Studies of the water-gas-shift reaction on ceria-supported Pt, Pd, and Rh: implications for oxygen-storage properties

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Abstract

Steady-state, water-gas-shift kinetics were measured on model, ceria-supported, Pd, Pt, and Rh catalysts and compared to rates obtained on alumina-supported catalysts. When ceria was calcined at low temperatures prior to addition of the precious metal, the specific rates were found to be identical for each of the metals, with an activation energy of 11 ± 1 kcal/mol and reaction orders of zero and one for CO and H_2O respectively. For comparison, specific rates on Rh/alumina were at least two orders of magnitude lower. However, ceria structure strongly affected the results. When ceria was calcined to high temperatures to increase crystallite size, prior to the addition of Pd, specific rates were a factor of 50 lower at 515 K and the activation energy was found to be much higher, 21 ± 1 kcal/mol. By comparison with results from an earlier study of CO oxidation [17], we propose that water-gas shift on ceria-supported metals occurs primarily through a bifunctional mechanism in which CO adsorbed on the precious metal is oxidized by ceria, which in turn is oxidized by water. Deactivation of the catalyst following growth in the ceria crystallite size is due to the decreased reducibility of large ceria crystallites. The implications of these results for automotive, emission-control catalysts is discussed. © 1998 Elsevier Science B.V.

Keywords: Water-gas shift; CO oxidation; Oxygen storage; Ceria-supported catalyst; Platinum; Palladium; Rhodium

1. Introduction

Ceria is a crucial component of modern automotive, emission-control catalysts, primarily for its role in oxygen storage, the taking up of oxygen under oxidizing conditions and releasing oxygen under reducing conditions. However, it also promotes precious-metal catalysts for the water-gas-shift reaction [1–7]. Water-gas shift provides an additional pathway for oxidizing

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CO, especially under fuel-rich conditions; and it produces H_2, a very effective reductant for removing NO. In simulated-exhaust studies, water and H_2 have been shown to be important in promoting the performance of the catalyst [8]. Questions remain as to how ceria promotes the reaction.

On ceria-supported, precious-metal catalysts, temperature-programmed desorption of adsorbed CO has shown that CO adsorbed on the metals can react with oxygen from ceria [9–11]. This ceria-mediated process can also lead to large rate enhancements for steady-state CO oxidation [12–14]. The normal reac-

tion pathway on precious metals requires gas phase CO and O_2 to compete for adsorption sites. In excess CO, particularly at lower temperatures, this competition leads to a rate which is inverse-first-order in CO, with an activation energy equal to the heat of adsorption for CO [15], indicating that O_2 adsorption onto the metals is suppressed by the strong adsorption of CO. The ceria-mediated process avoids this suppression of the rates by having O_2 oxidize ceria which in turn oxidizes adsorbed CO. The rate expression for this second pathway is zeroth-order in CO in excess CO and has a much lower activation energy, ~14 kcal/mol compared to 26 kcal/mol [13]. Furthermore, the rates in the ceria-mediated regime are the same for Pt, Pd, and Rh [14] and depend on the size of the metal crystallites [13], findings that are consistent with the limiting step in the second pathway being the transfer of oxygen to the metal interface. Finally, it was shown that the oxidation and reduction of ceria is highly sensitive to ceria structure. When ceria is calcined to high temperatures to form large ceria crystallites, the ceria-mediated pathway for CO oxidation disappears, even when the metal crystallite size remains constant [16,17]. Forming a mixed oxide of ceria and zirconia stabilizes the support so that the second pathway is maintained to higher temperatures [17].

In addition to providing enhanced rates for CO oxidation, the ceria-mediated oxidation of CO appears to be related to the ability of the catalyst to utilize its oxygen storage component. The loss of the second rate process in CO oxidation following high-temperature treatment of the ceria corresponds well with the deactivation of the oxygen-storage component of the catalyst observed during catalyst aging [18]. Furthermore, the stabilization of oxygen-storage capacity by zirconia is paralleled by a similar stabilization of the second rate process for CO oxidation by zirconia [19]. Therefore, the transfer of oxygen from ceria to the precious metal, observed in CO oxidation, is likely to be an important part of oxygen management in the catalyst.

