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Keywords
Water-gas shift, Pd, CeO2, Fe2O3, Oxygen transfer

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The Effect of Fe and Other Promoters on the Activity of Pd/Ceria for the Water-Gas Shift Reaction

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Abstract

The effect of adding oxide promoters, at monolayer coverages, to Pd/ceria catalysts was studied for the water-gas-shift reaction in 25 torr each of H_2O and CO under differential conditions. Oxides of Fe, Tb, Gd, Y, Sn, Sm, Pr, Eu, Bi, Cr, V, Pb, and Mo were added to ceria by wet impregnation of aqueous salts and calcined to 873 K prior to addition of 1 wt% Pd. While most of the oxides had a negligible effect on the water-gas-shift rates, rates on the Fe-promoted sample were 8 times higher than on the unpromoted Pd/ceria at 473 K, while rates on the Mo- and Pb-promoted cerias were significantly lower than on pure Pd/ceria. By varying the Fe loading, it was found that the maximum catalytic activity was achieved at the monolayer coverage. Addition of Fe in bulk ceria through sol-gel and preparation of Fe_2O_3-CeO_2 physical mixtures had no effect on the catalytic activity.

Key Words: Water-gas shift, Pd, CeO_2, Fe_2O_3, oxygen transfer

Introduction

Commercial, Cu/ZnO-based, water-gas-shift (WGS) catalysts are not always applicable for fuel processors because they require special activation procedures, are pyrophoric, and are intolerant of poisons, condensation, and oxidation [1,2]. By contrast, ceria-supported precious metals (PM) are much less sensitive and can show even higher WGS activities than the Cu/ZnO catalysts under conditions of interest for fuel processors, such as low CO pressures [1-6]. The high activity that PM-ceria catalysts show can be explained by the following mechanism:

$$CO + \sigma \rightarrow CO_{ad} \quad (1)$$

$$H_2O + Ce_2O_3 \rightarrow 2\,CeO_2 + H_2 \quad (2)$$

$$CO_{ad} + 2\,CeO_2 \rightarrow CO_2 + Ce_2O_3 + \sigma \quad (3)$$

According to this picture, CO adsorbs on the precious-metal sites (σ) and adsorbed CO is oxidized with oxygen from the ceria; the reduced ceria is then re-oxidized by H_2O. Support for this mechanism comes from a number of observations. First, the reaction order in CO is zeroth-order, as expected for strong adsorption on precious metals [6]. Second, high-temperature calcination of ceria, which is known to cause irreversible loss in the reducibility of ceria [7], also severely poisons specific rates for the WGS reaction [3]. Third, WGS rates for ceria-supported Pt, Pd, and Rh catalysts are essentially identical [3], as should be expected if re-oxidation of ceria or oxygen transfer from ceria is rate limiting. Finally, oxygen transfer from ceria to Pd has been observed directly in spectroscopic measurements [8].

Since the transfer of oxygen from CeO_2 to a precious metal must be endothermic [9], there must be a barrier to the oxygen-transfer reaction. Furthermore, it is reasonable to assume that one might lower the height of this barrier by allowing the transfer to occur in two steps, as might occur when a third component is inserted between the ceria and the precious metal. Effectively, oxygen would be transferred from ceria to the additive and from the additive to the precious metal. According to Xie, et al [10], monolayer oxide phases should be stable on ceria. In the present work, we have tested this hypothesis by preparing a series of Pd/ceria catalysts in which the ceria surface has been modified by metal-oxide monolayers and then measuring the WGS activities of these modified samples.

Experimental

Most of the catalysts used in this study were prepared from ceria powder that was synthesized by decomposition of $Ce(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99.5%) in air at 873 K [11]. The

ceria prepared in this way with a specific surface area of 37 m^2/g and its catalytic properties have been well characterized in previous work. This support was then modified by aqueous impregnation with one of the following: $Fe(NO_3)_3 \bullet 9H_2O$ (Aldrich, 98+%), $Tb(NO_3)_3 \bullet xH_2O$ (Alfa Aesar, 99.9%), $Gd(NO_3)_3 \bullet xH_2O$ (Alfa Aesar, 99.9%), $Y(NO_3)_3 \bullet 6H_2O$ (Alfa Aesar, 99.9%), SnC_2O_4 (Aldrich, 98%), $Sm(NO_3)_3 \bullet xH_2O$ (Alfa Aesar, 99.99%), $Pr(NO_3)_3 \bullet xH_2O$ (Alfa Aesar, 99.9%), $Eu(NO_3)_3 \bullet xH_2O$ (Alfa Aesar, 99.99%), $Bi(NO_3)_3 \bullet 5H_2O$ (Aldrich, 98%), $Cr(NO_3)_3 \bullet 9H_2O$ (J. T. Baker, 99.6%), NH_4VO_3 (Sigma), $Pb(NO_3)_2$ (Fischer Scientific, 100%) or $(NH_4)_6Mo_7O_{24}$ (Alfa Aesar, 99.999%). In all cases, the M:Ce molar ratio was fixed at 0.05:1, which corresponds approximately to a monolayer coverage for this particular ceria powder. After impregnation with the second oxide, the materials were dried at 383 K overnight and then calcined at 873 K in air for 6 h.

