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Studies of the water-gas-shift reaction with ceria-supported precious metals

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Abstract

Ceria-supported precious metals have great potential for use as water-gas-shift (WGS) catalysts in fuel processors for fuel-cell applications. In this paper, we review the mechanisms that have been proposed for these catalysts and discuss the deactivation that has been observed. Since a redox mechanism appears to explain the observations about the reaction best, we briefly review what is known about ceria reduction. We also discuss methods for enhancing catalytic activity through the use of additives.

Keywords: Water-gas-shift reaction; Ceria; Pd; Redox properties; Deactivation; Dopants

1. Introduction

There is a need for better water-gas-shift (WGS) catalysts for the development of efficient fuel processors for fuel-cell applications [1,2]. Getting higher WGS activities is crucial because it would allow the reaction to be carried out at lower temperatures where the equilibrium concentration of CO, a serious poison for low-temperature fuel cells, is decreased. Materials that are typically used for the WGS reaction in large-scale operations, such as Cu/ZnO, are not applicable for many fuel-cell applications due to the fact that they are sensitive to start-up/shut-down cycles and may be pyrophoric [1,2]. Ceria-supported, precious-metal catalysts are one class of materials that have been identified as exhibiting very interesting properties for the WGS reaction with fuel cells [1–6]. Under some conditions relevant to H_2 production, the WGS reaction rates were observed to be higher on ceria-supported, precious metals than on commercial catalysts [1,4].

While the properties of ceria-supported precious metals are well known because of their use in automotive, emissions-control catalysts; the application of these materials to low-temperature WGS will require optimization in a very different manner. In automotive catalysis, ceria is used as an oxygen-storage capacitor (OSC). In this application, ceria gives up oxygen under rich engine operating conditions and accepts oxygen under lean conditions. While work from our laboratory has shown that there seems to be a direct relationship between WGS activity and OSC [7], the activity of the automotive catalysts does not need to be particularly high because of the high operating temperatures. The primary issue in optimizing automotive catalysts is stability following severe hydrothermal aging, not the initial activity. Because pure ceria loses its ability to provide OSC after a relatively short time under automotive conditions [8], much effort has gone into stabilizing the redox properties of ceria through the formation of mixed oxides with zirconia [8]. Catalysts used for the WGS reaction will not be exposed to conditions as harsh as those experienced in the catalytic converter. While deactivation of Pt/ceria under low-temperature WGS conditions has been observed [9], it seems unlikely that the deactivation mechanisms are the same in the two applications.

One of the complications with ceria-based catalysts is that the activity can vary dramatically with pretreatment conditions and dopant levels [10–19]. This observation represents a challenge on the research side for understanding these materials and an opportunity on the applications side for developing new materials that exhibit superior performance. In this paper, we will attempt to outline some of the issues we have found from our work involved with ceria-

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based catalysts for the WGS reaction, with the goal of guiding future research towards the development of catalysts with higher activity and better stability.

2. Reaction mechanism

The question concerning how the WGS reaction proceeds is important, particularly for ceria-supported metals, because it provides the basis for how to develop better, more stable catalysts. With ceria-supported precious metals, Fig. 1 shows that it is crucial to have both ceria and the precious metal, in contact, to obtain high WGS activities. These experiments were carried out in a flow system under differential-reaction conditions with partial pressures for CO and H_2O of 25 Torr each. At a temperature of 500 K, the differential-reaction rates are more than 50 times higher on Pd/ceria than on either ceria or Pd/alumina individually. Since the activation energies are similar on each of the catalysts (48 kJ/mol on Pd/ceria, 58 kJ/mol on ceria, and 65 kJ/mol on Pd/alumina), this large enhancement in activity associated with having Pd and ceria together is observed at a wide range of temperatures. Unfortunately, the mechanistic details for the WGS reaction remain controversial in that two distinctly different mechanisms have been proposed. This is true for traditional catalysts based on Fe and Cu/ZnO [2] and also for the ceria-based catalysts [5,20].