We investigated the water-gas-shift reaction because it seemed feasible that the reaction proceeds by a similar mechanism as that observed for the second pathway for CO oxidation on ceria-supported metals. Precious metals like Pt, Rh, and Pd are not, in general, good shift catalysts because they are not easily oxidized by water. In contrast, the oxidation of Ce_2O_3 by water to give hydrogen is thermodynamically favorable and has been observed in low-pressure adsorption studies [20]. Since metal-adsorbed CO can be oxidized by CeO_2, the overall reaction should occur in the following steps, each of which have been observed in adsorption measurements:

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

$$H_2O + Ce_2O_3 = 2CeO_2 + H_2 \tag{2}$$

$$CO_{ad} + 2CeO_2 = CO_2 + Ce_2O_3 + \sigma \tag{3}$$
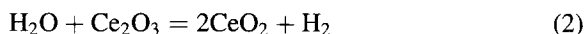
where σ represents adsorption sites on the metal. Similar redox mechanisms for water-gas shift have been proposed for ceria alone [21].

In this paper, we will show that the above mechanism is consistent with the measured reaction rates. Water-gas-shift rates are significantly higher over ceria-supported Pt, Pd, and Rh than over either ceria by itself or the alumina-supported metals. The rates are also zeroth-order in CO and first-order in water, as would be expected based on the mechanism. Similar to findings for CO oxidation, rates are essentially the same for ceria-supported Pt, Pd, and Rh [14]. Finally, as with the ceria-mediated process for CO oxidation, high-temperature calcination of the ceria leads to a loss in the rate enhancement. These results suggest that the water-gas-shift reaction, in addition to providing another mechanism for oxidizing CO, may play a role in the management of oxygen in three-way, emissions-control catalysis.

2. Experimental

Most of the model-catalyst samples examined in this study were used in earlier measurements of CO oxidation kinetics. Ceria films, ~10 μm in thickness, were prepared by spray pyrolysis of 0.1 M, aqueous solutions of $Ce(NO_3)_3$ onto nonporous, α-alumina wafers, held at ~530 K, using an air brush with an N_2 carrier [13]. The films were then calcined in air, at either 570 or 1670 K, and exhibited the fluorite structure in XRD. High-temperature calcination did increase the ceria crystallite size from 10 nm to 70 nm, as determined from XRD line broadening,

and changed the appearance of the films in SEM from rough and featureless to smooth with well-defined crystallites [16,17]. Alumina supports were prepared by simply calcining an Al foil at 770 K. Precious metals, either Pt, Pd, or Rh, were introduced by vapor deposition onto the oxide films, using methods described previously [13,14]. Each of the Pt and Rh catalysts were prepared with 5×10^{15} atoms/cm^2, while the Pd catalysts were prepared with 2×10^{15}/cm^2. Vapor deposition ensured that the precious metals were present only at the external surfaces of the oxides, which limited the potential problem of diffusion gradients affecting the rates. For the ceria deactivation studies, this method of catalyst preparation allowed the oxide to be calcined to high temperatures before the addition of the metal, so that the interfacial contact between the metal and ceria was essentially the same on the deactivated ceria. After the addition of the metals, no other pretreatments were performed prior to placing the samples into the reactor and measuring the rates.

Rates for the water-gas-shift reaction were measured by placing the catalysts into a 1/4-inch, quartz, tubular reactor. The total pressure in the reactor was maintained at one atmosphere, but the partial pressures of CO, water, and N$_2$ could be controlled by the flow rates to the reactor. Differential conditions were maintained at all times, with the conversions being typically less than 1% of the limiting reagent in all these studies. Rates were highly reproducible and remained constant over a period of several hours. Also, there was no hysteresis in the rates following changes in the partial pressures and no observable deactivation of the catalysts under reaction conditions. Water vapor was fed to the reactor by bubbling N$_2$ through deionized, distilled water. The CO fed to the reactor was first cleaned by passing it through an activated-carbon trap to remove carbonyls and through a packed bed of NaOH pellets to remove residual CO$_2$. CO and CO$_2$ compositions leaving the reactor were measured with an on-line gas chromatograph, equipped with a methanator and an FID detector. All reported rates have been normalized to the external surface area of the wafers.

Estimates of metal surface area, and therefore the average metal particle size, were obtained from absolute CO oxidation rates under pressure–temperature

conditions not influenced by the oxide, using specific rates from the (111) surfaces as references [15]. CO oxidation has been shown to be structure-insensitive, at least on Rh and Pd [22,23]. While the reaction is structure-sensitive on Pt for very small crystallites [24], the particle-size estimates obtained in our study for Pt are similar to that obtained for the other metals.