Because the Fe_2O_3-promoted catalyst showed enhanced activity, several additional supports based on mixed oxides of Fe and Ce were prepared. In addition to preparing materials with higher and lower Fe contents by aqueous impregnation, we also prepared mixed oxides using sol-gel methods and by physically mixing CeO_2 and Fe_2O_3 powders. Using the sol-gel method, we prepared an aqueous solution of $Fe(NO_3)_3$ and $Ce(NO_3)_3$, having an Fe:Ce ratio of 0.05, dried it at 383 K, and then calcined it at 873 K. With physical mixing, CeO_2 and Fe_2O_3 powders were mixed and ground together for 1 h, followed by calcination at 873 K. For clarification, these two supports are denoted Fe-ceria(sg) and Fe-ceria(pm). The Fe_2O_3 powder, by itself, was found to have a surface area of 25 m^2/g, which is comparable to the specific surface area of the ceria.

After preparing the support, Pd was added by wet impregnation using aqueous solutions of $Pd(NH_3)_4(NO_3)_2$ (Aldrich, 99.99%). The Pd content of the final catalysts was 1 wt% in all cases. Following impregnation, the catalysts were dried at 383 K and calcined at 873 K. The Pd surface areas were determined by CO adsorption at room temperature, using a procedure that has been described in detail elsewhere [12]. Because CO on Pd can react with oxidized ceria at near room temperature and because the CO_2 that is formed can then adsorb on reduced ceria [13], it was necessary to rigorously reduce the catalysts in H_2 at 673 K, prior to the room-temperature exposure of the catalysts to CO. To ensure that CO adsorption was associated with Pd and not the oxide promoters, we measured CO uptakes on the mixed-oxide supports in the absence of Pd and observed no measurable adsorption of CO. In determining the Pd surface area, we assumed

an adsorption stoichiometry of one CO molecule per surface Pd [14] and $5x10^{18}$ CO molecules/m^2 Pd.

Kinetic measurements for the WGS reaction were performed in a ¼-inch, Pyrex glass, tubular reactor using approximately 0.10 g of catalyst. Water was introduced by saturation of a He carrier gas flowing through a de-ionized water saturator. While the reactor pressure was always atmospheric, the partial pressures of CO, H_2O and He were controlled by adjusting the relative flow rates of each component. All of the reaction measurements in this study were collected with partial pressures for CO and H_2O of 25 torr. For all rate measurements, the conversions of CO and H_2O were kept well below 10%, so that differential conditions could be assumed. Before analyzing the products, we always allowed the reaction to run for at least 30 min to avoid potential transients associated with catalyst conditioning. To ensure that the results were reproducible, the rates at each point were measured at least three times. The concentration of the effluent from the reactor was determined using an on-line gas chromatograph, SRI8610C, equipped with a Hayesep Q column and a TCD detector.

Result and Discussion

In Fig. 1, we show the Arrhenius plot of the WGS rates for several selected catalysts to demonstrate the effect oxide modifiers can have. For comparison purposes, data are shown for a commercial-type, Cu/ZnO catalyst (Süd-Chemie, T-2650) and pure ceria. In a previous publication [13], we reported that rates for 1 wt% Pd/silica was even less active than ceria. While the Pd/ceria catalyst was not as active as the commercial-type Cu/ZnO catalyst for the particular reaction conditions that we used in this study, it has been shown that ceria-supported precious metals can be much more active than Cu/ZnO catalysts under some conditions [1]. Obviously, the rates observed on Pd/ceria are much higher than those on either pure ceria or 1 wt% Pd on silica, demonstrating the importance of having the precious metal in contact with ceria. Of more interest, modification of the ceria through the addition a monolayer (2 wt%) of Fe_2O_3 prior the addition of Pd increased rates by a factor of ~8 at 473 K, while the addition of a monolayer (2 wt%) of MoO_3 decreased rates by more than a factor of 5 under these same conditions. Clearly, changes this large are significant and worth investigating.

