Water Gas Shift Activity of Noble Metals Supported on Ceria-Zirconia Oxides

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Fuel processing systems that are used in conjunction with polymer electrolyte membrane (PEM) fuel cells require high activity water gas shift (WGS) catalysts that remove carbon monoxide, a poison for membranes in the fuel cell stacks. WGS activity of various noble metals supported on cubic, nanocrystalline, high surface area, large pore ceria-zirconia was measured at a space velocity of 312,000 hr^{-1}, under two feed gas compositions that simulated the high temperature shift (HTS) and the low temperature shift (LTS) conditions found in a typical fuel processing system. The (HTS) feed composition was 4.9% CO, 10.5% CO_2, 33% H_2O, 30.3% H_2; and the low temperature gas composition (LTS) was 1.5% CO, 5% CO_2, 45% H_2O, 25% H_2, with the balance of the stream being N_2 in both cases. The activity trend under both feed gases over a broad range of temperatures (200°C-320°C) was Pt > Rh > Ru ~ Pd > Ir > Au. This trend did not agree with those previously reported in literature or with CO uptake data for these samples. We hypothesize that this reflects the dominance of different reaction mechanisms under different gas compositions and temperatures. The discrepancy in the activities observed in this study and those reported in literature might also be attributed to differences in the synthesis techniques of the oxide supports and metal loading. Our study also found that the turnover rate (TOR) for the Pt catalyst was maximized in the range between 1-2 wt% loading under both HTS and LTS conditions. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 1888–1894, 2006
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Introduction

Water gas shift (WGS) reactors are critical components in fuel processors used to convert hydrocarbon fuels (natural gas, gasoline, and so on) to CO free (<10 PPM) fuel gas for proton exchange membrane (PEM) Fuel Cells power systems. The WGS reaction:

$$CO + H_2O \rightleftarrows CO_2 + H_2,\ \Delta H^o = -41.2\ \text{kJ mol}^{-1}$$

is an equilibrium limited, exothermic reaction that requires high activity, high selectivity catalysts to maximize CO conversion to CO_2 while minimizing the formation of byproducts, like CH_4. Supported CuO-ZnO catalysts have been the most commonly used WGS catalysts within an operating range of 180°C to 350°C.[1,2] Ceria based oxide systems are key materials in three way catalysts in automobiles because of their ability to release and uptake oxygen.[3] These oxides have also been identified as promoters for the WGS reaction.[4,5,6] Grenoble et al. studied the effect of different metals on WGS activity over Al_2O_3 and SiO_2 supports.[7] There have been limited studies done on the trends in WGS activity of ceria supported precious metal catalysts. These studies have concentrated on Pt,[5,6,8] Pd,[5,8] Rh,[8,9] and Au.[6]

The present article reports part of the work done at United Technologies Research Center (UTRC)[10] to support the development of a fuel processor (Figure 1) that had two water gas shift reactors, a high temperature stage that operated at

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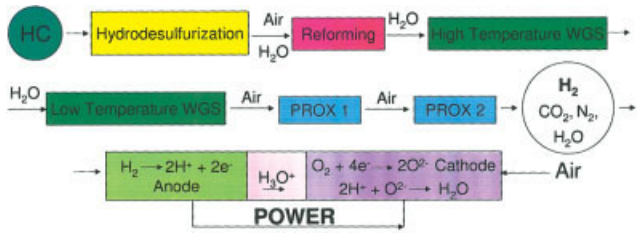

Figure 1. Fuel processing system for hydrogen production for PEM fuel cells.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

~320°C (exit temperature fuel) and a low temperature that operated at ~240°C. The results from the studies done on the impact of various noble metals (Pt, Pd, Ru, Rh, Ir, and Au) on the water gas shift activity of ceria-zirconia oxide systems under high temperature and low temperature shift (HTS, LTS) conditions are presented. The WGS activity trends observed are compared to those previously reported in literature. The results from studies performed to optimize noble metal loading on a turnover number (cost) and performance (CO conversion) under HTS and LTS conditions are also reported.

Experimental Procedures

Catalyst preparation and characterization

The key objective in the synthesis of the catalysts was to create high surface area supports with an engineered bimodal pore distribution that provided the maximum active site density per unit reactor volume with the minimum of mass-transfer resistance. This was accomplished by a network of 1 micron macro-pores that through a network of ~0.05 micron pores provided ready access to ~0.1 micron porous aggregates of ~3.5 nm crytallites with ~5 nm diameter pores between the crystallites. The surface of these cubic ceria-zirconian crystallites supported very high dispersion of nanometer sized noble metal rafts.