All specific rates reported in this paper were normalized using the external surface of the catalyst wafers. Since the external surface area is comparable to the precious-metal surface area for each of the supported-metal catalysts, this normalization provides a reasonable method for comparing the metal-containing catalysts. However, the alumina and ceria supports were porous. For example, in the case of ceria, it is reasonable to assume that the film has a surface area of approximately 12 m^2/g after calcination at the lower temperatures [16], so that the actual surface area of the 10 μm film is nearly 500 times the external surface area. Therefore, the actual specific rates reported in this paper for the oxide films in the absence of metal catalyst are too high, by a factor of 500 in the case of ceria.

3. Results

An Arrhenius plot with rates for each of the catalysts examined is shown in Fig. 1 and reaction orders and activation energies for each of the different catalysts are listed in Table 1. The rates in Fig. 1 were measured using partial pressures for CO and H$_2$O of 20 and 15 torr, respectively. Note, first, that the rates for Rh/alumina and alumina alone are identical. (For the alumina catalyst, the conversion changed in proportion to the amount of catalyst, so that these rates do not represent a baseline for the reactor.) The unexpectedly high specific rates on alumina are due in part to underestimating the surface area of the oxide film and, probably, to impurities in the foil. The fact that identical rates were obtained for Rh/alumina as for alumina is consistent with previous observations that Rh is a very poor catalyst for the water-gas-shift reaction. Extrapolating rates for Rh/alumina from the literature to our reaction conditions suggests that specific rates for Rh at 573 K should be a factor of 4 lower than reported here [25]. Therefore, the rates on
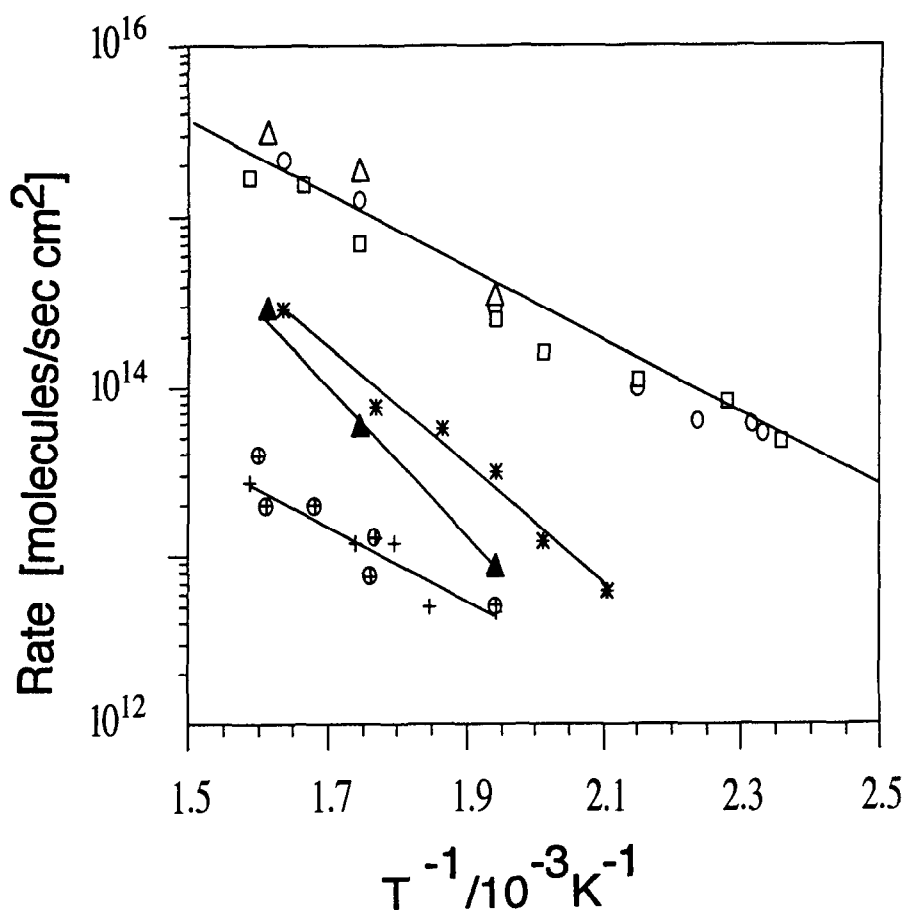
Fig. 1. An Arrhenius plot for the water-gas-shift rates on alumina (+), ceria(*), $5 \times 10^{15} Rh/cm^2$ on alumina (⊕), $2 \times 10^{15} Pd/cm^2$ on ceria (calcined at 570 K) (△), $2 \times 10^{15} Pd/cm^2$ on ceria (1670 K) (▲), $5 \times 10^{15} Rh/cm^2$ on ceria(570 K) (○), and $5 \times 10^{15} Pt/cm^2$ on ceria (570 K) (□). The CO and H_2O partial pressures were 20 and 15 torr, respectively.