Based primarily on evidence from FTIR measurements, it has been postulated that WGS occurs through a formate intermediate [20]. Using σ to designate an adsorption site, this mechanism can be written as follows:

$$CO + \sigma \rightarrow CO_{ad} \tag{1}$$

$$H_2O + 2\sigma \rightarrow H_{ad} + OH_{ad} \tag{2}$$

$$OH_{ad} + CO_{ad} \rightarrow HCOO_{ad} + \sigma \tag{3}$$

$$HCOO_{ad} + \sigma \rightarrow CO_{2,ad} + H_{ad} \tag{4}$$

$$2H_{ad} \rightarrow H_2 + 2\sigma \tag{5}$$

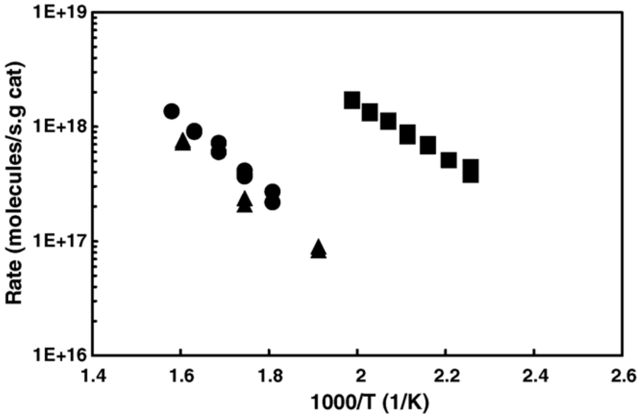

Fig. 1. Differential rates for the WGS reaction on ceria (▲), 1 wt.%Pd/Al_2O_3 (●) and 1 wt.% Pd/ceria (■) in 25 Torr each of CO and H_2O.

Proponents of this mechanism have argued that the rate-determining step is the decomposition of the formate, $HCOO_{ad}$, based on the observation that the intensities of features assigned to the formate decrease with water pressure [20] and that the rates exhibit a normal kinetic-isotope effect [21]. However, it should be noted that some who have studied the WGS reaction over Pt/ceria using FTIR have argued that the formate is a spectator species only and not involved in the mechanism [22].

The second postulated mechanism is essentially a redox process. If one assumes a single type of adsorption site, this mechanism can be written in a simplified form as follows:

$$CO + \sigma \rightarrow CO_{ad} \tag{6}$$

$$H_2O + \sigma \rightarrow O_{ad} + H_2 \tag{7}$$

$$CO_{ad} + O_{ad} \rightarrow CO_2 + 2\sigma \tag{8}$$

The key point is that the catalyst is oxidized by H_2O and reduced by CO. In principle, the adsorption sites for CO_{ad} and O_{ad} need not be the same. For example, with Pd/ceria catalysts, Bunluesin et al. have suggested that CO adsorbs on the Pd and then reduces the ceria near the Pd interface; subsequently, H_2O re-oxidizes the reduced ceria [5]. Also, a more complete statement of the mechanism would separate the dissociation of water into the formation of H_{ad} and OH_{ad}. The formation of OH_{ad} would imply formal oxidation of the catalyst and could subsequently dissociate into H_{ad} and O_{ad}. Even with the redox mechanism, Mavrikakis and Greely used Density Functional Theory to suggest that OH_{ad} need not dissociate further, at least on Cu catalysts, but could react directly with CO_{ad} to form a carboxylate species, $COOH_{ad}$ [23], which then decomposes to H_{ad} and CO_2. Mavrikakis went on to propose that formate intermediates form under different conditions and lead to methanol as the product.

While the debate over the mechanism is likely to continue, we favor the redox mechanism for the WGS reaction over ceria-supported precious metals for a number of reasons. First, formates have limited thermal stability [24], so that rates for WGS should probably exhibit a maximum at relatively low temperatures if this mechanism was operative. This does not agree with the observation that WGS rates increase steadily with increasing temperature. It is interesting to contrast the results for the WGS reaction and the methanol-synthesis reaction, where the formate intermediate is almost certainly involved. Both Cu and Pd/ceria can be used for production of methanol [25,26], but the selectivity towards methanol production occurs under different reaction conditions from that for WGS and appears to exhibit a maximum at intermediate temperatures [26].

