion, CO selectivity, and O₂ conversion are independent of Fe loading. This suggests that lower inlet temperatures were needed.

Figure 2 in the Executive Summary shows an example of catalyst performance at \( T_{\text{in}} = 100°C \), CO inlet concentration = 1.0, O₂/CO ratio = 1.1, and a gas hourly space velocity (GHSV) = 30,000 hr⁻¹. At these conditions, there are very distinct differences in the conversions and selectivity. At low Fe loading (pure Pt catalyst, 0.05 wt% Fe), the catalysts gave low activity; the CO conversion was less than 40%, and the O₂ conversion was less than 30%. At higher Fe loadings (0.5 wt%, 1.0 wt% Fe), the activity of the catalysts increased significantly; the CO conversion was approximately 80%, and the O₂ conversion close to 100%.

Since the stoichiometric ratio of the O₂/CO reaction is 0.5, it is not possible to achieve a high CO selectivity with a large excess of oxygen. With an O₂/CO ratio = 1.0, the 0.5 wt% and 1.0 wt% Fe promoted catalysts achieved 40% and 42% CO selectivity, respectively.

### 4.2 Reverse Water-Gas-Shift (rWGS) Reaction

The decrease in CO conversion at higher temperatures suggests that CO is formed by the reverse water-gas-shift (rWGS) reaction. Experiments with no CO concentration in the inlet (shutting off the CO inlet line) were carried out to determine the adiabatic temperature rise (\( \Delta T_{\text{ad}} \)) for these reactions. The theoretical \( \Delta T_{\text{ad}} \) can be calculated as follows:
\[ \Delta T_{ad} = \frac{-F_{AO} X \times 2 \times \Delta H_{RX}^0}{F_0 \sum_{i=1}^{n} \theta_i \hat{C}_{pi}} \]  

(10)

Where \( F_{AO} \) is the flow rate of CO, \( F_0 \) is the total flow rate, \( X \) is the CO conversion, \( \Delta H_{RX}^0 \) is the heat of reaction, \( \theta_i \) is the fractional composition of species \( i \) in the gas stream, and \( \hat{C}_{pi} \) is the average heat capacity of species \( i \) in the gas stream.

The inlet feed gas stream for our reactor is modeled after the reformate gas stream in a PROX fuel cell. For reformate gas stream compositions (i.e. 40-75% \( \text{H}_2 \), 15-20% \( \text{CO}_2 \), ~10% \( \text{H}_2\text{O} \), 0-35% \( \text{N}_2 \), and 0.5-1.0% \( \text{CO} \)), the rWGS reaction can severely limit the conversion of CO \([1,4,9]\). These limitations are more significant at higher temperature (i.e. > 170°C), where the oxidation catalyst is moderately active for the rWGS reaction:

\[ \text{H}_2 + \text{CO}_2 \xrightleftharpoons{} \text{H}_2\text{O} + \text{CO} \]  

(11)

Korotkikh and Farrauto \([1]\) carried out tests without \( \text{CO}_2 \) in the inlet gas in order to eliminate the possibility of forming CO by the rWGS reaction.

To test the activity of our catalysts for the rWGS reaction, CO was removed from the inlet stream. Therefore, any CO detected in the outlet stream can be attributed to the rWGS reaction. The equilibrium limitations were computed through a theoretical model, with the following assumptions:

1) All oxygen was consumed by the oxidation reactions (equations 1 and 2)
2) The ideal gas law (\( \text{PV} = \text{nRT} \)) was valid
3) The \( C_p \)'s and \( \Delta H_{rxn} \) are constant over our given range of temperatures

Figure 4 shows the measured outlet CO concentration, and the calculated CO concentration for the shift equilibrium, for a 5 wt% Pt, 0.5 wt% Fe catalyst. When there is no hydrogen oxidation present, the outlet CO concentration remains at a low value, around 158 ppm. As the inlet \( \text{O}_2 \) concentration increases, the outlet temperature is significantly increased, generating more CO in the outlet stream because of the temperature dependency in the rWGS reaction.

Although the CO concentration is below the equilibrium value for the rWGS reaction, the trend with temperature follows the equilibrium. This equilibrium line gives us a limit to the minimum level of CO exiting the PROX reactor. Figure
A5 in Appendix A gives similar data for the CO outlet concentration for all the ceramic monolith data.

The Fe promoted 5 wt% Pt catalysts have the following activity order:

\[ 0.5 \text{ wt}\% \text{ Fe} < 1.0 \text{ wt}\% \text{ Fe} < 0.0 \text{ wt}\% \text{ Fe} < 0.05 \text{ wt}\% \text{ Fe} \]

No obvious relationship has been discovered between the iron loading and the shift reaction activity. Based on these results, in addition to the catalyst performance study on the ceramic monoliths, we chose to use a 5 wt% Pt, 0.5 wt% Fe as the catalyst formulation for the metal foam support study.

### 4.3 Comparison of Metal Foam and Ceramic Monolith

#### 4.3.1 Pt-Fe catalyst (No Pretreatment, Metal Foam)

A 5% Pt-0.5% Fe catalyst was washcoated on a series of metal foams with the same volumetric washcoat loading (1.6 g/in³). The four different metal foams, all with 1” ID and 2” length, were 40 ppi 4% density, 40 ppi 12% density, 20 ppi 4% density, and 20 ppi 12% density. Figure 5 shows the CO conversion for these different metal foams.

From the data, it can be seen that higher ppi, higher void volume (consequently lower density) has higher CO conversion and CO selectivity compared to their counterparts for all three inlet temperatures studied. O₂ conversion was nearly 100% for all cases, excluding the two lower conversions from the 12% density foams.

Note that at the \( T_{\text{in}} = 100^\circ C \), you the 12% density foams have an extremely low CO conversion (< 22%). The order of activity for CO oxidation is:

\[ 20 \text{ ppi, 4% density} < 20 \text{ ppi, 12% density} < 40 \text{ ppi, 12% density} < 40 \text{ ppi, 4% density} \]

The higher the ppi, the more tortuous the flow path, allowing more mixing both axially and radially.
Increasing temperature results in decreasing CO conversion and CO selectivity. As the inlet temperature is increased, the probability of CO desorption from the Pt surface increases [4,9]. The CO desorption temperature from Pt is T~160°C [9]. Therefore, as temperature increases, CO desorbs while more H₂ is adsorbed onto the Pt surface, thereby decreasing the overall CO conversion. Because the O₂ conversion is approximately 100%, this decrease in CO conversion leads to a decrease in CO selectivity for the metal foam support.