Table 1
Summary of reaction orders and activation energies for the water-gas-shift reaction

	E. [a] (kcal/mol)	H_2O order [b]	CO order [c]
Ceria	15 ± 1	*	0.3
Rh/ceria	11 ± 1	1	0
Pt/ceria	11 ± 1	1	0
Pd/ceria (Low-Temp)	11 ± 1	*	0
Pd/ceria (High-Temp)	21 ± 1	*	0

[a] CO and H_2O pressures were 20 and 15 torr, respectively.
[b] Measured at 573 K using P_{CO} of 20 torr.
[c] Measured at 573 K using P_{H_2O} of 15 torr.

Rh were too low to measure in our apparatus, with our alumina support. While water-gas-shift rates for Pt and Pd are reported to be somewhat higher than that for Rh [25], we did not investigate the alumina-supported catalysts further.

The specific rates for ceria in Fig. 1 are approximately 1000 times higher than estimates based on literature data [26]. However, since the surface areas of our films are likely 500 times higher than the external surface area used in normalizing the rates, the agreement is actually reasonably good. The activation energy, 15 ± 1 kcal/mol, also agrees well with previous work, as does the reaction order for CO

which was determined to be 0.3. The most important point for the purposes of this study is that the rates on pure ceria are *much* lower than those of the ceria-supported metals, particularly when surface areas are properly normalized.

Rates on Rh/ceria, with $5 \times 10^{15} Rh/cm^2$, were approximately one order of magnitude higher than those on ceria alone and two orders of magnitude higher than the rates for our Rh/alumina catalyst over the temperature range investigated. Based on CO-oxidation rates on this Rh/ceria catalyst under conditions not affected by ceria [13], the Rh dispersion was estimated to be 0.36. Since the Rh surface area is so small, the enhancement over the rates reported for ceria alone are remarkable, given the low activity of Rh/alumina. The rates for Rh/ceria at 573 K are again in good agreement with reports from the literature [3], although we found an activation energy of 11 ± 1 kcal/mol, which is higher than the value reported previously.

More interesting is the fact that the Rh/ceria and Pt/ceria catalysts, both having 5×10^{15} metal atoms/cm^2, exhibited essentially identical rates. Rates were also essentially identical for the Pd/ceria catalyst containing 2×10^{15} Pd/cm^2, when the low-temperature ceria was used. (It should be noted that rates for ceria-mediated, CO oxidation with Rh were shown to depend only weakly on the metal coverage, so that changing the Pd coverage from $2 \times 10^{15}/cm^2$ to $5 \times 10^{15}/cm^2$ would not significantly change the rates [13].) The reaction orders for CO and H$_2$O were zero and one, respectively, on each of the three catalysts. Previously, we had shown that CO oxidation rates for each of the ceria-supported metals were identical in the ceria-mediated regime, with reaction orders of zero for CO and ~0.4 for O$_2$, and an activation energy of 14 ± 1 kcal/mol [14]. The similarity between the results for CO oxidation and water-gas shift are therefore striking. Furthermore, the results for both reactions can be understood by assuming that CO is oxidized indirectly, using oxygen from ceria, with the ceria then reoxidized by either H$_2$O or O$_2$, as discussed in the mechanism shown in the Introduction.

Fig. 1 also shows that calcining ceria to 1670 K prior to Pd deposition leads to a catalyst which is significantly less active, by more than a factor of 50 at 515 K, even though the Pd dispersions were similar on

both materials [17]. Furthermore, the activation energy on the catalyst prepared from ceria calcined to high temperatures was 21 ± 1 kcal/mol, similar to that reported for Pd/alumina in the literature [25] and much higher than the 11 kcal/mol found on the low-temperature ceria catalysts. Comparing the absolute rates for this Pd catalyst to literature values for Pd/alumina, the Pd/ceria catalyst still has an activity ~20 times higher, suggesting that ceria may still exhibit a promotional effect, although similar differences in activity are observed between silica- and alumina-supported catalysts [25].