Second, each of the proposed mechanistic steps with the redox mechanism has been observed in pulse-reactor measurements. Fig. 2 shows the effluent from a reactor loaded with a Pd (1 wt.%)–ceria catalyst exposed to CO and H_2O pulses at 723 K, a temperature above which the formate

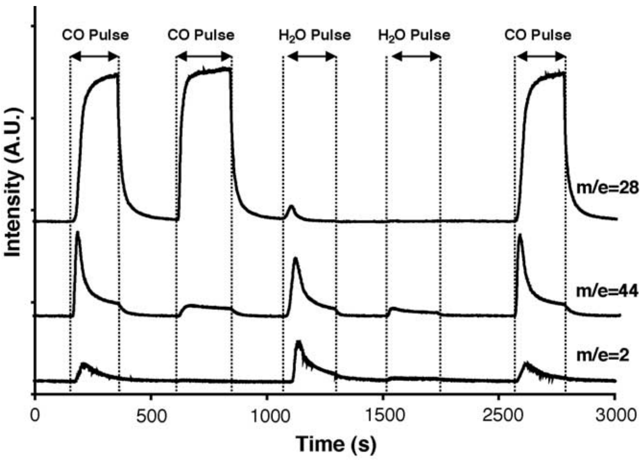

Fig. 2. Pulse measurements on a 1 wt.% Pd/ceria catalysts at 723 K. The data are for two pulses of CO (*m*/*e* = 28), followed by two pulses of H_2O and another of CO.

is reported to be stable. (The *m*/*e* = 18 peak is not shown because of the difficulty of monitoring water with a mass spectrometer.) While the pulse-reactor measurement shown here is at a somewhat higher temperature than the rate data in Fig. 1, it has been shown elsewhere that Pd/ceria exhibits significantly enhanced activities over Pd/alumina and ceria at this temperature as well [27] and the higher temperatures make the results of the pulse-reactor studies clearer.

Starting from a fresh Pd/ceria catalyst oxidized in water, $\sim$200 μmol/g of CO_2 and $\sim$100 μmol/g of H_2 are formed during the first CO pulse (5% CO in He) that is shown (this is essentially Reaction 8). When this reduced catalyst was exposed to 2% H_2O in He, an additional 150 μmol/g of CO_2 and 250 μmol/g of H_2 were formed at the leading edge of the water pulse (this is Reaction 7). Finally, the last CO pulse shows that the sequence is repeatable. In the initial CO pulse, CO_2 is formed primarily by reduction of ceria. Since the reduction of ceria by CO is accompanied by the formation of surface carbonates, the H_2 formation results from decomposition of hydroxyls that become unstable on the reduced ceria surface or in the presence of carbonates. The formation of CO_2 in the first H_2O pulse is due to re-oxidation of ceria. This is confirmed by FTIR measurements that show the removal of carbonates that are only stable on reduced ceria [6]. The oxidation of ceria by H_2O obviously requires the production of H_2.

Third, for ceria-supported precious metals, the redox mechanism accurately predicts the observed rate expression for the conditions used in our laboratory studies. The reaction order in CO is zeroth-order, as expected for strong adsorption on precious metals [6]. WGS rates for ceria-supported Pt, Pd, and Rh catalysts are essentially identical, as should be expected if re-oxidation of ceria or oxygen transfer from ceria is rate limiting. Finally, high-temperature calcination of ceria, which is known to cause irreversible loss in the reducibility of ceria [14], also severely poisons specific rates for the WGS reaction [5].

3. Oxidation and reduction of ceria

As discussed in the previous section, the reduction of oxidized ceria with adsorbed CO and the oxidation of reduced ceria with H_2O are crucial steps in the WGS reaction mechanism. This implies that one must understand the redox properties of ceria in order to completely understand this reaction. However, even though the redox properties of ceria have been studied extensively, for application with both automotive catalysts and ion-conducting membranes, the properties are not well understood. We will discuss two examples to show the problem.

First, there appear to be major discrepancies between the catalytic literature and the thermodynamic literature on ceria reduction. A recent review of thermodynamic measurements suggests that reduction of ceria should be insignificant at 973 K and lower temperatures, even at very low $P(O_2)$ [28]. For example, based on the measurements from several groups, $CeO_{1.99}$ is given as the equilibrium stoichiometry at 973 K and an O_2 fugacity of 10^{-22} atm, a fugacity that is established by a H_2:H_2O ratio of approximately 3 at this temperature. Reduction is predicted to be even less if the H_2:H_2O ratio is less than this. This conclusion completely contradicts the observation that ceria absorbs and releases oxygen in the automotive catalytic converter, where steam is always present at partial pressures much higher than the partial pressures of the reductants. (Note: The presence of small quantities of precious metals in the catalytic application would be expected to change the rate of ceria reduction but not the equilibrium state of ceria.)