### 4.3.2 Pt-Fe catalyst (No Pretreatment, Foam/Monolith)

The 400 cpsi ceramic monolith with the 40 ppi, 4% density metal foam were compared. Recall that these two catalysts have the same nominal Pt/Fe washcoat loading of 1.6 g/in³. Both have a 1” ID and 2” length, with the following conditions: CO = 1.0%, O₂/CO = 1.0, and GHSV = 30,000 hr⁻¹. [The results are summarized in Figure 1 located in the Executive Summary.]

Overall, the CO conversion and selectivity was slightly higher on the metal foam catalyst. At a Tₘᵢₙ=100°C, the metal foam achieved a 83% CO conversion and a 41% CO selectivity, compared to 79% CO conversion and a 40% CO selectivity on the ceramic monolith. At a higher Tₘᵢₙ=170°C, the CO conversion and selectivity decreased for both supports, but the metal foam catalyst was still higher for both CO conversion and selectivity – 70% vs. 53%, and 34% vs. 27%, respectively.

Because of the O₂/CO ratio of 1/1 (i.e. twice stoichiometric), the CO selectivity was not high for either temperature. Under all conditions studied, the O₂ conversion reached 90-100%. Since hydrogen oxidation is preferred at higher temperatures, both CO conversion and selectivity decreased when the inlet temperature was increased from 100°C to 170°C.

### 4.3.3 Pt-Fe catalyst (Pretreatment, Foam/Monolith)

In the case of the 20 ppi, 12% density metal foam, the dramatic drop in CO conversion at Tₘᵢₙ = 100°C led to an examination of the influence of the pretreatment procedure. The catalysts tested in Figure 5 were not pretreated. Because of the low activity of the 12% density materials, a pretreatment procedure was examined, consisting of two steps: oxidation and reduction. The oxidation consisted of a flow of 10% O₂/balance N₂ gas stream at 230°C for 2 hours to purge and oxidize the catalyst surface. Next, the reduction consisted of a flow of 15% H₂/balance N₂ gas stream, also at 230°C and 2 hours, to reduce the catalyst surface from its’ oxidized state. No obvious reactor temperature rise was observed under each pretreatment step.

A retest of the 20 ppi, 12% density metal foam catalyst revealed that after the pretreatment, the CO conversion was much higher than without the pretreatment. At Tₘᵢₙ=100°C, the CO conversion increased from 15% to 84%. At Tₘᵢₙ=170°C, the increase was much less, from 62% to 67%. Overall, the CO selectivity was higher for the pretreated catalyst. The effect of the pretreatment on this metal foam is summarized in Figure 6. This increase in activity was permanent; a repeat experiment for the 20 ppi, 12% density foam produced similar results to our first trial.
To see if similar results of pretreatment could be achieved for the catalysts with higher initial activity, the same pretreatment was applied to the 5 wt% Pt-0.5 wt% Fe, 400 cpsi, ceramic straight-channel monolith. There was no significant difference. The ceramic monolith was taken out of the reactor, exposed it to air, and then placed it back in the reactor. This also had no effect. Figures A6 and A7 in Appendix A summarizes these tests.

These data seem to indicate that the use of the pretreatment procedure activated the 20 ppi, 12% density metal foam at low inlet temperatures, but did not effect the catalysts with high activity. Further characterization studies on these supported catalysts are needed to understand the effect of this pretreatment procedure. Information such as washcoat layer thickness, Pt/Fe existing state on the catalyst surface, and Pt/Fe distribution on the metal foam would provide more information to help us understand the effect of pretreatment.

4.3.4 Pt-Fe catalyst (Transients, Foam/Monolith)
To examine any differences between the metal foam and ceramic monolith, a transient study was carried out to test the effect of $\Delta T_{ad}$ as a function of time, using a 20 ppi, 12% density metal foam, and a 400 cpsi ceramic monolith. The study was carried out by cutting off the $O_2$ input, allowing for the outlet temperature to equal the inlet temperature, and then turning the $O_2$ input back on at time zero. Figure 7 shows the CO and $O_2$ concentration and outlet temperature from 0 to 15 minutes.

![Fig. 6. Effect of Pretreatment on 20 ppi, 12% density metal foam](image_url)
The results show that the metal foam responds somewhat more rapidly than the ceramic monolith. This may be caused by the higher thermal conductivity and better radial/axial mixing in metal foams. The CO outlet concentration response is similar for the different supports. More data on the transient behavior can be found in Appendix C.

### 4.4 Effect of Operating Conditions

#### 4.4.1 O₂/CO Ratio

The effect of the O₂/CO ratio on the CO conversion and selectivity was studied. Figure 8 shows this effect for both the metal foam and ceramic monolith at Tᵢₙ=80°C. For both supports, as the O₂/CO ratio increases, the CO selectivity decreases. This is because more hydrogen is oxidized at higher O₂/CO ratios, especially above stoichiometric values. At higher O₂/CO ratio, the CO conversion increases because of the higher O₂ content in the inlet gas stream.

Figure A8 in Appendix A shows a performance comparison between the same metal foam and ceramic monolith in Figure 8. In general, the two catalysts were quite
comparable. However, at an \( \text{O}_2/\text{CO} \) ratio = 1.0, the CO conversion for the ceramic monolith was substantially higher than that of the metal foam.

The 40 ppi, 4% density metal foam and the 400 cpsi ceramic monolith used here are not the same piece used in Section 4.3 of this report. We believe that there may be subtle differences between the two different pieces of the same support, despite a conscious effort to synthesize identical catalysts.

4.4.2 Space Velocity / Linear Velocity

A study of GHSV and linear velocity was carried out using 2” and 6” lengths of both the 40 ppi, 4% density metal foam and 400 cpsi ceramic monolith. Figure 9 shows the effect of space velocity on the 40 ppi, 4% density metal foam for a 2” length catalyst piece.

