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Pt-Re bimetallic supported on CeO_2-ZrO_2 mixed oxides as water–gas shift catalysts[☆]

Sara Yu Choung, Magali Ferrandon, Theodore Krause*

Electrochemical Technology Program, Chemical Engineering Division, Argonne National Laboratory,
9700 South Cass Avenue, Argonne, IL 60439, USA

Abstract

The addition of Re to Pt/$Ce_{0.46}Zr_{0.54}O_2$ was shown to enhance the water–gas shift (WGS) rate compared with the rate observed with Pt alone supported on either $Ce_{0.46}Zr_{0.54}O_2$ or $Ce_{0.6}Zr_{0.4}O_2$ at similar Pt weight loadings. The results from CO chemisorption showed that the Pt was more highly dispersed on Pt-Re/$Ce_{0.46}Zr_{0.54}O_2$ than on the Pt/$Ce_{0.46}Zr_{0.54}O_2$ or Pt/$Ce_{0.6}Zr_{0.4}O_2$. Based on this Pt dispersion, the exposed Pt surface area was calculated for Pt-Re/$Ce_{0.46}Zr_{0.54}O_2$, Pt/$Ce_{0.46}Zr_{0.54}O_2$ and Pt/$Ce_{0.6}Zr_{0.4}O_2$. The WGS rate was observed to be proportional to the exposed Pt surface area for the Pt-Re and Pt catalysts; however, the rate per m^2 of exposed Pt for Pt-Re/ $Ce_{0.46}Zr_{0.54}O_2$ was higher than that of Pt/$Ce_{0.46}Zr_{0.54}O_2$ or Pt/$Ce_{0.6}Zr_{0.4}O_2$. The difference in the rates upon the addition of Re to Pt WGS catalysts suggests that the role of Re in enhancing the WGS activity of Pt is more complex than to just increase the Pt dispersion.

1. Introduction

Reforming of natural gas, propane, gasoline or other hydrocarbon fuels is one option being pursued to generate hydrogen for use in automotive or stationary polymer electrolyte fuel cells (PEFCs) or for other applications. Because the fuel gas exiting the reformer contains from 5 to 20 vol.% CO, additional processing of the reformate is required to reduce the CO concentration to ~10 ppm to minimize losses in performance due to CO poisoning of the PEFC anode catalyst. The water–gas shift (WGS) reaction ($CO + H_2O \equiv CO_2 + H_2$) is used in many fuel-processing schemes to reduce the concentration of CO to 0.5–1%, with preferential oxidation or methanation of the remaining CO to further reduce its concentration to <10 ppm. Commercial Cu-Zn and Fe-Cr oxide WGS catalysts have certain drawbacks that make them unsuited for use in fuel processors being developed for use onboard a vehicle or for distributed power or hydrogen production. First, these catalysts require an activation step consisting of a controlled in situ reduction. In the reduced state, these catalysts may be pyrophoric or at least exhibit a large rise in temperature when exposed to air. This temperature rise can cause the catalysts to sinter, resulting in loss in activity. During shutdown, these catalysts may be exposed to condensing steam, which can cause the catalysts to reoxidize. Because of frequent startups and shutdowns, these catalysts may be exposed to many condensation and vaporization cycles that can lead to poor mechanical stability. Finally, the activity of these current catalysts is not sufficient to permit operation of the water–gas shift reactor at high gas hourly space velocities (GHSVs) of 30,000 h^{-1} or more, which are needed to yield compact fuel processors.

Catalyst formulations based on platinum supported on ceria have been shown to exhibit high WGS activity [1] and address many of the issues associated with using commercial WGS catalysts mentioned above [2]. The high WGS activity of these catalysts has been attributed to a synergism between the platinum and the ceria for the WGS reaction. A bifunctional redox mechanism is used to explain this synergism [3]. In this mechanism, CO is adsorbed on the platinum, then oxygen is

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* Corresponding author. Tel.: +1 630 252 4356; fax: +1 630 972 4463.
E-mail address: krause@cmt.anl.gov (T. Krause).

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transferred from the ceria to the platinum, where the CO is oxidized (CO_2) and the ceria is reduced ($Ce^{4+} \rightarrow Ce^{3+}$); finally, the reduced ceria is reoxidized ($Ce^{3+} \rightarrow Ce^{4+}$) by the dissociative adsorption of H_2O, releasing H_2 in the process. Although ceria-supported platinum shift catalysts are very active, the cost of catalyst required for a 50 kW_e onboard fuel processor, which is estimated to be about \$2.50/kW_e [4], is higher than the \$1/kWe target that the U.S. Department of Energy had established [5].