A second, very dramatic example comes from the results of Smirnov and Graham [12], who showed that Pd films that had been vapor deposited onto ceria–zirconia substrates could be completely oxidized by heating to 423 K in ultra-high vacuum. What makes the oxidation of Pd by ceria–zirconia so surprising is that the reaction, $2CeO_2 + Pd = PdO + Ce_2O_3$, is endothermic by 295 kJ/mol [29]. Given that the activation energy for transferring one mole of O must be at least as large as the heat of reaction, the reaction should not occur except possibly at very high temperatures. Since the enthalpy of forming O_2 from $CeO_{(2-x)}$ has been reported to be essentially independent of x [30], the results cannot be explained by assuming that it is energetically easier to reduce CeO_2 to an oxide intermediate between CeO_2 and Ce_2O_3. One must conclude that the enthalpy change for transfer of oxygen from ceria–zirconia to Pd is much less than would be predicted by the thermodynamic values typically reported for ceria. (Note: It may be significant that older handbooks report the heat of reaction for $Ce_2O_3 + 1/2O_2 \rightarrow 2CeO_2$ to be -232 kJ/mol [31], while a value of -380 kJ/mol is found in newer references [29].)

The key factor in the above results is not the presence of zirconia. Although pure ceria is unstable, it can provide OSC prior to high-temperature treatments [13]. Furthermore, evidence for oxygen transfer from ceria to precious metals has been observed with pure ceria [10,11]. Also, the apparent discrepancies between the catalytic and thermodynamic results cannot be explained by surface effects, since active materials often have low surface areas.

One possible explanation for the observations described above is that the reduction of ceria is structure sensitive. Evidence for this comes from the observation that ceria becomes much more difficult to reduce after it has been heated to high temperatures [14]. Also, ceria single crystals [14] and vapor-deposited ceria films on alumina [14] have been shown to be very difficult to reduce compared to low-temperature powders and ceria films on zirconia [32].

Finally, it should be mentioned that it is a common practice to modify the properties of CeO_2 by doping the oxide, particularly with +3 ions like La^{3+}, Sm^{3+}, or Gd^{3+} that are known to affect the ionic conductivity [33]. However, in our laboratory, we found that rates for *n*-butane oxidation actually decreased significantly upon addition of Yb_2O_3, Y_2O_3, Sm_2O_3, Gd_2O_3, La_2O_3, Nb_2O_5, Ta_2O_5, and Pr_6O_{11} to ceria [34]. It is, therefore, important that one not simply assume that the addition of dopants will enhance either the reducibility of ceria or its activity.

4. Deactivation of WGS

The long-term stability is a concern with all WGS catalysts and particularly so with ceria-supported precious metals [9]. While it seems likely that considerable industrial effort has been expended to understand these deactivation processes, relatively little has been published on this with ceria-supported metals. Based on the published work, there is still no consensus on what processes are most important.

An initial proposal by Loffler et al. is that deactivation occurs as a result of ceria over-reduction [9]. Using literature values for the thermodynamic properties of ceria, this is certainly not possible; typical WGS reaction conditions are too oxidizing. However, as we pointed out in the previous section, catalytic forms of ceria may not be well described by the published thermodynamic values. For the conditions we have used in tests in our laboratory [6], the ceria-supported metals were not highly reduced. The color of ceria goes from light yellow to almost black when it is reduced and all of the catalysts in our study were yellow when taken out of the reactor. Furthermore, it should be relatively easy to restore the activity of a deactivated catalyst by oxidation if deactivation were due to over-reduction. Since this is not the case [35], there must be other processes involved.

A more recent study of reverse WGS on Pt/ceria catalysts has suggested that deactivation in that case is due to formation of large amounts of carbon for reaction at 400 °C [36]. Furthermore, the carbon formed under these conditions was reported to be amazingly reactive, oxidizing between 260 °C and 290 °C in temperature-programmed oxidation measurements. Since minimal carbon formation was observed on Pt/silica, the authors argued that carbon formed initially on the ceria. While the authors of this study did not explicitly claim that carbon formation is responsible for WGS deactivation, they did argue that the carbon formed as a result of CO dissociation, so that a similar deactivation process could presumably be responsible for deactivation under WGS conditions. It is noteworthy that, if the claims for carbon formation on Pt/ceria at such mild conditions prove to be true, this catalyst is more effective for CO dissociation than is a Ni catalyst, one of the most active methanation catalysts. Since bulk carbonates could exhibit properties similar to that which were claimed for carbon, we believe the claim about carbon formation needs to be verified.