In order to increase the space velocity, the volumetric flowrate through the catalyst was increased; for example, to increase the GHSV from 10,000 hr\(^{-1}\) to 30,000 hr\(^{-1}\), the flowrate was increased by a factor of 3, but this also increases the linear velocity by the same factor, shown in equations 13 and 14.

\[
\tau = \frac{1}{\text{GHSV}} \quad \text{(12)}
\]

\[
\text{GHSV} = \frac{\dot{V}}{V} \quad \text{(13)}
\]

\[
\dot{V} = \bar{v}A_{xs} \quad \text{(14)}
\]

\( \tau \) is defined as the residence (retention) time, GHSV is the gas hourly space velocity, \( \dot{V} \) is the volumetric flowrate, \( V \) is the catalyst support volume, \( \bar{v} \) is the linear velocity, and \( A_{xs} \) is the cross-sectional area of the reactor. The linear velocity and space velocity effects are thus coupled in this data, and further tests were carried out in order to decouple the two effects.

The CO and O\(_2\) conversion decreased as the GHSV is increased, while the CO selectivity increased, as expected. CO oxidation is thought to be a faster reaction kinetically than \( \text{H}_2 \) under certain conditions [22]. Therefore, with a shorter retention time, CO selectivity would increase. However, the CO conversion line is flatter than we expected.

To examine this point, CO oxidation is assumed to be a first-order reaction, and the reactor is assumed to be isothermal, which allows the use of a constant value for the reaction rate constant. With these assumptions, the CO conversion at a GHSV of 10,000 hr\(^{-1}\) can be calculated to a range of 60%-70%, which is much higher than the measured value of 51%, shown in Figure 9.
Also, the $\Delta T_{ad}$ is higher at 10,000 hr$^{-1}$ than at 45,000 hr$^{-1}$ because of the higher O$_2$ conversion, giving a higher outlet reactor temperature at lower GHSV. Therefore, because of our isothermal assumption, this calculated CO conversion serves as a lower bound on the actual conversion. Calculations are in Appendix D.

One explanation for the “flatness” of the curve of CO conversion as a function of space velocity may be the result of the rWGS reaction, discussed in section 4.2. As the space velocity was reduced, the outlet temperature increased. Therefore, the rWGS reaction may be more important as the GHSV is reduced, potentially accounting for the lowered sensitivity of CO conversion to space velocity.

Another possible explanation is that there are transport effects occurring within our reactor. If the reaction rate is limited by mass transfer of CO or O$_2$ from the inlet gas stream to the catalyst surface, then the linear velocity through the reactor ($\bar{v}$) would affect the CO conversion. Heat and mass transfer coefficients are positive functions of linear velocity, so as linear/space velocity increases, space velocity reduces the contact time in the reactor, but linear velocity increases the mass transfer coefficient. These competitive effects may cause the behavior of the CO conversion curve as a function of GHSV.

In order to decouple these effects, tests were carried out at fixed space velocity, but varying linear velocities. This was accomplished by placing three 2” 40 ppi, 4% density metal foams together to form a 6” length. The performance of the individual 2” and the 6” metal foam were analyzed. Experimental constraints limited this comparison to GHSV of 10,000 hr$^{-1}$ and 15,000 hr$^{-1}$. At these GHSV, the 6” piece had a linear velocity that was three times higher than the 2” piece. The results of this comparison are shown in Figure 10.

At a constant GHSV, the 6” length reactor piece has an overall higher CO conversion and selectivity, and O$_2$ conversion, for both GHSV values. This result is consistent with a significant transport resistance between the inlet gas and the surface of the catalyst. The CO and O$_2$ conversion increases with higher linear velocity because of the increase in the mass transfer coefficient. The CO selectivity is affected because H$_2$ oxidation is relatively slow compared to the CO oxidation, and therefore not as sensitive to the transport resistance.
Similarly, the linear velocity can be held constant to show the effect of GHSV for the 40/4 metal foam. The linear velocity for a 6” length of catalyst operating at a given space velocity is the same as that for a 2” length of catalyst operating a three times the space velocity. For example, a 6” catalyst running at a GHSV of 5,000 hr⁻¹ has the same linear velocity as a 2” catalyst running at a GHSV of 15,000 hr⁻¹. Similarly, the points of 10,000 hr⁻¹ and 30,000 hr⁻¹, and 15,000 hr⁻¹ and 45,000 hr⁻¹, respectively, have constant linear velocity. [See Equation 13.] Figure 11 shows the results.

The CO conversion (solid lines), at a constant linear velocity, is much more sensitive to space velocity than seen in Figure 9. From 5,000 hr⁻¹ to 15,000 hr⁻¹, at a constant linear velocity of 21.3 cm/sec, the CO conversion drops from 73% to 45%, respectively. Also, note that the CO selectivity (dashed lines) is a function of space velocity. At a linear velocity of 64.0 cm/sec, the CO selectivity increases, but at lower linear velocities (21.3 and 42.7 cm/sec), the CO selectivity decreases or is constant at higher GHSV. At higher space velocities, the CO selectivity should increase because of the shorter retention time and the kinetically faster reaction of CO oxidation, relative to the H₂ oxidation, as explained above.

For the constant linear velocity of 21.3 cm/sec (5,000 hr⁻¹ and 15,000 hr⁻¹), the CO conversion would be expected to increase. The O₂ conversion also increases (not shown), from 84% to 100%. However, it seems unlikely that the selectivity for CO oxidation would increase dramatically. Since the reactor is essentially adiabatic, the temperature in the added catalyst segments is higher, and the CO and O₂ concentrations are lower. In general, selectivity would be expected to decrease with increasing temperature and with decreasing CO concentration.

The rWGS reaction offers a possible explanation for this behavior. At lower linear velocities, the catalyst surface can be much hotter than the gas stream temperature. Moreover, the gas stream contains a substantial concentration of H₂, the surface of the catalyst can be higher than the observed ΔTad. Consequently, the rWGS may be taking place in the first catalyst segment at a higher temperature than that observed leaving the reactor. This will decrease the observed CO conversion and selectivity. However, at lower space velocities, as the gas passes through the second and third section of the 6” catalyst, heat is dissipated as it flows through the different sections, and the temperature difference between the gas stream and the catalyst surface becomes smaller. This allows the rWGS reaction to re-equilibrate at a lower temperature, hence permitting a lower decrease in CO conversion and selectivity.
This effect described above is mitigated at a linear velocity of 64.0 cm/sec. In both the 6” and 2” length reactors, there is much more incomplete combustion (100% and 33% \(O_2\) conversion, respectively), so the \(\Delta T_{ad}\) is lower for the 2” length, and the catalyst surface may not be significantly hotter than the gas stream. This leads to a higher CO selectivity at faster GHSV, as expected.