Several different R&D efforts are focused on increasing the activity of ceria-supported platinum catalysts to reduce their cost [3,4,6–8]. Kinetic studies have suggested that either oxygen transfer from ceria or reoxidation of ceria is the rate-limiting step for Pt, Pd or Rh supported on ceria [3]. One potential approach to increasing the rate of oxygen transfer from ceria is to modify the redox properties of the ceria by replacing some of the cerium cations with a different rare earth cation, such as lanthanum, gadolinium or zirconium, or an alkaline earth metal cation; this approach is referred to as "doping". Zirconium is a common dopant for ceria because its smaller ionic radius (0.84 Å for Zr^{4+} versus 0.97 Å for Ce^{4+}) introduces lattice strain, which promotes both the formation of oxygen vacancies and the reduction of Ce^{4+}–Ce^{3+} [10]. We have reported in a previous study, however, that there is little difference in the WGS activities of 1 wt.% Pt supported on undoped CeO_2, zirconia-doped ceria ($Ce_{0.8}Zr_{0.2}O_2$, $Ce_{0.6}Zr_{0.4}ZrO_2$, $Ce_{0.56}Zr_{0.54}ZrO_2$ and $Ce_{0.4}Zr_{0.6}ZrO_2$), or gadolinium-doped ceria ($Ce_{0.8}Gd_{0.2}O_{1.9}$) over the temperature range of 250–400 °C [9,11].

An alternative approach is to enhance the activity of platinum through the use of bimetallic formulations. A theoretical study conducted by Ishikawa et al. [12] predicted that the energetics of H_2O dehydrogenation are lower and the $CO_{ads} + OH_{ads}$ reaction is more favorable, on certain Pt-mixed metal clusters than on Pt alone. In previous studies, the WGS activity of different platinum-containing bimetallic formulations, Pt-Re, Pt-Co, Pt-Mo, Pt-Sn and Pt-Cu, supported on a zirconia-doped ceria were evaluated and compared with the WGS activity of Pt alone supported on the same zirconia-doped ceria [9,11]. Catalysts containing Pt-Re and Pt-Co exhibited a higher WGS activity than Pt (on a per-gram-of-Pt basis), whereas Pt-Mo, Pt-Sn and Pt-Cu exhibited a lower WGS activity. Although Pt-Re and Pt-Co were shown to be more active than Pt, the Pt-Re catalyst was less prone to deactivation than the Pt-Co catalyst. The mechanism by which Re promotes the WGS activity of Pt is not well understood, although it has been reported that Re increases the Pt dispersion on TiO_2 [13] and Al_2O_3, and inhibits Pt sintering on Pt-Re/Al_2O_3 [14]. Recently, both Matsushita Electric Works and Süd-Chemie, Inc. have filed U.S. patent applications for Pt-Re WGS catalysts [15,16].

Our research is focused on developing WGS catalysts to address the drawbacks with using commercial Cu-Zn and Fe-Cr oxide WGS catalysts in fuel processors being developed for automotive and distributed hydrogen and power production applications. In this paper, we report some results from our study to investigate reasons for the enhancement in the WGS activity of ceria-supported Pt catalysts when Re is added.

2. Experimental methods

$Ce_{0.6}Zr_{0.4}O_2$ was prepared by a coprecipitation process. In this process, cerium and zirconium nitrate were dissolved into 800 mL deionized water and then heated to 100 °C. Ammonium hydroxide was added dropwise until the pH of the solution reached 8–9. The solution was centrifuged at 2500–3000 rpm for 5 min and then the liquid was decanted off yielding a gel. The gel was dried overnight at 110 °C and then calcined in air at 500 °C for 1 h. Samples with different Pt weight loadings (0.87, 1.51 and 2.86 wt.% Pt) were prepared by the incipient wetness technique using tetraammineplatinum(II) nitrate [$Pt(NH_3)_4(NO_3)_2$]. After impregnation of Pt, the samples were dried at 110 °C overnight and then calcined at 500 °C for 1 h.

$Ce_{0.46}Zr_{0.54}O_2$ was purchased from Rhodia and calcined in air at 500 °C before the metals were impregnated. Samples consisting of Pt, Re or Pt-Re were prepared by the incipient wetness technique using hydrogen hexachloroplatinate(IV) [H_2PtCl_6] (Aldrich, 8 wt.% solution in water) and ammonium perrhenate [NH_4ReO_4] (Aldrich, 99+%). The samples were dried in air at 120 °C overnight and then calcined in air at 500 °C for 2 h. The weight loading of Pt in the sample that contained only platinum was 1.05 wt.%. The weight loading of Re in the sample that contained only rhenium was 0.90 wt.%. The weight loadings of the samples that contained both platinum and rhenium were (1) 0.91 wt.% Pt, 0.95 wt.% Re; (2) 0.92 wt.% Pt, 1.79 wt.% Re ;(3) 1.81 wt.% Pt, 1.77 wt.% Re.