The following describes the method of preparation for the ceria-zirconia nanocrystalline support material described in this article, and the resulting properties. A $Ce_{0.58}Zr_{0.42}O_2$ catalyst support was prepared by dissolving 47.7014 g of $(NH_4)_2Ce(NO_3)_6$, 17.0999 g of $ZrO(NO_3)_2$. $\times$ H_2O and 1152 g of urea in 9600 mL of de-ionized water. The solution is heated to its boiling temperature while stirring until co-precipitation is observed. The mixture is then aged at boiling temperature for 7 h and then is left stirring at room temperature for 16 h. The mixture is filtered using a Büchner funnel. The resulting filter cake is washed twice with 1000 mL of de-ionized water at boiling temperature while stirring for 10 min, and then filtered again after each washing step. Then the filter cake is washed three times with 200 mL of dried 2-propanol while in the Büchner funnel. Then, if necessary, the precipitate is mixed with 800 mL of dried 2-propanol and heated to reflux for 45 min and then filtered again before being extruded, as through a syringe. The extrudates are dried in a vacuum oven at 70°C for 3 h and then left in the oven at 70°C (overnight) for 16 h without vacuum. The extrudates are then calcined in air at 400°C for 4 h with a heating rate of 2°C/min. After calcination at 400°C, the surface area of the support was measured to be 211 m^2/g. The pore volume was 0.23 cm^3/g, and the average pore diameter was 44 Å (4.4 nm).

A portion of the calcined $Ce_{0.58}Zr_{0.42}O_2$ support was then prepared for loading with ruthenium. 1.9298 g of the oxide support, comminuted to an 80-120 mesh size, was heated at 50°C for 15 min in 4 mL of an 0.2M malic acid in ethanol solution. The support was then rinsed with ethanol until the pH was >4. After rinsing, the support was submerged or immersed in 6.4173 g of a 1.5 wt% Ru solution made from ruthenium nitrosyl nitrate for 2 h at room temperature. The loaded support material was washed with ethanol and acetone and vacuum dried overnight (about 16 h) at 70°C. The loaded support was then calcined at 380°C for 4 h with a heating rate of 2°C/min. ICP analysis was conducted on the loaded support, giving an Ru loading value of 0.72 wt%.

A second portion of the calcined $Ce_{0.58}Zr_{0.42}O_2$ support was prepared for loading with rhodium. 2.1738 g of the oxide support, comminuted to an 80-120 mesh size, was heated at 50°C for 15 min in 4 mL of an 0.2M malic acid in ethanol solution. The support was then rinsed with ethanol until the pH was >4. After rinsing, the support was submerged or immersed in 4.3476 g of a 0.92 wt% Rh solution made from rhodium (III) nitrate for 2 h at room temperature. The loaded support material was washed with ethanol and acetone and vacuum dried overnight (about 16 h) at 70°C. The loaded support was then calcined at 380°C for 4 h with a heating rate of about 2°C/min. ICP analysis was conducted on the loaded support, giving an Rh loading value of 0.88 wt%.

A third portion of the calcined $Ce_{0.58}Zr_{0.42}O_2$ support was prepared for loading with iridium. 1.9941 g of the oxide support, comminuted to an 80-120 mesh size, was heated at 50°C for 15 min in 4 mL of an 0.2M malic acid in ethanol solution. The support was then rinsed with ethanol until the pH was >4. After rinsing, the support was submerged or immersed in 6.02689 g of a 0.99 wt% Ir solution made from tris(acetonylacetonate)iridium(III) for 1.5 h at 50°C. The loaded support material was washed with ethanol and acetone and vacuum dried overnight (about 16 h) at 70°C. The loaded support was then calcined at 380°C for 4 h with a heating rate of about 2°C/min. ICP analysis was conducted on the loaded support, giving an Ir loading value of 0.59 wt%.