The 400 cpsi ceramic monolith produced similar results to the 40/4 metal foam. Figures A9, A10a, and A10b in Appendix A shows similar results as Figures 9, 10, and 11.

Finally, a comparison of the 40 ppi, 4% density metal foam and the 400 cpsi ceramic monolith reveals that the metal foam is comparable in all aspects to the ceramic monolith. This is depicted in Figure 12.

4.5 Testing of “Identical” Individual Pieces (Ceramic Monolith and Metal Foam)
As noted in section 4.4, the evaluation of the 6” length reactor consisted of three separate, nominally “identical” catalysts for both the metal foam and ceramic monolith reactor. The three pieces are made up of two “new” pieces placed at the beginning and middle of the 6” reactor and one “old” piece placed at the end of the reactor. One of the new pieces was used in section 4.4, while the old piece was used in section 4.3.

The performance of the two “new” pieces of metal foam catalyst was almost identical, but both the CO conversion and selectivity were substantially poorer than those for the original “old” piece. The performance of the two “new” pieces of the ceramic monolith catalyst was not the same. Data is shown in Appendix E.

4.6 Metal Monolith and Ceramic Foam
5% Pt / 0.5% Fe catalysts have also been prepared with the same washcoat loading on a corrugated metal monolith, and a 20 ppi, 11% density ceramic foam. The tests were completed under these conditions: \(T_{in}=80°C\) and \(150°C\), GHSV=15,000-45,000 hr\(^{-1}\), CO inlet = 1.0%, and \(O_2/CO\) ratio = 0.5 and 1.0. The ceramic foam was 1” ID and 2” length, while the metal monolith was 1” ID and 1.5” length. The data is shown in Appendix F.

Under all conditions, the CO and \(O_2\) conversions for the ceramic foam and metal monolith were substantially lower than for the 40/4 “new” metal foam and 400 cpsi “new” ceramic monolith. At \(T_{in}=80°C\), the metal monolith performed higher than the
ceramic monolith in all aspects, but worse than the metal foam and ceramic monolith. At 
$T_m=150^\circ C$, the metal monolith and ceramic foam had similar CO conversion and 
selectivity, which were at the same level as the metal foam.

There is no obvious reason why the metal foam and ceramic monolith are distinctly 
superior. It may be because the preparation techniques for catalysts on ceramic 
monoliths have been well studied, while the techniques for the newer supports require 
more study until they are improved.

4.7. ICP/BET (NCSU)
Section 3.2 outlines the procedure used to impregnate the Pt/promoter material and to 
washcoat the catalyst onto the metal foam. Because metal foams are not of a size that can 
be fit into characterization systems designed for powder samples, conventional 
characterization techniques can not be used. Therefore, the powder catalysts prepared 
were analyzed by two methods. An Inductively Coupled Plasma (ICP)-Emission 
Spectrometer, at NC State Department of Soil Science, was used to determine bulk 
elemental composition. Secondly, an in-house Micrometrics Flowsorb II 2300, with 
Brunauer-Emmett-Teller (BET) capability, was used to determine the total surface area. 
The results are summarized in Appendix G.

The ICP results show variation between each sample from the projected composition and 
the determined elemental composition. One sample of specific interest is lab i.d. 80, 
which is a slurry provided by the Pt-Fe washcoating company. The Fe loading 
determined is much higher than the projected composition, with a 200% error. This 
suggests that the samples are not identical.

The BET results show minor variations between each group of samples. The major 
differences lie within the 5% Pt, varying Fe loadings. This problem is because of 
inconsistent balance readings.

4.8 BET Surface Area (Clemson)
The BET surface area of the 5 wt% Pt/$\gamma$-Al$_2$O$_3$ after calcination was 295 m$^2$/g.

4.9 X-ray Powder Diffusion
The XRD pattern of the Pt catalyst after calcination showed peaks corresponding to $\gamma$-
Al$_2$O$_3$. No peaks for Pt metal were seen. This was due to the high dispersion of the Pt 
since Cu K$_\alpha$ XRD is not able to detect metal particle sizes less than ca. 5 nm. 
Overlapping $\gamma$-Al$_2$O$_3$ peaks also make the detection of Pt peaks even harder.

4.10 Hydrogen Chemisorption
The amount of hydrogen irreversibly chemisorbed on Pt atoms extrapolated to zero 
pressure was found to be 69.7 $\mu$moles H$_2$/g cat. The metal dispersion of reduced 
platinum catalyst was determined to be 54.5%, corresponding to an average Pt particle 
size of 2.0 nm. This latter quantity was calculated based on the correlation between % 
dispersion and metal particle size, 
\[ \tilde{d}_{wa} = 6 \frac{V_m}{a_m} D_m, \]
where $V_m/a_m$ is the volume per area
of metal atom \( V_m = 1.46 \times 10^{-23} \text{ cm}^3/\text{Pt atom} \), \( a_m = 8 \times 10^{-16} \text{ cm}^2/\text{Pt atom} \) and \( D_m \) is the fractional dispersion.

4.11 Catalytic Oxidation of Carbon Monoxide in the Presence of Hydrogen

Time-on-stream (TOS) behavior of CO conversion, rate, and CO\(_2\) selectivity are shown in Figures 2, 3 and 4, respectively, in Appendix B. Both CO conversion and CO\(_2\) selectivity decreased rapidly with TOS. The CO conversion (Figure 2) for the reaction conditions used was 57% at 5-minute TOS and decreased to about 6.5% at reaction steady state. Reaction rate (Figure 3) decreased in a like manner. The results illustrate the rapid deactivation of Pt catalysts typically seen during the initial reaction period. The CO\(_2\) selectivity showed the same decreasing pattern, starting at 90% selectivity and then dropping to 27% within 50 minutes.