WGS activities of these catalysts were measured in a flow microreactor system over a temperature range of 250–400 °C using a synthetic reformate with the composition: 6.9% CO, 10.4% CO_2, 31.1% H_2, 31.0% H_2O and 20.7% N_2. The amount of catalyst (0.05–0.4 mL) and the GHSV (400,000–2,100,000 h^{-1}) were adjusted to maintain differential reactor conditions (conversion $\leq$15%) at the lower temperatures investigated. In order to maintain a constant bed volume of 0.5 mL, catalyst samples were diluted with α-alumina, which, by itself, was shown to have negligible WGS activity. The samples were reduced using a gas mixture consisting of 4% H_2/He at 400 °C for 1 h prior to the activity measurements. The temperatures were monitored at the top and the bottom of the catalyst bed and at the outside wall of the reactor, with the temperature at the bottom of the catalyst bed being the temperature reported. The concentrations of CO and CO_2 in the effluent were monitored continuously using an on-line infrared gas analyzer (California Analytical Instruments, Model ZRH infrared analyzer). Periodically, grab samples of the effluent were collected using a gas-tight syringe and analyzed using a gas chromatograph (Hewlett Packard 5890 Series II) equipped with thermal conductivity detectors. These measurements were used to verify the concentrations of the gases measured by the on-line infrared gas analyzer; the results were used to determine if significant methanation was occurring during the reaction. The CO_2 was separated on a J&W Scientific GS-CarbonPLOT column using He as the carrier gas. The other gases, CO, H_2, N_2 and CH_4, were separated on a J&W Scientific GS-MolSieve column using Ar as the carrier gas.

Some samples were exposed to air at a flowrate of 200 mL/min at 300 °C for 10 min after determining their WGS activity. After air exposure, the WGS activity of these samples was determined again to see if reoxidation at high temperatures had caused the catalyst to deactivate. These tests were conducted at a GHSV of 400,000 h^{-1}. To evaluate the long-term stability of the catalysts, the WGS activity of some of the samples was measured over a period of 60 h. These tests were conducted at a GHSV of 300,000–400,000 h^{-1}.

The Pt dispersion was measured by CO chemisorption using a commercial catalyst characterization system (Zelton Altamira, Model Ami-100) equipped with a thermal conductivity detector to measure CO uptake. The amount of sample used for each measurement was ~25 mg. Prior to measuring the CO uptake, the samples were oxidized in a flowing mixture of 4% O_2 in He from room temperature to 500 °C at a heating rate of 30 °C/min, flushed with He at 500 °C and then cooled to room temperature in He. The oxidation procedure was repeated. The samples were then reduced in a flowing mixture of 3% H_2 in Ar from room temperature to 500 °C at a rate of 5 °C/min, flushed with He at 500 °C and then cooled to room temperature in He. The reduction process was then repeated two more times. The CO uptake measurements were conducted at 30 °C by injecting a series of pulses containing 53 μL of CO into a He stream flowing over the sample at a rate of 25 mL/min and measuring the amount of CO absorbed per pulse.

A temperature-programmed reduction (TPR) study of the catalysts was performed using the Zelton Altamira system. The following procedure was used for the TPR: (1) the sample was oxidized in 4% O_2/He (50 mL/min) by heating the sample from ambient temperature to 500 °C at a rate of 5 °C/min and then holding the temperature at 500 °C for 1 h; (2) the sample was then cooled to ambient temperature in He (50 mL/min); (3) the TPR was conducted by heating the sample in 3% H_2/Ar (50 mL/min) from ambient temperature to 500 °C at 5 °C/min and then holding the temperature at 500 °C for 1 h; (4) the sample was cooled to ambient temperature in He (50 mL/min); and (5) steps (1) through (4) were repeated. The first TPR is referred to as TPR1 and the second TPR is referred to as TPR2. The sample size was ~0.1 g.