The work from our laboratory has suggested that another mechanism for deactivation of Pt/ceria and Pd/ceria catalysts under WGS conditions is the loss of metal dispersion [35]. First, as shown in Fig. 3, WGS rates on a series of Pd/ceria catalysts were found to increase linearly with the surface area of the Pd, so that a loss of dispersion could easily account for the loss in activity.

This linear dependence between the WGS rate and Pd surface area is somewhat surprising. Given that the WGS reaction on Pd/ceria appears to be due to a bifunctional mechanism, with ceria supplying oxygen from water to the Pd and CO oxidation occurring on the Pd surface, one might expect that the rates would depend on the circumferential area at the interface between Pd and ceria, similar to what has been reported for ceria-mediated rates of CO oxidation on Rh/ceria catalysts [44]. However, based on the paper by Smirnov and Graham, who showed that Pd particles were completely oxidized by a ceria–zirconia film upon mild heating in vacuum [12], it seems reasonable that the entire surface of the Pd particles could be effective for catalyzing the oxidation reaction if the rates of oxygen transfer from ceria to Pd were comparable to the overall reaction rate. Furthermore, we observed that

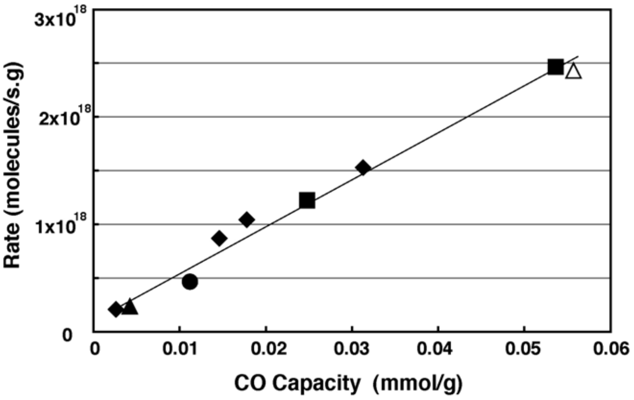

Fig. 3. A plot of differential, water-gas-shift rates as a function of CO adsorption capacity for a series of Pd/ceria catalysts in 25 Torr each of CO and H_2O at 523 K. Data are shown before and after deactivation for some of the catalysts. The symbols correspond to the following catalysts: (◆) 1 wt.% Pd/ceria, with ceria calcined at 873 K; (■) 6 wt.% Pd/ceria with ceria calcined at 873 K; (△) 1 wt.% Pd/ceria with ceria precipitated and calcined at 623 K; (●) 1 wt.% Pd/ceria with ceria calcined at 1073 K; (▲)1 wt.% Pd/ceria with ceria calcined at 1223 K.

Pd and Pt dispersion could change rather dramatically under WGS conditions at 673 K, even after less than 100 min. Additional evidence that ceria-supported Pd and Pt undergo sintering under these mild conditions was obtained by Shen et al. [37], who found even more dramatic increases in the size of Pd particles supported on ceria when the catalyst was used for methanol synthesis.

Finally, reduced ceria is known to form highly stable carbonates, and FTIR measurements performed under WGS conditions have shown that surface carbonates are present under reaction conditions [6]. At the present time, it is not clear how the presence of carbonates affects the reaction and whether formation of bulk carbonates might be involved in deactivation.

5. Promoter effects

In our attempts to find promoters to enhance WGS activity for ceria-supported precious metals, we found that the addition of Tb^{3+}, Gd^{3+}, Y^{3+}, Sm^{3+}, Pr^{3+}, Eu^{3+}, and Bi^{3+} to ceria had no effect on WGS rates [38]. The most interesting additives that did dramatically affect WGS rates were Fe and Mo. This is shown in Fig. 4, which is an Arrhenius plot of differential WGS rates for 1 wt.% Pd on ceria, Fe–ceria, and Mo–ceria. For these experiments, Fe and Mo were added to the ceria support by aqueous impregnation with $Fe(NO_3)_3 \cdot 9H_2O$ and $(NH_4)_2MoO_4$, respectively. After impregnation, the samples were dried at 383 K overnight and then calcined in air at 873 K for 4 h. Then the precious metal Pd was added to the oxide support by impregnating $Pd(NH_4)_4(NO_3)_2$. Following the impregnation, the samples were dried at 383 K and calcined at 873 K. In the case of Fe-containing samples, small quantities of Fe were found to increase WGS rates of Pd catalysts rather dramatically [39]. With the addition of Mo, WGS rates were found to decrease through poisoning of the redox properties of ceria [40]. Each of these two cases will be discussed individually.