Table 1 summarizes the WGS rate data for all of the catalysts prepared with 1 wt% Pd on the ceria powders prepared by impregnation with 1 monolayer of the modifier. The rates and activation energies reported at 473 K were all measured in 25 torr of CO and 25 torr of H_2O

under differential reaction conditions. With the exception of Fe_2O_3, MoO_3, and PbO, the additives had a minimal effect on the rates. The rates at 473 K for the other oxides differed by less than a factor of 2 from the unmodified Pd/ceria and the activation energies were 43±5 kJ/mol. Both MoO_3 and PbO decreased reaction rates at 473 K. With MoO_3, the activation energy remained the same, suggesting that the rate-limiting step was unaffected and that the lower rates were due to a decrease in the active surface area. This kind of effect might be expected if the MoO_3-covered surface was inactive for the WGS reaction but part of the surface remained uncovered. With PbO, the activation energy decreased significantly to 25 kJ/mol; but the rates were very low at all temperatures.

For the Fe_2O_3-promoted Pd/ceria, both the rate and the activation energy increased significantly. Therefore, we investigated this system more thoroughly, with selected data shown in Fig. 2 and summarized in Table 2. We consider first the WGS rates on pure Fe_2O_3, 1 wt% Pd on Fe_2O_3, and 2 wt% Fe_2O_3 on ceria. The Fe_2O_3-impregnated ceria is not significantly more active than pure ceria; and pure Fe_2O_3, while more active than ceria, is significantly less active than Pd/ceria. It is interesting that 1 wt% Pd/Fe_2O_3 is reasonably active for the WGS reaction. While we did not investigate this in detail, it seems likely that the mechanistic steps listed in the Introduction for the WGS reaction over Pd/ceria could also apply to Pd/Fe_2O_3, since Fe can also exist in multiple oxidation states. Furthermore, precedence exists for the idea that oxygen transfer can occur from Fe_2O_3 to a supported precious metal. Fe_2O_3-promoted Pt/alumina catalysts are active for the selective oxidation of CO in H_2 and an oxygen-transfer mechanism has been invoked to explain the role of Fe in this catalysts [15].

Also in Fig. 2 are WGS rates for 1 wt% Pd supported on Fe_2O_3-impregnated ceria having 1, 2 and 10 wt.% Fe_2O_3. These Fe_2O_3 coverages correspond to 0.5, 1 and 5 monolayers of Fe_2O_3 on the surface of the ceria. Table 2 shows additional results for catalysts prepared with ceria supports having 0.5 and 4 wt% Fe_2O_3. The catalysts with Pd on the Fe_2O_3-impregnated ceria were all more active than Pd/ceria or Pd/Fe_2O_3. Furthermore, the catalysts prepared with approximately one monolayer of Fe_2O_3, the 2-wt% and 4-wt% samples, were considerably more active than the other samples. Those catalysts having a significant excess of Fe_2O_3 over the monolayer coverage and those without sufficient Fe_2O_3 to form a monolayer were less active. Finally, it is noteworthy that the activation energies for the catalysts prepared with Fe-impregnated ceria were all somewhat higher than were observed on Pd/ceria.

Because oxygen diffusivity in ceria is affected by dopants [16], it is common practice to add dopants to ceria catalysts, even though at least one study has shown that dopants can significantly *decrease* the oxidation activity of ceria [17]. To test whether Fe might act as a dopant in enhancing ceria, we examined WGS rates for 1 wt% Pd on Fe-ceria(sg) and Fe-ceria(pm). Fe-ceria(sg) was prepared by sol-gel methods and should have Fe present in the bulk of the ceria, while Fe-ceria(pm) was a physical mixture that was prepared to provide a reference. The rates and activation energies for these samples were almost indistinguishable from that on the Pd/ceria catalyst without Fe. This provides additional evidence that Fe_2O_3 must be on the surface of the ceria, in contact with the Pd, in order to provide rate enhancements.

Finally, since WGS rates for Pd/ceria catalysts have been shown to increase with the Pd dispersion [12], it is possible that the enhancement observed for the catalysts prepared with Fe_2O_3-impregnated ceria could be caused by an increased dispersion. Therefore, the Pd dispersion was measured for 1 wt% Pd supported on ceria, on 2 wt% Fe_2O_3-ceria, and on 2 wt% MoO_3-ceria. The dispersions for Pd on ceria and on 2 wt% Fe_2O_3-ceria were found to be very similar, 0.25 and 0.20 respectively. Enhanced activity can therefore not be due to enhanced dispersion. However, with Pd on the MoO_3-ceria, the apparent dispersion measured by CO adsorption was only 0.02. Since it seems unlikely that the Pd particles would be so large as to give a dispersion this low, Pd must be covered by MoO_3 or have reacted with MoO_3 following the pretreatment conditions that we used. Indeed, Susic, et al [18] demonstrated that Pd may react with MoO_3 in the presence of H_2 to form Pd/H_xMoO_3 bronze.