3. Results and discussion

A comparison of the WGS rates observed with 1.05 wt.% Pt/$Ce_{0.46}Zr_{0.54}O_2$, 0.90 wt.% Re/$Ce_{0.46}Zr_{0.54}O_2$ and 0.91 wt.% Pt–0.95 wt.% Re/$Ce_{0.46}Zr_{0.54}O_2$ showed that the rate observed with the Pt-Re catalyst is greater than the sum of the rates of the Pt and Re catalysts, as shown in Fig. 1, indicating that the addition of Re enhances the WGS activity of the Pt catalyst. Similar results have been reported by others for Pt, Re and Pt-Re supported on ceria-based oxides [16].

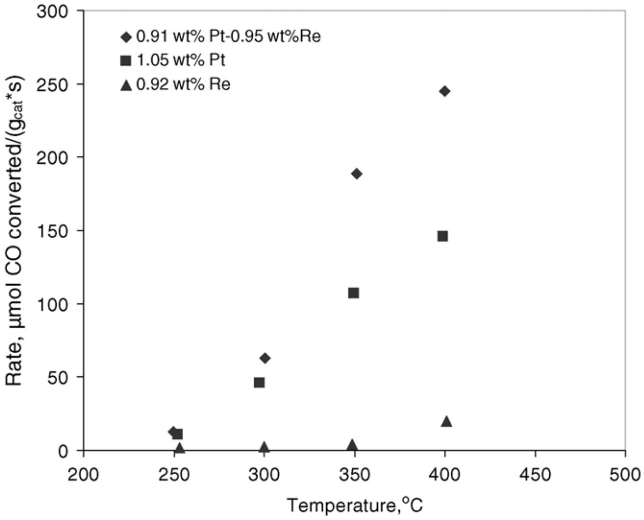

Fig. 1. WGS activity (per gram of catalyst) of Pt, Pt-Re and Re supported on $Ce_{0.46}Zr_{0.54}O_2$.

Iida et al. [13] has suggested that the increase in the WGS activity observed when Re was added to Pt/TiO_2 was to due to smaller particle sizes being present on Pt-Re/TiO_2 compared to Pt/TiO_2, which led to an increase in the number of active sites. This was based on results from CO chemisorption and transmission electron microscopy studies to determine the average particle size on the Pt/TiO_2 and Pt-Re/TiO_2 catalysts. We measured the WGS rate, in terms of micromoles of CO converted per gram of catalyst, for the

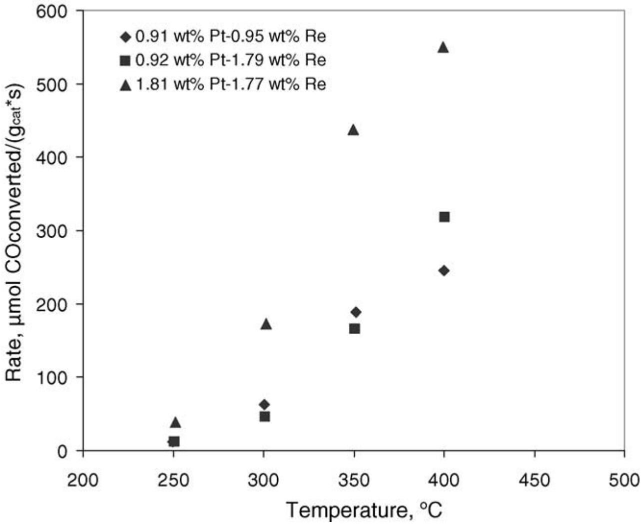

Fig. 2. WGS activity (per gram of catalyst) of Pt-Re/ $Ce_{0.46}Zr_{0.54}O_2$ at different Pt and Re weight loadings.

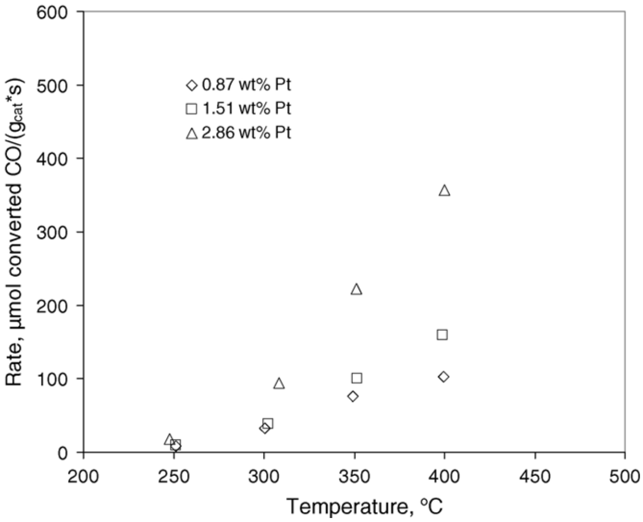

Fig. 3. WGS activity (per gram of catalyst) of $Pt/Ce_{0.6}Zr_{0.4}O_2$ at different Pt weight loadings.