Isotopic transient kinetic analysis was used to decouple the deactivation behavior of Pt catalyst into the contributions from site activity and concentration of surface intermediates. Figure 5 in Appendix B gives typical transients for CO, CO\(_2\) and the inert tracer Ar following a step change in the isotopic label on the CO feed. The average surface residence times and concentrations of CO\(_2\) intermediates and reversibly adsorbed CO were calculated using (SS)ITKA software. The switching was conducted at 5 min TOS and periodically afterwards until steady state reaction was reached.

A Langmuir-Hinshelwood single site mechanism is widely accepted to explain CO oxidation on Pt [2,14,19]. Adsorbed CO is assumed to react with adsorbed O on an adjacent Pt site. At low reaction temperatures, the noble metal surface is believed to be predominantly covered with adsorbed CO [14,19] and the irreversible molecular adsorption of oxygen is suggested to be the rate-determining step. As determined by Nibbelke et al. [19], at temperatures between 163-230\(^\circ\)C the rate of CO oxidation can be expressed as

\[
R_{\text{CO}_2} = \text{const.} \cdot P_{\text{O}_2} / P_{\text{CO}}.
\]

Although surface reaction is not the rate-determining step, at steady state condition, the rates of all steps including surface reaction are equal and are equivalent to the overall rate of CO oxidation. Therefore the reaction rate can be expressed by

\[
R_{\text{CO}_2} = \text{const.} \cdot P_{\text{O}_2} / P_{\text{CO}} = k_{\text{CO}_2} \cdot N_{\text{t-CO}_2} \cdot N_o
\]

where \( N_{\text{t-CO}_2} \) and \( N_o \) are the surface concentrations of CO\(_2\) intermediates and adsorbed oxygen, respectively. Since the surface residence time of CO\(_2\) reaction intermediate

\[
\tau_{\text{CO}_2} = N_{\text{t-CO}_2} / R_{\text{CO}_2},
\]

the relationship between the intrinsic rate constant \( k_{\text{CO}_2} \) and \( \tau_{\text{CO}_2} \) is

\[
1 / \tau_{\text{CO}_2} = k_{\text{CO}_2} \cdot N_o = k = R_{\text{CO}_2} / N_{\text{t-CO}_2},
\]

Thus, the reciprocal of the surface residence time of CO\(_2\) intermediate \((1 / \tau_{\text{CO}_2})\) is equivalent to a pseudo-first-order intrinsic rate constant, \( k \), and represents the intrinsic activity of the catalyst (a type of turnover frequency, TOF), although it also includes the oxygen surface concentration dependence, as seen above. However, after varying the
oxygen concentration, it was found that $k$ was weakly dependent on the oxygen concentration.

The dependency of surface concentration and consequent the pseudo-first-order intrinsic rate constant on the partial pressure of oxygen in feed stream is shown in Figure 6 in Appendix B.

Figure 7 in Appendix B shows the TOS behavior of the pseudo-first-order intrinsic rate constant, $k$. It is obvious that the average intrinsic activity of the Pt sites did not vary greatly with TOS. With the exception of the first data point, $k$ was relatively constant with TOS. The first data point is probably higher due to a higher initial surface concentration of oxygen. On the other hand, as seen in Figure 8 in Appendix B, the concentration of CO$_2$ surface intermediates decreased with TOS in a similar fashion as the reaction rate (Figure 3, Appendix B). It can be concluded that the deactivation of this Pt catalyst is mainly the result of a decrease in the concentration of active intermediates for CO oxidation (related to the available active Pt sites), not the intrinsic activity.

The concentration of surface Pt atoms calculated from the hydrogen chemisorption measurement was 139 µmoles/g cat. ITKA determined the concentration of surface CO (both reversibly adsorbed, $N_{co}$ and CO$_2$ intermediates, $N_{I-CO_2}$) at 5 min TOS to be 132 µmoles/g cat, about 95% of surface Pt atoms would have been occupied by CO initially. If one assumes that every site was available for reaction at 5 min TOS, this would leave only 7 µmoles/g cat available for the adsorption of hydrogen and oxygen, suggesting the reason for the high selectivity for CO$_2$ formation. Considering the concentration of surface CO$_2$ intermediates, $N_{I-CO_2}$, it would appear that the surface coverage in intermediates, calculated by dividing $N_{I-CO_2}$ with the concentration of surface Pt atoms, was only 41% at 5 minute TOS. At steady state, the concentration of active CO$_2$ intermediates decreased to about 7% coverage. This decrease is reflected in the decrease in CO oxidation rate and CO$_2$ selectivity. Although the surface coverage of CO$_2$ intermediates decreased about 80%, the surface coverage of reversibly adsorbed CO increased only 30%. Although the CO oxidation rate decreased, the H$_2$ oxidation rate increased from ca. 0.92 µmoles/g cat/s at 5 min TOS to ca. 2.4 µmoles/g cat/s at steady state. This might suggest that hydrogen has better able to compete for oxygen because of the decrease in concentration of CO$_2$ intermediates. The decrease in CO$_2$ selectivity is, thus, the result of the decrease in CO oxidation rate and the concomitant increase in H$_2$ oxidation rate. By assuming that all Pt surface atoms are active for CO oxidation, the TOF based on hydrogen chemisorption calculated (~0.007 sec$^{-1}$) was about 12 times lower than the pseudo-first-order steady state rate constant (~0.09 sec$^{-1}$) at steady state condition.
4.12 Characteristics of the catalyst surface at steady state
In order to determine the cause of deactivation, additional experiments were conducted to try to determine the surface composition of the catalyst after reaction.

4.12.1 Effect of regeneration temperature
The deactivated catalyst was regenerated at different temperatures in a stream of hydrogen for 1 h. As shown in Figure 9 in Appendix B, some of initial activity was recovered using regeneration temperatures lower than 300°C. On the other hand, regeneration at temperatures higher than or equal to 300°C resulted in a complete recovery of the initial activity.

4.12.2 Effect of CO addition before oxygen
The catalyst bed was flushed with the reactant stream excluding oxygen for 1 h before adding oxygen and starting the CO oxidation reaction. At 5 minute TOS (after oxygen was fed), the CO oxidation rate was found to be approximately the same as the rate at steady state (after deactivation) in the normal run. This result suggests that CO is the source of the species that deactivates the catalyst.