A fourth portion of the calcined $Ce_{0.58}Zr_{0.42}O_2$ support was prepared for loading with gold. 2.5103 g of the oxide support, comminuted to an 80-120 mesh size, was submerged or immersed in 14.9169 g of a 6.0 wt% Au solution made from chloroauric acid ($HAuCl_4$) for 1.5 h at room temperature. The loaded support material was washed with water until no chlorine was detectable by a silver nitrate test. The material was further washed with ethanol and acetone and vacuum dried overnight (about 16 h) at 70°C. The loaded support was then calcined at 380°C for 4 h with a heating rate of about 2°C/min. ICP analysis was conducted on the loaded support, giving an Au loading value of 3.33 wt%.

The ceria-zirconia oxide prepared for platinum loading had a similar synthesis procedure, with a slight difference. The extrudates formed were ground to a coarse powder, spread across a quartz boat to maximize surface area, and calcined under the following steps: 10°C/min up to 380°C in a CO_2 environment (2L/min flow rate across furnace cavity, overnight soak at 380°C in a CO_2/O_2 environment (50:50 volume %)), and a 20 h isotherm in O_2 (2 L/min). The sample was removed

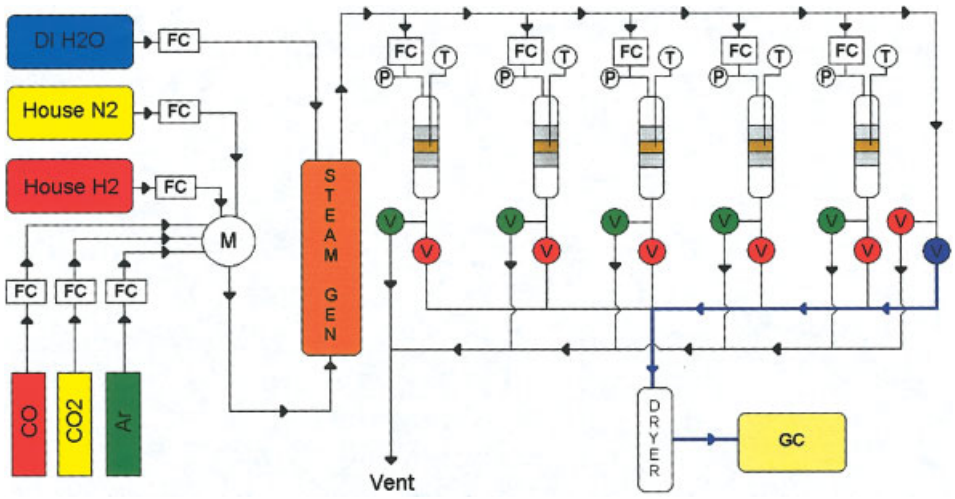

Figure 2. Catalyst screening rig.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

from the furnace at 380°C without a ramp down step. After calcination, the surface area of the support was measured to be 218 m^2/g.

A portion of the calcined $Ce_{0.58}Zr_{0.42}O_2$ support was then prepared for loading with platinum. 1.0831 g of the oxide support, comminuted to an 80-120 mesh size, was heated at 50°C for 15 min in 2 mL of an 0.2M malic acid in ethanol solution. The support was then rinsed with ethanol until the pH was >4. After rinsing, the support was submerged or immersed in 1.1124 g of a 1.0 wt% Pt solution made from tetraaminplatinum nitrate for 2 h at room temperature. The supernatant solution was filtered through a 10 μm Teflon® membrane filter and saved for ICP analysis. The loaded support material was washed with ethanol and acetone and vacuum dried overnight (about 16 h) at 70°C and then calcined at 380°C for 4 h with a heating rate of 2°C/min. ICP analysis conducted on the original Pt solution and compared with the supernatant solution after loading gave a Pt loading value of 0.87 wt%. The other loadings of Pt were prepared using the same method using varying amounts of the Pt precursor.

A portion of the calcined $Ce_{0.58}Zr_{0.42}O_2$ support (used in Pt sample preparations) was prepared for loading with palladium. 1.2345 grams of the oxide support, comminuted to an 80-120 mesh size, was heated at 50°C for 15 min in 2.5 mL of an 0.2M malic acid in ethanol solution. The support was then rinsed with ethanol until the pH was >4. After rinsing, the support was submerged or immersed in 2.5532 g of a 0.45 wt% Pd solution made from tetraaminepalladium nitrate for 2 h at room temperature. The supernatant solution was filtered through a 10 μm Teflon® membrane filter and saved for ICP analysis. The loaded support material was washed with ethanol and acetone and vacuum dried overnight (about 16 h) at 70°C and then calcined at 380°C for 4 h with a heating rate of 2°C/min. ICP analysis conducted on the original Pd solution and compared with the supernatant solution after loading gave a Pd loading value of 0.67 wt%.