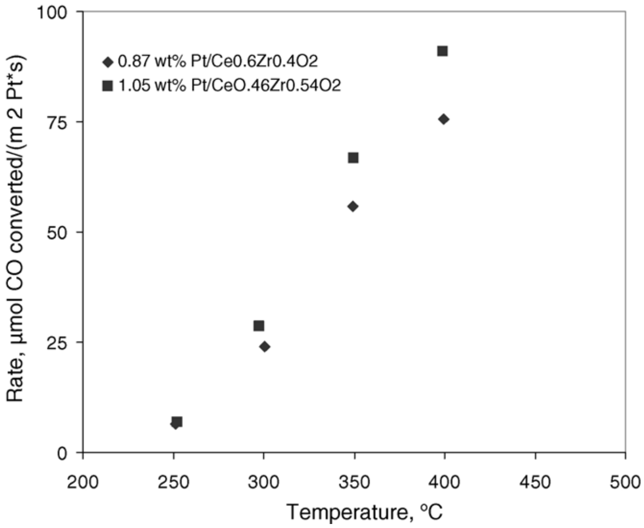

Fig. 4. Comparison of the effect of the composition of the mixed ceria-zirconia oxide support on the WGS activity of the Pt catalysts.

three different Pt-Re ratios investigated (0.91 wt.% Pt–0.95 wt.% Re, 0.92 wt.% Pt–1.77 wt.% Re and 1.81–1.77 wt.% Re). Our results showed that the CO conversion rate per gram of catalyst increased with the Pt loading as shown in Fig. 2. Similar results were reported by Wagner et al. [16] for Pt-Re supported on a ceria-based oxide, although in that study the total weight loadings of Pt and Re were constant. We then measured the WGS activity of $Pt/Ce_{0.6}Zr_{0.4}O_2$ for three different Pt weight loadings (0.87, 1.51 and 2.86 wt.% Pt). The WGS rate, in terms of micromoles of CO converted per gram of catalyst was observed to increase with increasing Pt loading, as was observed with the Pt-Re catalysts, as shown in Fig. 3. Fig. 4 shows that a difference in the composition of the mixed ceria-zirconia oxide support ($Ce_{0.46}Zr_{0.54}O_2$ or $Ce_{0.6}Zr_{0.4}O_2$) had minimal effect on the WGS activity for the Pt catalysts.

CO chemisorption was used to estimate the Pt dispersion on both the Pt-Re and Pt catalysts. The Pt-Re catalysts exhibited a greater CO uptake than the Pt catalysts for similar Pt weight loadings which suggests that Pt is more highly dispersed as $Pt\text{-}Re/Ce_{0.46}Zr_{0.54}O_2$ than as $Pt/Ce_{0.6}Zr_{0.4}O_2$, as shown in Table 1. For example, 0.91 wt.% Pt–0.95 wt.% $Re/Ce_{0.46}Zr_{0.54}O_2$ exhibited a CO uptake of 38.5 µmol/g$_{cat}$, which correlates to a Pt dispersion of 83% (assuming that Re does not adsorb CO), compared to a CO uptake of 26.8 µmol/g$_{cat}$, which correlates to a Pt dispersion of 60%, exhibited by 0.87 wt.% $Pt/Ce_{0.6}Zr_{0.4}O_2$. For the Pt-Re catalysts, it is possible that both Pt and Re can contribute to the CO uptake. However, the small CO uptake (5.1 µmol/g$_{cat}$) exhibited by 0.95 wt.% $Re/Ce_{0.46}Zr_{0.54}O_2$ suggests that the amount of CO uptake by Re compared to the amount of CO uptake by Pt is minimal. Even if CO uptake by Re is accounted for (assuming 0.95 wt.% Re adsorbs 5.1 µmol/g$_{cat}$), the Pt dispersion would still be 72% for 0.91 wt.% Pt–0.95 wt.% $Re/Ce_{0.46}Zr_{0.54}O_2$.