4.12.3 Hydrogen reaction with the deactivated catalyst
About 50% hydrogen in helium was fed through the bed of partially deactivated catalyst after reaching steady state while the temperature in the reactor was raised from the reaction temperature to 550°C. A mass spectrometer was used to detect the gas outlet composition from the reactor. Small amounts of methane were detected in the temperature range of 230°C to 280°C.

4.12.4 Determination of carbon content
After reaching steady state reaction rate, a sample of the deactivated catalyst was removed and sent to Galbraith, Inc. for carbon determination. The amount of carbon determined by from the combustion/coulometric titration was 16.7 µmole/g cat, equivalent to 12% coverage of the surface Pt atoms by carbon atoms.
5. Conclusions
A series of Fe-promoted Pt/Al₂O₃ catalysts were synthesized and evaluated for the selective oxidation of a low concentration of CO in the presence of a high concentration of H₂. Very strong inhibition by CO was observed for catalyst with a 0.5 wt% Pt / 0.005 wt% Fe / Al₂O₃ washcoat, with a 1.6 g/in³ loading on the support. The CO in the inlet gas stream poisons the catalyst, but the inhibition is reversible, as seen when CO is removed from the inlet gas stream.

A ceramic monolith support with a washcoat loading containing 5 wt% Pt and 0.5 wt% Fe proved to have a high activity for CO conversion, along with a moderate selectivity for CO over H₂. With an inlet temperature of 100°C, and 1.0% CO and an O₂/CO ratio = 1.0 in the feed gas, this catalyst was able to achieve 80% conversion with a selectivity of about 40%. Because the tests were carried out above stoichiometric O₂ concentrations, the CO selectivity can only reach a maximum of 50% if all the O₂ is oxidized.

Different metallic foams were tested as catalyst supports. In general, the best foam structure was the 40 ppi, 4% density. Catalysts prepared on this foam had comparable activity and selectivity to the 400 cpsi ceramic, straight-channel monolith. Catalysts prepared on the 40/4 foam gave a slightly higher performance than the 20/4 foam, and significantly higher than the 40/12 and 20/12 catalysts. However, the apparent differences between these four supports, and the individual “identical” pieces of the 6” reactor study, may reflect the inconsistencies of reproducible catalyst preparation on a novel support. Further attention is required on the techniques for both catalyst preparation and catalyst characterization. To increase the CO conversion, a pretreatment method increased the activity of low performance catalysts, but did not impact already high performance catalysts.

Studies on catalyst prepared with the 5 wt% Pt/0.5 wt% Fe washcoat showed that the reverse water-gas-shift reaction played an important role in determining CO conversion and selectivity, especially at higher inlet temperatures. This reaction needs to be suppressed in order for us to reach feasible CO concentrations.

Metal monoliths and 20/11 density ceramic foams were also evaluated, but had lower activity and selectivity. Further work was done on transient behaviors in order to discover differences between the metal foam and ceramic monolith support, but no significant difference was determined.

Various operating conditions were examined, specifically: O₂/CO ratio, space velocity, and linear velocity. Studies showed that the performance of the catalysts prepared on both the ceramic monolith and the metal foam was influenced by mass and heat transport, to some extent. The transport characteristics of straight-channel monoliths are reasonably well understood. However, additional work to quantify the mass- and heat-transfer characteristics of the metal foams is necessary.

The selective oxidation of CO in the presence of hydrogen using 5% Pt/γ-Al₂O₃ exhibited high initial partial deactivation before reaching steady state. The observed rate and CO₂
selectivity were very high during the initial reaction period, but decreased significantly with time-on-stream. By using isotopic transient analysis, the pseudo-first-order intrinsic rate constant was found to be relatively constant compared to the concentration of surface CO₂ reaction intermediates. It can be concluded that the deactivation of this Pt catalyst is mainly the result of a decrease in the concentration of surface intermediates, not the intrinsic activity. In addition, regeneration of the catalyst in the stream of hydrogen at temperatures higher than or equal to 300ºC can completely recover the initial activity and selectivity of the deactivated catalyst. Approximately 12% of surface Pt was likely covered with carbonaceous species during initial deactivation. From this result, we suggest that the deactivation of Pt is due to carbon deposition on the Pt surface and that this carbon deposition also caused a significant decrease in CO₂ selectivity. Possibly CO₂ selectivity is decreased because CO adsorption is affected more than H₂ and O₂ adsorption.
6. Recommendations

a) **Develop reproducible techniques for catalyst preparation.** The Pt/Fe system that was investigated appears to have promise and is worthy of further study, but the results on nominally identical foams were somewhat different. Re-evaluate other foam structures once reproducible catalyst preparation techniques have been established.

b) In connection with catalyst preparation research, **develop techniques to characterize these catalysts**, including measuring washcoat uniformity, Pt metal area, and Fe dispersion, and other surface properties. Typical characterization techniques are not feasible with these support systems because of their shapes and sizes. Novel methods will be needed to characterize the foams used in these tests.

c) **Carry out additional research to define the transport effects on metal foams and ceramic straight-channel monoliths.** This includes measuring the mass transfer characteristics of the foams.

d) **Evaluate the need for an isothermal reactor.** The adiabatic temperature rise plays a significant role in the RWGS reaction. To suppress this reaction, catalysts on metal foams with cooling tubes inserted metallurgically should be reviewed.

e) **Evaluate the reactions in the kinetic regime** to determine kinetic rate constants and develop a model. This involves the use of a differential reactor.

f) **Assess the use of other metal promoters from the Straschil and Egbert patent [3], such as Mn, Co, Sn.**
7. References