The CO uptake of the catalysts was measured to establish a pre-screening tool for catalyst WGS activity. These measurements were carried out in a Micromeritics ASAP 2010C unit. The analysis procedure involved degassing the catalyst sample to 10^{-5} atm and 150°C to remove moisture. The sample was then pre-treated in oxygen flow at 200°C for 1 h to remove any organic impurities on the surface. This was followed by an evacuation under flowing He at 200°C for 0.5 h. Following the He evacuation, the sample was reduced under hydrogen flow for 5 minutes at 200°C, 230°C, and 260°C. This was followed by an evacuation at 10^{-5} atm at 260°C and a cool down under vacuum to the analysis temperature. The CO chemisorption amounts were measured at 35°C.

WGS activity experiments

The WGS activity measurements were conducted in a catalyst screening rig used to evaluate five different catalysts simultaneously under identical inlet gas compositions and space velocities. Catalyst (0.6 g), or 0.5 cc by volume, of the 80-120 mesh catalyst loaded with noble metal, was uniformly blended with 5 cc, or 9.4 g, of +40 mesh Strem Chemical alpha alumina granules and charged into a 0.5 inch O.D. 316L Stainless Steel reactor tube with 0.049 in walls with a 0.402 inch I.D. equipped with a 0.125 inch O.D. Axial Thermowell. The net cross sectional area of the reactor was 0.74 cm^2. The catalyst charge was separated from the bottom frit by a 5.25 inch length of 10 mesh alundum granules and a thin wad of borosilicate glass wool. The catalyst and 40 mesh alumina diluent bed together was 3.0 inches long, and topped with a thin wad of borosilicate glass, above which was loaded about 5 in. more of 10 mesh alundum granules. As this was a down flow reactor, this 5 in. top section served to preheat the reaction gas mixture to reaction temperature before it contacted the dilute catalyst. This was confirmed during the initial heating and reduction by the internal, 0.0625 inch K type thermocouple in the internal, axial thermowell. The 0.5 in. O.D. reactor tube was placed inside a tight fitting aluminum block to minimize axial temperature gradients, and no axial thermal gradient was found at 320°C under 20% hydrogen, 80% nitrogen flowing at 2.6 standard liters per minute (SLM). Figure 2 presents a schematic of a fully automated multi-reactor rig used in these experiments. The experiments were conducted at a space velocity of 312,000 hr^{-1} and the temperature of the catalyst bed

Table 1. Catalyst Characterization Data

NM/ wt%	SA Support/ (m^2 g^{-1})	T_{chem} (°C)	CO Uptake (μmol g^{-1})	CO/NM
Pt/0.87	218	35	38	0.80
Pd/0.67	218	35	82	1.30
Ru/0.72	211	35	296	4.20
Rh/0.88	211	35	156	1.80
Ir/0.59	211	35	58	1.80
Pt/3.31	218	35	96	0.60
Au/3.31	211	35	9	0.10

was measured by the K-type thermocouple in the axial thermowell. The flow of UHP grade compressed gases N_2, Ar, H_2, CO, and CO_2 was controlled by Brooks Flow Controllers (Model 5850E) and combined at ambient conditions in a mixing manifold. De-ionized water was fed to a steam generator that operates at approximately 270°C. The mixed dry gas were then contacted with the steam in the steam generator to obtain the final gas mixture. This hot gas mix was metered to the individual reactors by MKS Model M330 mass flow controllers. The experimental protocol used had the following features:

(a) Preliminary drying of the gases in nitrogen flow at 150°C.

(b) Reduction of the catalyst in 8-40% hydrogen, with a balance of N_2 in the 240-330°C range.

(c) Stepwise addition of steam from a concentration of 0% to 33% with 30% H_2 and balance N_2 at 320°C.

(d) Determination of the WGS activity at high CO conditions (4.9% CO, 33% H_2O, 30% H_2, 10.5% CO_2, with balance N_2 and Ar) while varying temperatures from 320°C to 200°C.

(e) Determination of the WGS activity at high CO conditions (1.5% CO, 45% H_2O, 25% H_2, 5% CO_2, with balance N_2 and Ar) while varying temperatures from 320°C to 200°C.