Finally, we compared the WGS activity of the various $Pt\text{-}Re/Ce_{0.46}Zr_{0.54}O_2$ and $Pt/Ce_{0.6}Zr_{0.4}O_2$ catalysts on the basis of micromole of CO converted per m^2 of Pt surface area, as shown in Fig. 5. The three $Pt/Ce_{0.6}Zr_{0.4}O_2$ catalysts, which differ only in the Pt weight loading, exhibited the same WGS activity as a function of temperature, which suggests that the rate is a function of the exposed Pt surface area. Similarly, Wang et al. [18] reported that the WGS rate depends only on exposed metal surface area for ceria-supported palladium. The three $Pt\text{-}Re/Ce_{0.46}Zr_{0.54}O_2$ catalysts also exhibited the same WGS activity as a function of

Table 1
Results of CO chemisorption study to measure the Pt dispersion and exposed Pt surface area for $Pt/Ce_{0.6}Zr_{0.4}O_2$ and $Pt\text{-}Re/Ce_{0.46}Zr_{0.54}O_2$

Sample	CO uptake (µmol/g$_{cat}$)	CO uptake (µmol/g$_{Pt}$)	Dispersion (%)	Number of exposed Pt (atoms/g$_{cat}$)	Pt surface area (m^2/g$_{cat}$)[a]
0.87 wt.% $Pt/Ce_{0.6}Zr_{0.4}O_2$	26.8	3080	60	1.6×10^{19}	1.4
1.51 wt.% $Pt/Ce_{0.6}Zr_{0.4}O_2$	36.8	2430	48	2.2×10^{19}	1.9
2.86 wt.% $Pt/Ce_{0.6}Zr_{0.4}O_2$	87.9	3070	60	5.3×10^{19}	4.5
1.05 wt.% $Pt/Ce_{0.46}Zr_{0.54}O_2$	32.1	3060	60	1.9×10^{19}	1.6
0.95 wt.% $Re/Ce_{0.46}Zr_{0.54}O_2$	5.1	–	–	–	–
0.91 wt.% Pt–0.95 wt.% $Re/Ce_{0.46}Zr_{0.54}O_2$	38.5	4230	83	2.3×10^{19}	2.0
0.92 wt.% Pt–1.79 wt.% $Re/Ce_{0.46}Zr_{0.54}O_2$	32.7	3560	69	2.0×10^{19}	1.7
1.81 wt.% Pt–1.77 wt.% $Re/Ce_{0.46}Zr_{0.54}O_2$	80.3	4440	86	4.8×10^{19}	4.1

[a] Assumes a surface area per surface Pt atom of 0.0841 nm^2 [17].

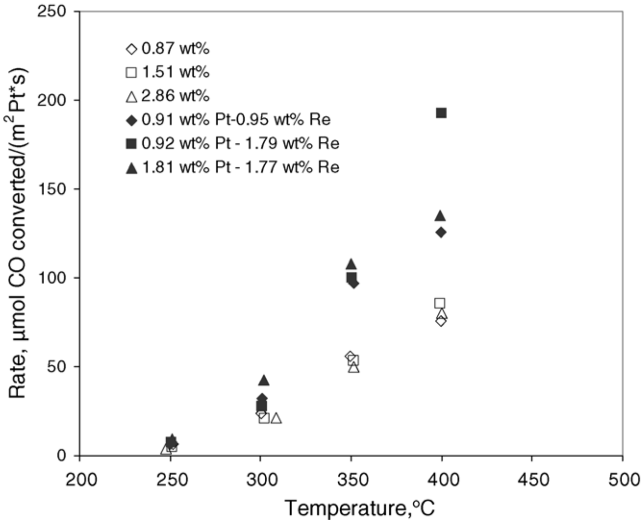

Fig. 5. Comparison of the WGS activity (per m^2 of Pt) of $Pt/Ce_{0.6}Zr_{0.4}O_2$ and $Pt\text{-}Re/Ce_{0.46}Zr_{0.54}O_2$ at various Pt weight loadings.

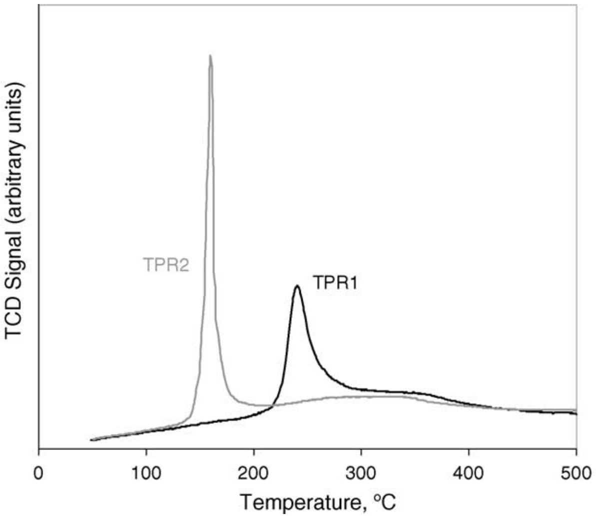

Fig. 7. TPR of $Pt/Ce_{0.46}Zr_{0.54}O_2$ [TPR1: 3% H_2/Ar, 50 mL/min, 5 °C/min; TPO: 4% O_2/He, 50 mL/min, 5 °C/min; TPR2: 3% H_2/Ar, 50 mL/min, 5 °C/min].