8. Bibliography
## 9. List of Acronyms and Abbreviations

<table>
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<td>40/4</td>
<td>40 ppi, 4% density foam</td>
</tr>
<tr>
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<td>20 ppi, 4% density foam</td>
</tr>
<tr>
<td>40/12</td>
<td>40 ppi, 12% density foam</td>
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<tr>
<td>20/12</td>
<td>20 ppi, 12% density foam</td>
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<tr>
<td>$\Delta H_{\text{rxn}}$</td>
<td>Heat of Reaction</td>
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<td>$\Delta T_{\text{ad}}$</td>
<td>Adiabatic Temperature Rise</td>
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<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
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<tr>
<td>$C_{\text{p}}$</td>
<td>Heat Capacity</td>
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<td>cpsi</td>
<td>Cells Per Square Inch</td>
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<td>GHSV</td>
<td>Gas Hourly Space Velocity</td>
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<td>ICP</td>
<td>Inductively Coupled Plasma</td>
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<td>ITKA</td>
<td>Isotopic-Transient Kinetic Analysis</td>
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<td>I.D.</td>
<td>Inner Diameter</td>
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<td>LV</td>
<td>Linear Velocity</td>
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<td>NDIR</td>
<td>Nondispersive Infrared</td>
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<td>Proton Exchange Membrane</td>
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<td>ppi</td>
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<td>Preferential Oxidation</td>
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<td>Reverse Water-Gas-Shift</td>
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<td>$S_{\text{CO}}$</td>
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<td>SSITKA</td>
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<tr>
<td>$T_{\text{in}}$</td>
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<td>Thermal Conductivity Detector</td>
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<td>Turnover Frequency</td>
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<td>Time-On-Stream</td>
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<td>X-Ray Powder Diffusion</td>
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Appendix A

NCSU Figures
Fig. A1. Pictures of (a) open cells in metal foam, (b) shapes of metal foams, and (c) metal tubes inserted into metal foams
Fig. A2. 400 cpsi Ceramic Straight-Channel Monolith ("monolith") and a 40 ppi, 4% density Metal Foam ("foam")
Fig. A3. Process Flowsheet for our PROX System
Fig. A4. Reactor Design Schematic
Fig. A5. Effect of rWGS on 400 cpsi ceramic monolith, varying Fe wt% loading
Fig. A6. Effect of Pretreatment on 400 cps Straight-Channel Ceramic Monolith
THE EFFECT OF PRETREATMENT (based on CO conversion)

20 ppi, 12% density metal foam support

<table>
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<td>83.70%</td>
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<td>55.40%</td>
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<td>67.00%</td>
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<tr>
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<td>54.50%</td>
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400 cpsi ceramic monolith

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<th>After Pretreatment (Re.)</th>
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<td>88.00%</td>
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<td>CO/O₂ = 0.5</td>
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<td>52.10%</td>
<td>59.40%</td>
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<td>49.00%</td>
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Main Conclusions:

1. Pretreatment improved 20 ppi, 12% density metal foam catalyst performance. This improvement also seems to be permanent since the CO conversion was considerably same before and after air exposure for the pretreated sample.

2. Pretreatment slightly improved ceramic monolith performance with some conditions (O₂/CO = 1). With O₂/CO = 0.5 condition, CO conversion was even marginally lower than before (without pretreatment). Overall, pretreatment did not have an impressive effect on the performance of ceramic monolith.
Fig. A8. Comparison of Effect of O$_2$/CO on 40/4 metal foam and 400 cpsi ceramic monolith
Fig. A9. Effects of GHSV and linear velocity on 400 cpsi ceramic monolith
Fig. A10a. Effect of GHSV, constant linear velocity

Fig. A10b. Effect of linear velocity, constant GHSV
Appendix B

Clemson Figures
Table 1. Isotopic transient kinetic analysis results

<table>
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<tr>
<th>TOS (min)</th>
<th>CO Conversion (%)</th>
<th>Rate(^a) (µmole/g cat/sec)</th>
<th>(\tau_{CO_2}) (sec)</th>
<th>(\tau_{CO}) (sec)</th>
<th>(N_{1-CO}) (µmol/g cat)</th>
<th>(N_{CO}) (µmol/g cat)</th>
<th>(k)(^b) (sec(^{-1}))</th>
<th>(N_{(1-CO_2+C-O)}) (µmol/g cat)</th>
<th>(\theta_{1-CO_2})(^c)</th>
<th>(\theta_{CO})(^c)</th>
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\(^{a}\) Rate = micromoles of CO consumed per gram of catalyst per second at 90°C; 1.8 atm; 45% H\(_2\), 1% O\(_2\), 1% CO by mole and balance He

\(^{b}\) \(k=1/\tau_{CO_2}\), pseudo-first-order intrinsic rate constant. Error estimated at ±5%

\(^{c}\) \(\theta_i = N_i/(irreversibly adsorbed H atom)\), the surface coverage of species i. Error estimated at ±10%
Figure Captions

Figure 1: Schematic diagram of the ITKA CO oxidation system.

Figure 2: Time-on-stream behavior for CO conversion at 90°C.

Figure 3: Time-on-stream behavior for the CO oxidation rate at 90°C.

Figure 4: Time-on-stream behavior for CO₂ selectivity during CO oxidation at 90°C.

Figure 5: Isotopic transients during CO oxidation at 90°C on 5% Pt/γ-Al₂O₃ at steady state.

Figure 6. Oxygen partial pressure dependency of surface oxygen concentration

Figure 7: Time-on-stream behavior of the pseudo-first-order intrinsic rate constant at 90°C.

Figure 8: Time-on-stream behavior of the concentration of CO₂ surface intermediates, \( N_{I-CO_2} \), at 90°C.

Figure 9: Time-on-stream behavior of the CO oxidation rate after regeneration at different temperatures.
Fig. 1

Vent

Back Pressure Regulator

Pressure transducer

Switching Valve

Pressure Transducer

Reactor

Unlabeled CO → Labeled CO

He, H₂, CO₂, O₂

Vent

Back Pressure Regulator

3-way valve

6-port valve

GC

Vent

Vacuum pump

Pump

MS
Fig. 3

CO oxidation rate, µmole/g cat/sec vs TOS, min
Fig. 4

![Graph showing the relationship between TOS (min) and % CO2 selectivity.](image-url)
Fig. 6

Oxygen partial pressure, kPa

No/(No at 1% O₂)
Fig. 8

Concentration of surface CO$_2$ intermediates, $N_{CO_2}$, µmole/g cat.
Fig. 9

CO oxidation rate, µmole/g cat/sec

TOS, min

- fresh
- regeneration at 150°C
- regeneration at 200°C
- regeneration at 250°C
- regeneration at 300°C
Appendix C

Transient (NCSU) Study
CO = 1%, O₂/CO = 1
### Transient Study:

Record the CO and O₂ concentration and outlet temperature from time zero to the time the reaction reaches steady state.

The preliminary study did not show significant transient difference for metal foam and ceramic monolith support.