The inlet and exit gases from the system were analyzed using a Varian GC equipped with three detectors (one FID and two TCDs), a methanizer, and six separation columns. The first two columns (61 cm and 92 cm Haysep DB 80/100 mesh columns, 1 mm ID), and the first TCD (H_2 carrier) were used to detect N_2, Ar, and CO_2. The vent from the second column was connected through a valve to two other separation columns (both 183 cm Mol Sieve 5A 80/100 mesh columns, 1 mm ID). These columns were used to separate CO, CO_2, and CH_4. The effluent from these columns was fed through the methanizer to the FID for detection. The final two columns (61 cm and 122 cm Haysep DB 80/100 mesh columns, 1 mm ID) and a second TCD (N_2 carrier gas) were used to detect H_2. The feed gas composition measured between product gas composition measurements was used in the determination of CO conversion. The turnover numbers presented in this article were calculated using the expression TOR = (% CO converted) * (Flow rate in mol/s)/(Total amount of metal loaded in moles). After initial activation, the catalysts that showed the highest activities were aged by running a series of temperature ramps over time under HTS and LTS conditions.

Results and Discussion

Table 1 presents the noble metal loading amounts along with corresponding BET surface areas and CO uptakes. The only Au supported sample tested had a loading of 3.3%, so a Pt sample with equivalent loading was tested and its characterization data is also reported in Table 1.

The interpretation of the CO uptake data is difficult because ceria is known to adsorb large amounts of CO[11] and noble metals can adsorb more than one CO atom per noble metal, a phenomenon dependent on the exposed crystal faces in the catalyst.[12] The purpose of this study was to evaluate the possibility of using CO chemisorption as a qualitative activity-screening tool for the WGS reaction. Consequently, the CO uptakes were normalized to the total amount of noble metal loaded on the catalysts and this value is reported as the CO/NM ratio. The heats of adsorption of CO on various metals has been tabulated by Vannice,[13] and the trend observed was Au $<$ Ru $<$ Pt $<$ Rh $<$ Ir $<$ Pd. The CO/NM values in this study follow the trend Au $<$ Pt $<$ Pd $<$ Rh $\sim$ Ir $<$ Ru.

The discrepancy in the trends observed through our studies and those in literature might be attributed to differences in synthesis techniques of the oxide supports and the metal loading techniques. There is no direct correlation between the CO uptakes and the heats of adsorption of CO on the pure metals due to possible metal-support interaction further complicated by CO adsorption on ceria and non-stoichiometric CO adsorption on some of the metals. A summary of CO chemisorption adsorption sites measured through LEED and CO stretching frequencies for single crystal noble metal surfaces is presented in the textbook by Somarjai.[12] This has shown the possibility of experimentally observing CO:NM ratios of 2:1 for Pd(100) and Pt(111) surfaces with a number as high as 3:1 observed for an Rh(111) surface. The catalysts prepared might have multiple surfaces with a variation of exposed crystal planes that might adsorb varying amounts of carbon monoxide. This, along with adsorption of CO by the support, made it difficult to use CO adsorption as an effective titration tool for measuring noble metal amounts on the support surface. Consequently, the total amount of metal loaded on the surface was used in estimating the turnover rates. This implies that the noble metal dispersion for each of the cases was near 100% (for metal loadings less than 3%). The assertion was corroborated for platinum catalysts through electron microscopy measurements (Figure 3).

Figure 4 presents the WGS activity of the catalysts under HTS conditions normalized to the total amount of noble metal loaded on the active metal oxide. The results from the Au

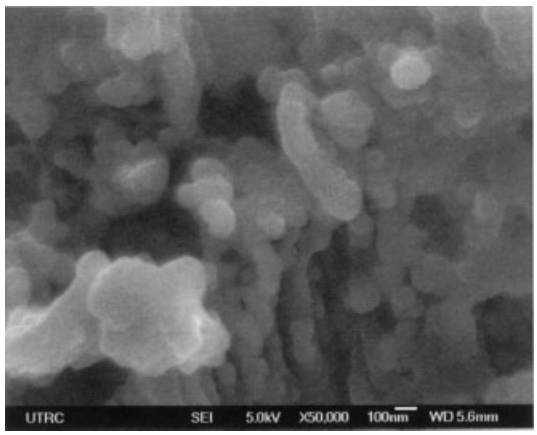

Figure 3. Catalyst micrograph pictures indicate no visible NM at 2% Pt loading.