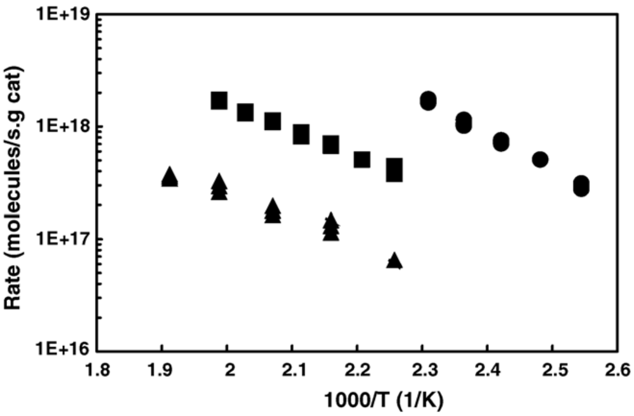

Fig. 4. Differential rates for the WGS reaction on 1 wt.% Pd/Mo–ceria (▲), 1 wt.%Pd/ceria (■) and 1 wt.% Pd/Fe–ceria (●) in 25 Torr CO and 25 Torr H_2O. The samples have an Fe:Ce molar ratio 0.05:1 and Mo:Ce molar ratio 0.05:1, respectively.

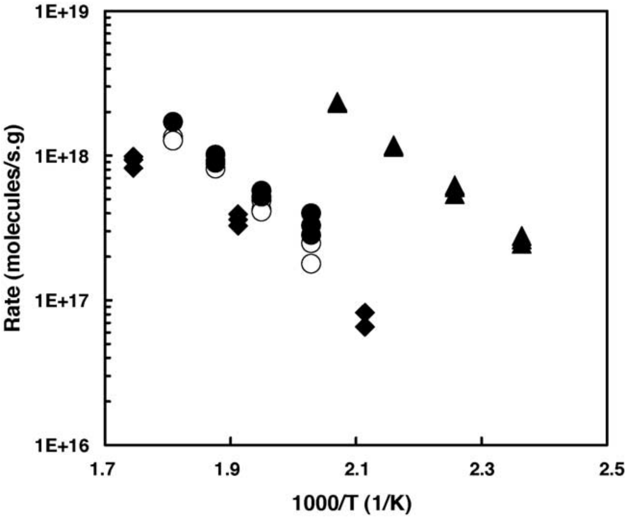

Fig. 5. Differential rates for the WGS reaction on Fe_2O_3 (◆), 1 wt.% Pd/Fe_2O_3 (▲), 1 wt.%Pt/Fe_2O_3 (●) and 1 wt.% Rh/Fe_2O_3 (○) in 25 Torr each of CO and H_2O.

5.1. Pd/Fe_2O_3–CeO_2

The strongest evidence for a direct, specific interaction between Pd and Fe, independent of ceria, comes from the rate data shown in Fig. 5. This Arrhenius plot shows WGS rates taken on Fe_2O_3 powder, before and after addition of 1 wt.% Pt, Pd, or Rh. The Fe_2O_3 sample was prepared by decomposing $Fe(NO_3)_3 \cdot 9H_2O$ at 873 K. Then the precious metals were added by wet impregnation using aqueous solutions of $Pd(NH_4)_4(NO_3)_2$, $Pt(NH_4)_4(NO_3)_2$, or $Rh(NO_3)_3$. Following the impregnation, the samples were dried at 383 K and then calcined at 873 K. The addition of Pt and Rh had no effect on the rates; by contrast, the addition of