temperature; however, the activity was higher than that of the $Pt/Ce_{0.6}Zr_{0.4}O_2$ catalysts, especially at temperatures above 300 °C. If the only function of Re was to increase the Pt dispersion, one would expect the same WGS activity for both Pt and Pt-Re catalysts. We have reported an activation energy of 67 kJ/mol and reaction orders of zero for CO and 0.40 for H_2O for $Pt\text{-}Re/Ce_{0.46}Zr_{0.54}O_2$, which is in reasonable agreement with the activation energy of 46 kJ/mol and reaction orders of zero for CO and 0.5 for H_2O for Pt/CeO_2 reported by Bunlunsein et al. [3], suggesting that the reaction mechanism is similar on both catalysts. The addition of Fe_2O_3 has been shown to enhance the WGS activity of ceria-supported Pd, which has been attributed to the formation of a Fe–Pd alloy [19]. While our data suggest that the addition of Re increases Pt dispersion, the WGS rates evaluated on the basis of the exposed Pt surface area suggest that there may also be a synergistic effect between Pt and Re. X-ray absorption spectroscopy studies are in progress to determine if the addition of Re to ceria-supported Pt results in the formation of a Pt–Re alloy.

The stabilities of the two catalysts, 0.91 wt.% Pt–0.95 wt.% $Re/Ce_{0.46}Zr_{0.54}O_2$ and 1.05 wt.% $Pt/Ce_{0.46}Zr_{0.54}O_2$, were compared by measuring the WGS rate for each catalyst at 300 °C over a period of 60 h, as shown in Fig. 6. At first, the $Pt/Ce_{0.46}Zr_{0.54}O_2$ deactivates rapidly, losing about 40% of its initial activity within 20 h but it then deactivates more slowly, losing only about 5% (of the activity measured at 20 h) over the next 40 h. The

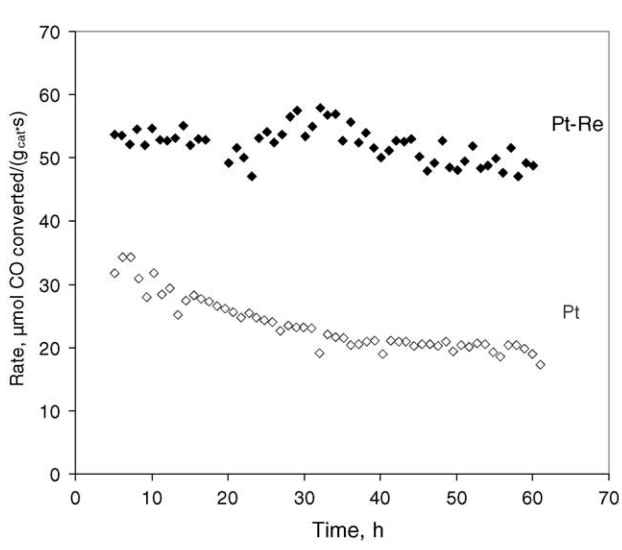

Fig. 6. Comparison of the WGS activity (per gram of catalyst) of $Pt/Ce_{0.46}Zr_{0.54}O_2$ and $Pt\text{-}Re/Ce_{0.46}Zr_{0.54}O_2$ as a function of time on stream.

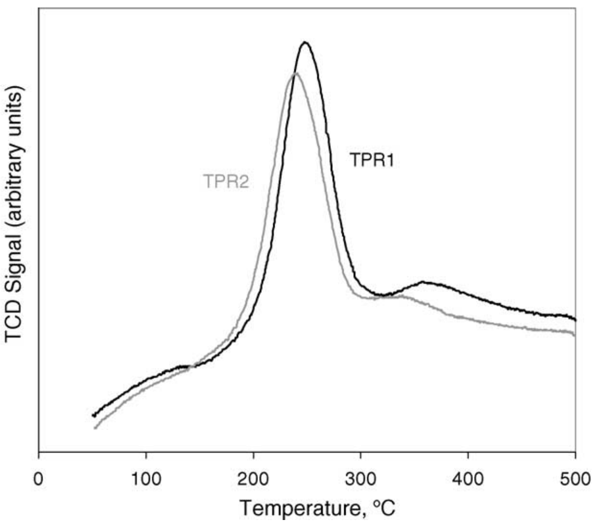

Fig. 8. TPR of $Pt\text{-}Re/Ce_{0.46}Zr_{0.54}O_2$ [TPR1: 3% H_2/Ar, 50 mL/min, 5 °C/min; TPO: 4% O_2/He, 50 mL/min, 5 °C/min; TPR2: 3% H_2/Ar, 50 mL/min, 5 °C/min].