The reaction kinetics for these two Pd catalysts are examined more closely in Fig. 2, which shows rates as a function of CO pressure for the water-gas-shift reaction at 515 K, with a H$_2$O pressure of 15 torr. Previous results for CO oxidation on the same two catalysts, with a fixed O$_2$ pressure of 0.3 torr, are shown for comparison [17]. CO oxidation rates over Pd on the low-temperature ceria are zeroth-order in CO and are much higher than would be observed for Pd/alumina, at least for high CO pressures. In contrast, the rates for Pd on the high-temperature ceria exhibit a reaction order of -1 for CO and the absolute rates are identical to what would be observed for Pd/alumina with a similar Pd dispersion. Following high-temperature calcination, the ceria has essentially no effect on the rates. The water-gas-shift rates again parallel the CO oxidation rates. While the CO dependence is approximately zeroth order on both catalysts, rates on the catalyst with low-temperature ceria are a factor of ~50 lower. Clearly, the structure of the underlying ceria strongly affects the activity of the catalyst for water-gas shift.

A comparison of the absolute rates for CO oxidation and water-gas shift for Pd on the low-temperature ceria are also of interest. The comparison in Fig. 2 is biased due to the much higher water pressure, 15 torr compared to 0.3 torr; but partial pressures of H$_2$O will also be much higher in the automotive exhaust streams. The rates for water-gas shift clearly approach that obtained for CO oxidation at 515 K. Assuming that the processes for the two rates are, indeed, related, it is likely that higher pressures of H$_2$O are required because H$_2$O is less effective for the oxidation of reduced ceria. The activation energy for the water-gas shift (11 kcal/mol) is similar to that for the ceria-mediated, CO-oxidation reaction
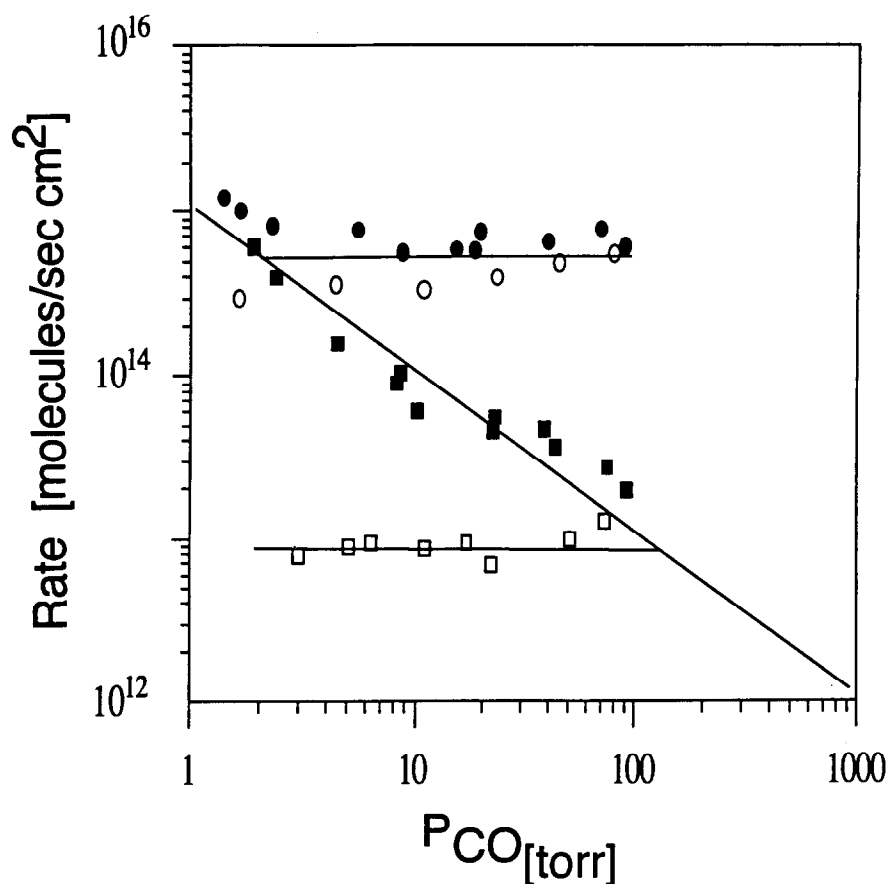
Fig. 2. Steady-state rates for CO oxidation (filled points) and water-gas shift (open points) as a function of the CO partial pressures at 515 K for 2×10^{15} Pd/cm^2 on ceria. The partial pressure of H_2O for water-gas-shift rates was 15 torr and the partial pressure of O_2 was 0.3 torr for CO oxidation. Circles correspond to ceria calcined at 570 K and squares to ceria calcined at 1670 K prior to Pd deposition.