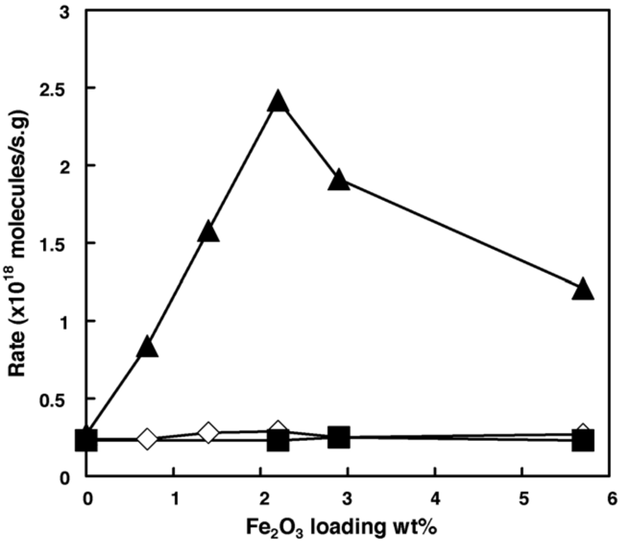

Fig. 6. A plot of differential, water-gas-shift rates as a function of Fe_2O_3 loading in 25 Torr CO and 25 Torr H_2O at 453 K on 1 wt.% Pd/Fe–ceria (▲), 1 wt.%Pt/Fe–ceria (◇) and 1 wt.%Rh/Fe–ceria (■).

1 wt.% Pd increased the rates by almost an order of magnitude. Fig. 6 shows the effect of adding different amounts of Fe to ceria-supported Pt, Pd, and Rh. The addition of various amounts of Fe to 1 wt.% Pt/ceria and 1 wt.% Rh/ceria gave rates that were indistinguishable from rates on the unpromoted catalysts; with 1 wt.% Pd/ceria, the enhancement was maximized by the addition of 2.2 wt.% Fe_2O_3. The enhancement associated with addition of Fe to Pd/ceria catalysts was obtained independent of the order in which Pd and Fe were added to the ceria. Based on the above observations, as well as XRD measurements [39], we suggested that the activity enhancement associated with Fe is due to formation of a Pd–Fe alloy.

That one might form an alloy with Pd and Fe under WGS conditions is extremely interesting, given that Fe normally exists as Fe_3O_4 under WGS conditions [41]. For the Fe–Pd alloy to form under the same conditions implies that formation of the alloy must provide an energetic driving force for reduction of Fe. Indeed, we suggest that there may be an equilibrium established between Fe_3O_4 and an Fe–Pd phase under WGS conditions. A similar proposal has been suggested for understanding the unique properties of Pd–Zn alloys for steam reforming of methanol [42]. A thermodynamic driving force for reducing Fe_3O_4 could explain the enhanced WGS activity that is observed for these catalysts. A key step in the redox mechanism proposed for precious metals on ceria involves oxidation of CO that is adsorbed on the metal by oxygen from the ceria. If Fe, by its intimate contact with Pd in the alloy, can enhance this transfer of oxygen from ceria to Pd, one should expect increased reaction rates for the alloy catalyst.

More work is obviously required to understand the Pd–Fe catalyst and the reasons for rate enhancements more completely; however, the large enhancement observed with the addition of Fe certainly make this an attractive direction for further investigation. For purposes of the discussion in this paper, it is also important to recognize that idea of examining Fe dopants was driven by the hypothesis of a redox mechanism for the WGS reaction.

5.2. Pd/MoO_3–CeO_2

Mo addition to Pd/ceria catalysts is interesting in that it is a surprisingly effective poison for the WGS reaction [40]. When varying levels of MoO_x were added to the surface of ceria in a series of Pd/ceria catalysts, rates were found to decrease linearly with Mo coverage, with loss of 90% of the activity upon addition of 1.8 Mo/nm^2. Furthermore, there was a direct correspondence between the loss in WGS activity and the loss of activity for 2-propanol dehydration in temperature-programmed desorption (TPD). In the absence of MoO_x, desorption of 2-propanol led to the formation of significant amounts of propene and water. Addition of MoO_x decreased the fraction of the 2-propanol that reacted, with addition of 1.8 Mo/nm^2 causing essentially all of the 2-propanol to desorb intact. The correspondence between the WGS rates and the 2-propanol TPD results is shown in Fig. 7. Finally CO–O_2 pulse measurements suggested that the Mo-containing surface is harder to reduce than pure ceria [40].