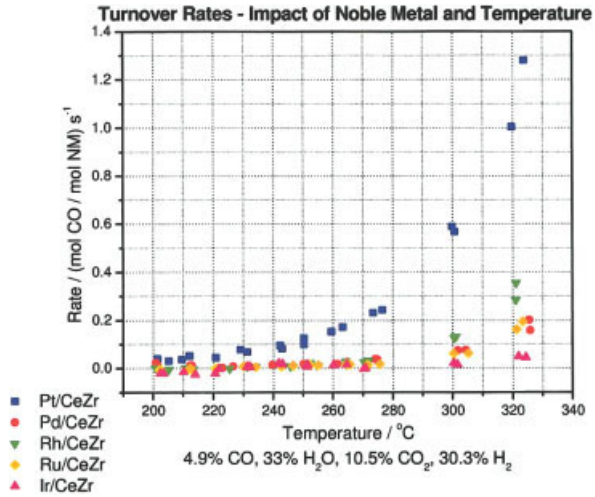

Figure 4. Effect of noble metals on HTS activity.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

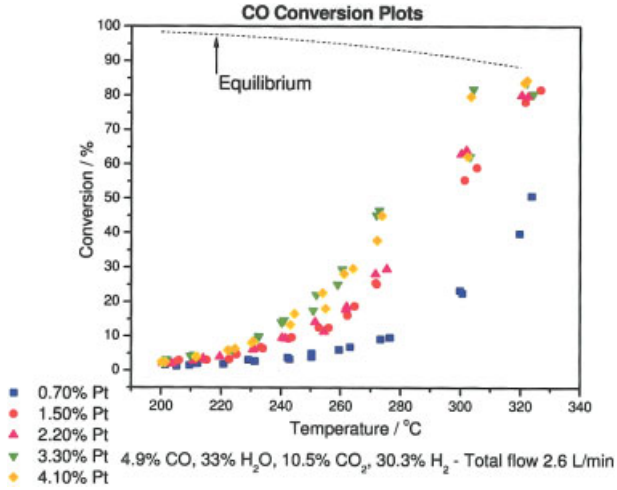

Figure 6. Effect of platinum loading on HTS CO conversions.

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catalyst are not presented because no significant WGS activity was observed for these catalysts. The supported Pt catalyst on ceria-zirconia gave the highest activity on a per noble metal basis. The order of WGS activity was Pt > Rh > Ru ~ Pd > Ir > Au. Methanation was a concern for both supported Rh and Ru catalysts. A similar trend in activity (Figure 5) was observed under LTS conditions. The activity trends for Al_2O_3 and SiO_2 supported catalysts observed by Grenoble et al.[7] followed the trend Ru > Pt > Au > Rh ~ Pd > Ir. Gorte et al.[5] found Pt, Pd, and Rh supported on ceria to be equally effective for the WGS activity at 1:1 H_2O/CO ratio. The Grenoble and Gorte work was done at a H_2O/CO ratio of 1 with no H_2 in the inlet stream. The activity tests for this study were done at a H_2O/CO ratio of 6.7 and 30 with the gas composition simulating a reformate stream that enters the two stages of WGS reactors in a fuel processor.

The discrepancy between the data in this study and those in literature might be attributed to the differences in gas and catalyst composition. In situ IR studies have indicated the existence of different types of adsorbed species under varying gas feed and catalyst compositions (unreported results), thereby suggesting the possible existence of competing reaction mechanisms on the surface of the catalyst that is dependent on the surface properties and the kinetic regime of operation. Another evidence for the existence of these mechanisms was the fact that both the supported Ru and Rh catalysts produced increasing amounts of methane with increasing temperatures that artificially enhanced the HTS and LTS rates, which were being calculated through CO conversion measurements.

Recent work by Stephanopolous et al.[6] has determined that non-metallic gold and platinum species strongly associated with cerium-oxygen groups are responsible for WGS activity in ceria supported gold and platinum catalysts. Although their observations regarding platinum WGS activity agrees with this current study, our supported gold catalysts had very low WGS activity. It is possible that at loadings >3%, the gold has a bulk crystalline structure that renders it inactive for the WGS reaction. The supported gold catalysts may also be sensitive to the presence of CO_2 and H_2 in the inlet gas stream similar to the Rh and Ru samples. The screening experiments indicated further pursuing Pt as the noble metal of choice, and dozens of samples with varying amounts of platinum were prepared and tested. The figures provided through the rest of the article use representative samples that help summarize information on the trends observed.