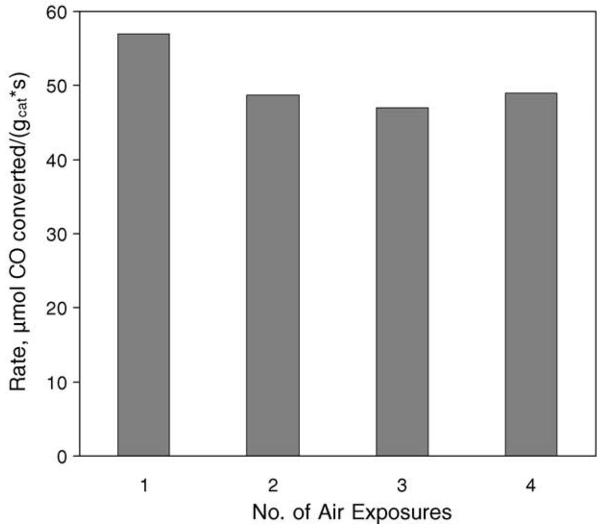

Fig. 9. WGS activity (per gram of catalyst) of Pt-Re/$Ce_{0.46}Zr_{0.54}O_2$ after exposure to air at 300 °C for 10 min/cycle.

Pt-Re/$Ce_{0.46}Zr_{0.54}O_2$ catalyst is more stable than Pt/$Ce_{0.46}Zr_{0.54}O_2$, losing less than 20% of its initial activity after 60 h. A TPR study of Pt and Pt-Re supported on $Ce_{0.46}Zr_{0.54}O_2$ was conducted to investigate the effect of the addition of Re on the reducibility and sintering of Pt on Pt-Re/$Ce_{0.46}Zr_{0.54}O_2$. For Pt/$Ce_{0.46}Zr_{0.54}O_2$, the temperature at which the reduction peak is observed during the second reduction cycle (TPR2) is lower than the temperature at which the reduction peak is observed during the first reduction cycle (TPR1), as shown in Fig. 7. The shift of the reduction peak to a lower temperature suggests that the Pt has sintered during the first reduction cycle, forming larger Pt particles, which are more easily reduced during the second reduction cycle. For Pt-Re/$Ce_{0.46}Zr_{0.54}O_2$, the reduction peak occurs at very similar temperatures during the first and second reduction cycles (TPR1 and TPR2), suggesting that the addition of Re inhibited Pt from sintering during the first reduction step (Fig. 8). Based on the TPR results, one possible explanation for the slower rate of deactivation of Pt-Re/$Ce_{0.46}Zr_{0.54}O_2$ compared with Pt/$Ce_{0.46}Zr_{0.54}O_2$ is that the Re may stabilize the Pt against sintering.

The stability of the 0.91 wt.% Pt–0.95 wt.% Re/$Ce_{0.46}Zr_{0.54}O_2$ catalyst after exposure to air at 300 °C was investigated. The WGS rates observed before and after successive air exposures are compared in Fig. 9. The WGS activity of Pt-Re/$Ce_{0.46}Zr_{0.54}O_2$ decreases after the initial air exposure, but is stable after further air exposures. Similar studies have shown that Cu/Zn oxide WGS catalyst loses almost 40% of its initial activity upon repeated exposure to oxidation–reduction cycles [20]. The stability of the Pt-Re catalyst in air is promising in light of the potential for exposure to O_2 at high temperature depending on the procedures used to start and shut down the fuel processor.

4. Conclusions

The addition of Re to Pt/$Ce_{0.46}Zr_{0.54}O_2$ was shown to enhance the WGS rate compared with the WGS rate observed with Pt/$Ce_{0.46}Zr_{0.54}O_2$ at similar Pt weight loadings. The Pt dispersion was higher on the Pt-Re catalysts than the Pt catalysts based on CO chemisorption measurements. The WGS rate for both the Pt-Re and Pt catalysts was observed to correlate with the exposed Pt surface area on the various catalysts; however, the enhancement in the rate observed upon the addition of Re could not be completely explained by just the higher Pt dispersion.

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