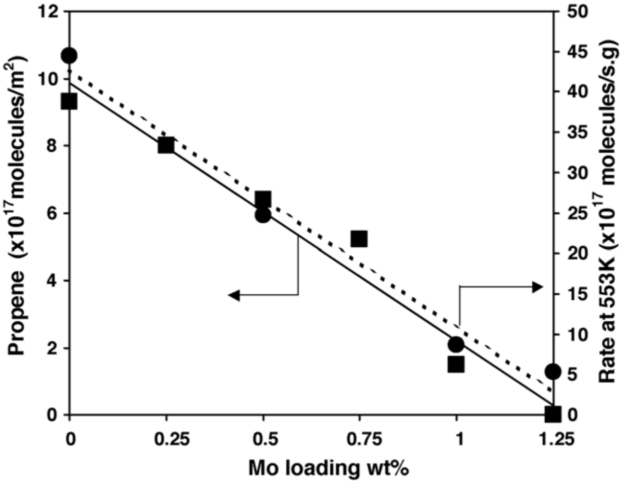

Fig. 7. WGS reaction rates and propene production from TPD-TGA is shown as a function of Mo loading. The WGS reaction rates at 553 K for different samples are shown as the circles, and the propene production in the temperature range 500 K–625 K from the 2-propanol TPD are shown as squares.

It is instructive to consider that the surface concentration of Mo^{6+} for the (1 0 0) surface of MoO_3 is 4.9 Mo/nm^2 based on crystallographic information. A similar value was obtained by Dong et al. for an MoO_3 monolayer on ceria [43]. Based on these values, the MoO_3 in our study is probably not poisoning the ceria surface by a simple blocking mechanism that makes the ceria surface inaccessible. However, 1.8 Mo/nm^2 is a sufficiently high coverage that, if the Mo^{6+} is evenly dispersed over the ceria surface, most of the surface O^{2-} ions could be associated with a Ce^{4+} that neighbors a Mo^{6+}. This is shown by the a model in Fig. 8 of the CeO_2(1 0 0) surface with Mo at a coverage of 1.2 Mo/nm^2. As to how this low coverage of Mo deactivates the redox properties of ceria, one obvious difference between Mo^{6+} and Ce^{4+} is the charge of the ion. It is tempting to suggest that the more positive ion withdraws charge from Ce^{4+}, making the Ce–O bond stronger and decreasing the ease with which CeO_2 reduces. Based on the redox mechanism for WGS, a decreased reducibility for ceria will result in decreased rates.

Perhaps the most important message from the work with Mo addition is that ceria-based catalysts exhibit interesting WGS properties that can be greatly modified by processing conditions and the addition of surface dopants. While the present study focused on a dopant that poisoned catalytic activity, we believe the insights gained in this work may lead to new approaches that enhance reactivity. Our study shows that Mo affects the activity by blocking the surface redox ability of ceria.

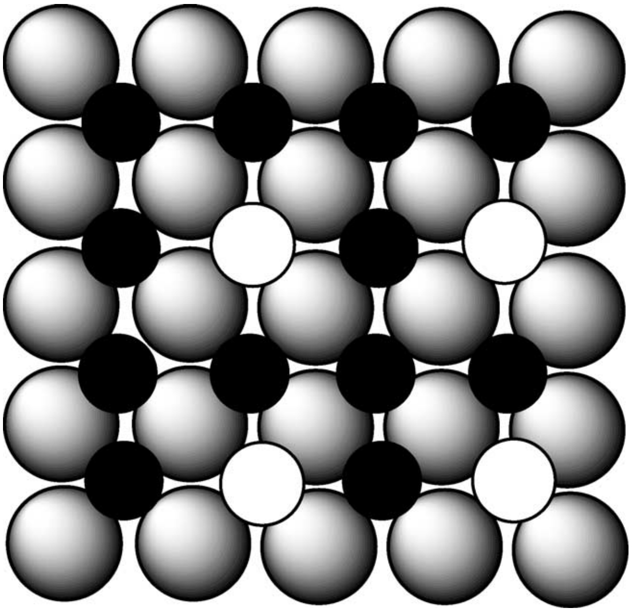

Fig. 8. Model of ceria (1 0 0), Mo coverage is 1.2 Mo/nm^2. The grey balls represent oxygen atoms, the black balls for cerium atoms and the white balls for molybdenum atoms.

6. Conclusions

Ceria-supported precious metals exhibit very interesting properties for use as water-gas-shift (WGS) catalysis with fuel processors for the fuel-cell applications. The activity of these materials can be modified significantly by pretreatment conditions and through the use of additives. However, surprisingly fast deactivation has been observed under WGS conditions. Given that the detailed mechanism by which these catalysts work remains controversial, more research is required to understand how to prepare and use these catalysts.

Acknowledgements

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