Figures 6 and 7 present the CO conversion and WGS turnover numbers under HTS conditions. The CO conversions indicate that at a temperature of 320°C, the catalyst with Pt loadings in the 2-4% range reached the equilibrium conversion predicted for that feed composition and temperature. The turnover numbers suggest an advantage for Pt loadings of less than 2%. This discrepancy can be explained by the fact that, while on a per noble metal basis the low loading catalysts do have an advantage, in practical terms one would require the higher loadings to achieve the desired CO conversion for the HTS

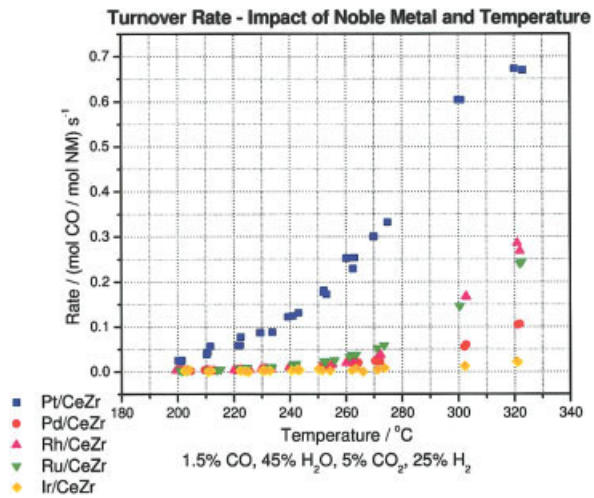

Figure 5. Effect of noble metals on LTS activity.

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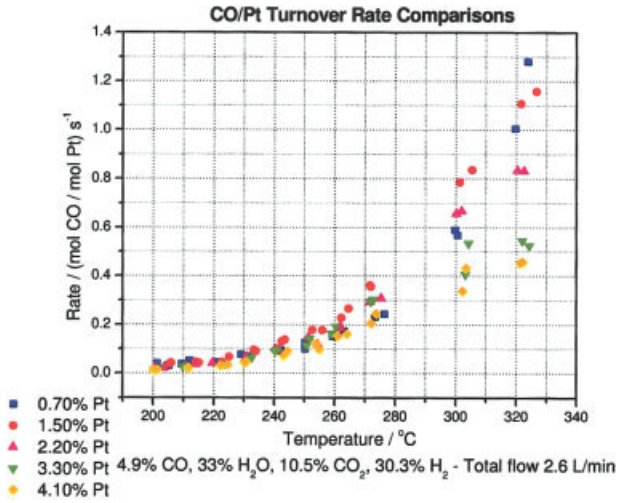

Figure 7. Effect of platinum loading on HTS turnover rates.

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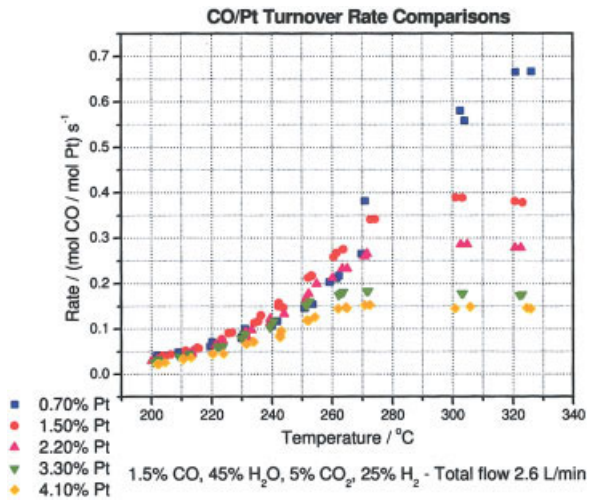

Figure 9. Effect of platinum loading on LTS turnover rates.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

condition. These results suggested that a catalyst with 2.2% Pt meets the requirements of adequate conversion and cost effectiveness for HTS conditions.

Figures 8 and 9 present the CO conversion and WGS turnover numbers under LTS conditions. None of the catalysts achieved the desired equilibrium conversion needed at 240°C. A Pt loading of at least 3% was needed to hit equilibrium conversion at ~260°C under LTS conditions, with the 2.2% catalyst approaching equilibrium in the 280- 290°C temperature range. Turnover numbers under LTS conditions indicated a cost and performance optimized catalyst would be in the 1-2% Pt loading range.