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</table>

**Temperature Transient**

**CO = 1%, O₂/CO = 1**

**CO = 1%, O₂/CO = 0.5**
Appendix D

First Order Kinetics
Assumption
Calculations
Assumptions
(1) First order kinetics \( r_{CO} = -k_{CO}[CO] \)
(2) Isothermal Reactor conditions \( k \) is constant

Mass Balance:
\[
F_{CO,\text{in}} = \left( F_{CO,\text{in}} + dF_{CO}\right) - r_{CO}dV \\
F_{CO,\text{in}} = \left[ F_{CO,\text{in}} + d\left[F_{CO,\text{in}}(1-X_{CO})\right] \right] - r_{CO}dV \\
F_{CO,\text{in}}dX_{CO} = r_{CO}dV
\]
\[
dF_{CO} = r_{CO}dV \\
dF_{CO} = [CO]\dot{V}_{CO}
\]
\[
\dot{V}_{CO}\frac{d[CO]}{dV} = -k_{CO}[CO]
\]
\[
d\frac{[CO]}{d\tau} = -k_{CO}[CO]
\]
\[
[CO] \frac{d[CO]}{[CO]_{o}} = -k_{CO} \int_{0}^{\tau} d\tau \\
\ln\left( \frac{[CO]}{[CO]_{o}} \right) = -k_{CO}\tau
\]
\[
\ln\left( \frac{[CO]_{o}(1-X_{CO})}{[CO]_{o}} \right) = -k_{CO}\tau
\]

Final Solution:
\[
\ln(1-X_{CO}) = -\frac{k_{CO}}{\text{GHSV}}
\]

Nomenclature
\( F_{CO,\text{in}} \) = Mass flowrate of CO, inlet 
\( F_{CO} \) = Mass flowrate of CO 
\( dF_{CO} \) = Differential mass flowrate of CO 
\( \dot{V}_{CO} \) = Volumetric Flowrate of CO 
\( [CO]_{o} \) = initial CO concentration 
\( \tau \) = residence time 
\( k_{CO} \) = CO reaction rate constant

GHSV = Gas Hourly Space Velocity
Appendix E

Individual “Identical” Pieces Data
Comparison of Catalyst Performance for Three “Identical” Metal Foam Pieces
(T$_{in}$ = 150°C, CO inlet = 1.0%, O$_2$/CO ratio = 1.0, GHSV = 30,000 hr$^{-1}$)

<table>
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<tr>
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<th>Xco (%)</th>
<th>Sco (%)</th>
<th>Xo$_2$ (%)</th>
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<td>“Old” Piece</td>
<td>51.3</td>
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Comparison of Catalyst Performance for Three “Identical” Ceramic Monolith Pieces
(T$_{in}$ = 150°C, CO inlet = 1.0%, O$_2$/CO ratio = 1.0, GHSV = 30,000 hr$^{-1}$)

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<th>Xco (%)</th>
<th>Sco (%)</th>
<th>Xo$_2$ (%)</th>
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+: T$_{in}$ = 170°C

Note: This is the only set operating condition that was tested for all three pieces catalyst, monolith and foam.
Fig. E1. (a) CO conversion and (b) CO selectivity for three individual “identical” 40 ppi, 4% density metal foams

Fig. E2. (a) CO conversion and (b) CO selectivity for three individual “identical” 400 cpsi ceramic monoliths
Appendix F

Comparison of Catalyst Performance for Different Supports
Comparison of Catalyst Performance for Ceramic Foam, Metal Monolith, Metal Foam and Ceramic Monolith

(CO inlet = 1.0%, O₂/CO ratio = 0.5)

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<th>Flow Rate</th>
<th>Ceramic Foam 20 ppi, 11% density</th>
<th>Metal Monolith</th>
<th>“new” Metal Foam 40 ppi, 4% density</th>
<th>“new” Ceramic Monolith 400 cpsi</th>
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Appendix G

ICP/BET Results
Analysis for Kyle bishop and Paul Chin, Chemical Engineering
Prepared By: Wayne P. Robarge
Date: July 28, 2002

Results for Fe and Ni are average of duplicate analyses.

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Digestion Procedure:
Sample Amount: 0.100 - 0.200 grams
React sample with 3 mL of concentrated HF acid in Teflon beaker.  Take to dryness.
Add 15 mL of aqua regia and allow to reflux on hot plate for 30 - 45 minutes.
Remove from hot plate and allow to cool. Make to volume in appropriate volumetric flask.
Dissolution of sample matrix is essentially complete except for few fine particles in solution.
Elemental analyses were conducted on Perkin-Elmer Model 2000 DV in axial mode.

Comment:
The Fe and Ni analyses are mean of true duplicates - separate samples weighed out and analyzed
on separate days. The sample size is very small since the material is dense. It is possible
that your material in not that homogeneous. Given the small sample size I use for the
analysis, I would need to do a fair number of replicates to get a better idea of the variability
in the composition of the material.
BET Results:

NCSU:

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Environex:

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<td>%Fe</td>
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<td>0.005</td>
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</table>

Note: The 5% Pt catalysts were tested last. During these runs I was unable to get consistent readings from the balance. This likely led to the diversity of the results. The 2% Pt and 0.5% Pt catalysts are more representative of the NCSU catalysts.
**BET Theory** [7]

\[
\frac{p}{n^s (p_o - p)} = \left( C - 1 \right) \frac{p}{n^s_m C} \frac{1}{p_o n^s_m C}
\]

- **C** constant related to the heat of adsorption into the first layer ($\Delta H_1$) and the heat of condensation of the adsorbate ($\Delta H_c$)
- **$n^s$** quantity of gas adsorbed at an equilibrium pressure
- **$n^s_m$** the value of $n^s$ at monolayer coverage
- **p** equilibrium pressure
- **$p_o$** vapour pressure of adsorbate in the condensed state at the adsorption temperature

\[
C = R^* \exp \left[ \frac{\Delta H_c - \Delta H_1}{RT} \right]
\]

- **R** constant being approximately $j_s/j_c$
- **$j_s$** partition function for the internal degrees of freedom for a molecule in the first adsorbed layer
- **$j_c$** partition function for the internal degrees of freedom for a molecule in the condensed phase
- **R** Universal Gas Law constant
- **T** adsorption temperature

\[
A = a_m n^s_m
\]

- **A** surface area of the adsorbent
- **$a_m$** effective area per molecule in the monolayer