(14 kcal/mol), but not identical, indicating that the rates are limited, in part, by the oxidation rate of ceria.

In interpreting these results, it is important to notice that the temperatures used in our study are much lower than typical automotive exhaust conditions. At higher temperatures, the dominant mechanism for CO oxidation will be the normal, metal-catalyzed process which has an activation energy of 26 kcal/mol. However, the rate processes involved in oxygen storage require oxygen transfer to and from the ceria. Since rates for ceria-mediated, CO oxidation and water-gas shift are similar, with similar activation energies, H_2O may play an equally important role to O_2 as an oxidant in these processes.

4. Discussion

The water-gas-shift rate measurements on the ceria-supported metals are consistent with the mechanism described in the Introduction, in which CO adsorbed on the metal is oxidized by ceria, which in turn is oxidized by water. In addition to the fact that rates on the ceria-supported metals are much higher than for either ceria or the metals individually, the similarities between CO oxidation and water-gas shift on these catalysts, especially the effect of calcination temperature for ceria, are apparent. Other mechanistic studies of water-gas shift on supported precious metals have also reported the bifunctional nature of this reaction and other key features of the reaction, even for non-

reducible supports like alumina and silica [25]. However, most studies also invoke formate species in additional intermediate steps [2,3,25]. These species probably play a key role on nonreducible supports, and may well be present on our catalysts as well.

We had previously shown that high-temperature calcination of the ceria, prior to the addition of the precious metal, eliminates the ceria-mediated process for CO oxidation for ceria-supported metals [16,17]. Temperature-programmed-desorption measurements of CO adsorbed on Rh deposited onto ceria also show that CO_2 formation is eliminated by high-temperature calcination of ceria [16]. Apparently, large ceria crystallites are more difficult to reduce. The water-gas-shift kinetics on the two Pd/ceria catalysts, both of which have a similar Pd dispersion, and therefore interfacial contact between the Pd and the ceria film, show this same effect.

Water is likely to play an important role in oxygen storage, especially since it will be present in much higher quantities than O_2 in automotive exhausts. Both the ceria-mediated processes for CO oxidation and water-gas shift appear to be controlled by the same two steps: the transfer of oxygen from ceria to the metal interface and the rate of reoxidation of the ceria. The two reactions are the same except that ceria is oxidized by O_2 in CO oxidation and H_2O in water-gas shift. At the higher temperatures used in real exhaust catalysts, the normal CO-oxidation process will dominate under stoichiometric or lean conditions. However, water may well be important for the control of the oxidation state of ceria and, therefore, play a key role in the management of oxygen storage.

The importance of both oxygen storage and water-gas shift in automotive catalysts derives from their contributions to the overall reaction which occurs during transient operation about stoichiometry. It has been established, for example, that both oxygen storage and water-gas shift contribute substantially to the rich-spike conversion of CO [5,6]. What is not as clear, however, is the relative degree to which water and oxygen are involved in restoring the oxygen level in ceria (or, in the case of water, maintaining it under rich conditions).

Steady-state, water-gas-shift kinetics appear to provide a convenient method for characterizing thermal deactivation of ceria due to catalyst aging. Since the rates on the metals and ceria separately are so low, the effect of the metal–ceria interactions on the water-gas-shift reaction rate may provide a more sensitive indicator of the ability of ceria to provide oxygen to the metal than in the case of ceria-mediated CO oxidation, discussed in a previous publication [17].

5. Summary

Water-gas-shift kinetics on ceria-supported, precious metals suggest that reaction occurs by a mechanism in which metal-adsorbed CO is oxidized by ceria, which in turn is oxidized by water. Pt, Pd, and Rh are equally effective as catalysts. Since the redox properties of ceria depend on ceria structure, growth of ceria crystallites due to high-temperature calcination strongly deactivates ceria-supported catalysts for water-gas shift.

Acknowledgements

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