Stability data for the catalysts (~2% Pt loading) under the HTS and LTS conditions (Figures 10 and 11) indicate a 20-30% activity drop in the period between 330 h and 500 h, time on stream that is in the time regime where the catalyst activity should have stabilized. All of these results further indicated the need for an improved catalyst for the WGS reactors, and this was accomplished by adding a metal promoter to the Pt loaded catalysts.[10]

Conclusions

Various noble metal supported ceria-zirconia oxides were tested for their water gas shift activities under HTS (4.9% CO, 10.5% CO_2, 33% H_2O, 30.3% H_2) and LTS (1.5% CO, 5% CO_2, 45% H_2O, 25% H_2) conditions in the temperature range between 200-320°C. The observed reaction rates were found to be highly dependent on the synthesis technique, surface composition, and kinetic regime of operation, which potentially resulted in different reaction mechanisms for the different

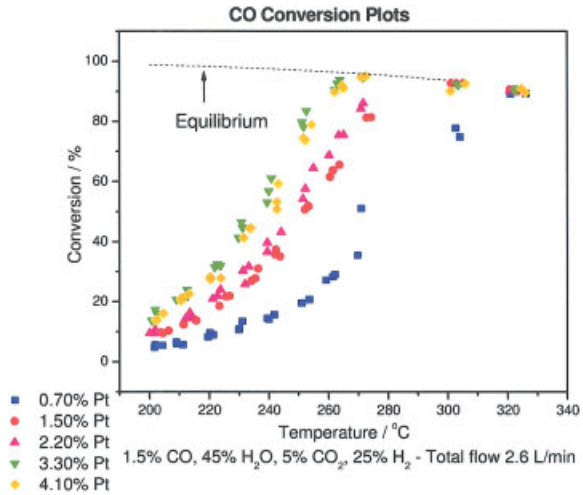

Figure 8. Effect of platinum loading on LTS CO conversions.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

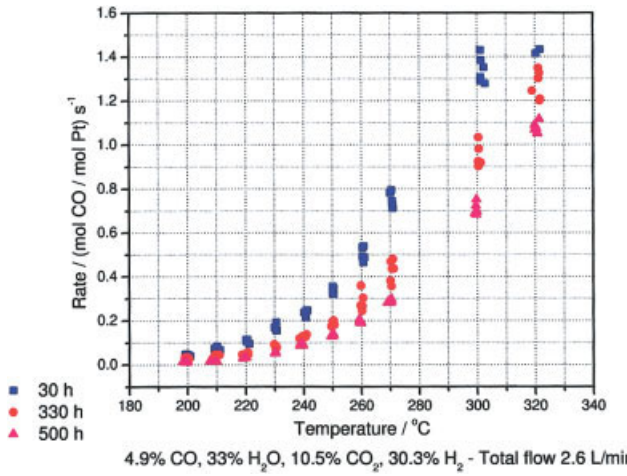

Figure 10. Stability of ~2% Pt/Ce/Zr catalyst at HTS conditions.

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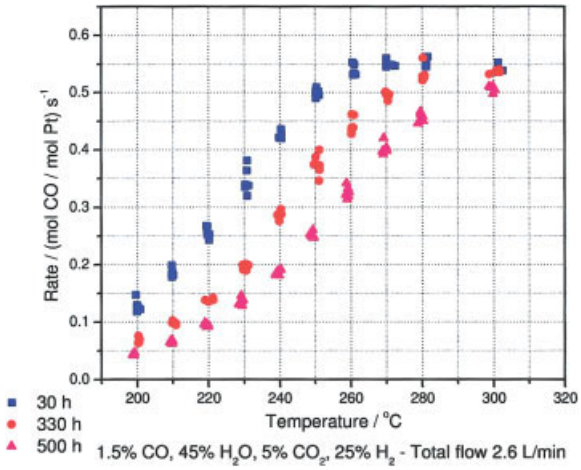

Figure 11. Stability of ~2% Pt/Ce/Zr catalyst at LTS conditions.

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catalysts. Platinum was identified as the noble metal with the highest activity under these conditions, with a cost and performance optimized loading identified to be in the 1-2 wt % range.

Acknowledgments

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