The results of our study clearly demonstrate that surface promotion of ceria can strongly affect WGS activity for supported Pd catalysts. Considering the WGS mechanism from the Introduction, the role of the promoters must be to affect the barrier for oxygen transfer from ceria to the Pd. Based on data from bulk compounds, the enthalpy change required to go from CeO_2 to Ce_2O_3 is 760 kJ/mol of O_2, the enthalpy change required to go from Fe_2O_3 to Fe_3O_4 is 460 kJ/mol of O_2, and the enthalpy change for PdO to Pd is 176 kJ/mol. While bulk data may not directly apply to surface species and small ceria crystallites [9], the calculated energies suggest that the Fe_2O_3 film may lower the barrier for oxygen transfer by providing an intermediate phase between CeO_2 and Pd.

Whatever mechanism is responsible for the enhanced rates, it is clear that the activity of ceria-supported, precious metal catalysts can be enhanced significantly through the addition of

surface promoters. We believe that this approach may be generally applicable to other catalyst systems as well.

Summary

We have demonstrated that the water-gas-shift activity of Pd/ceria catalysts can be enhanced by the addition of monolayer coverages of Fe_2O_3 on the ceria. The addition of monolayer oxides of Tb, Gd, Y, Sn, Sm, Pr, Eu, Bi, Cr, and V to ceria had minimal effect on the rates, while the addition of oxides of Pb, and Mo caused deactivation of Pd/ceria catalysts.

Acknowledgement

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Figure Captions

Fig.1 Differential rates for the WGS reaction on Ceria (♦), Pd/Mo-Ceria (●), Pd/Ceria (■), Pd/Fe-Ceria (○), and Cu/ZnO (▲).

Fig. 2. Differential rates for the WGS reaction on Fe(2 wt%)-Ceria (●), Fe_2O_3 (▲), Pd/Ceria (■), Pd/Fe_2O_3 (♦), Pd/Fe(10 wt%)-Ceria (◊), Pd/Fe(1 wt%)-Ceria (Δ), and Pd/ Fe(2 wt%)-Ceria (○).

Table 1. Differential Rates and Activation Energies for the Water-Gas-Shift Reaction on Promoted Pd/Ceria Catalysts.

Catalyst[a]	Rate at 473 K (x 10^{18} molecules/s.g cat)	Activation Energy (kJ/mol)
Pd/ceria	1.12	45
Pd/Fe-ceria[b]	9.36	60
Pd/Tb-ceria	1.81	46
Pd/Gd-ceria	1.56	46
Pd/Y-ceria	1.51	44
Pd/Sn-ceria	1.33	40
Pd/Sm-ceria	1.33	41
Pd/Pr-ceria	1.20	44
Pd/Eu-ceria	1.17	46
Pd/Bi-ceria	0.84	38
Pd/Cr-ceria	0.78	41
Pd/V-ceria	0.66	46
Pd/Pb-ceria	0.50	25
Pd/Mo-ceria	0.16	41

[a.] Pd loading was 1 wt%, while the M:Ce molar ratio was maintained at 0.05:1.
[b.] This rate was extrapolated from rates taken at lower temperatures where rates were differential.

Table 2. Differential rates and activation energies for the WGS reaction on Pd/ceria catalysts modified by Fe_2O_3.

Catalyst	Rate at 423 K (x 10^{18} molecules/s·g cat)	Activation Energy (kJ/mol)
Pd/ceria	0.30*	45
Pd/Fe-ceria, 0.5 wt % Fe_2O_3	0.84	55
Pd/Fe-ceria, 1 wt % Fe_2O_3	0.91	57
Pd/Fe-ceria, 2 wt % Fe_2O_3	2.21	60
Pd/Fe-ceria, 4 wt % Fe_2O_3	1.90	59
Pd/Fe-ceria, 10 wt % Fe_2O_3	0.34	70
Pd/Fe-ceria(sg), 2 wt % Fe_2O_3	0.38	44
Pd/Fe-ceria(pm), 2 wt % Fe_2O_3	0.39	46
Pd/Fe_2O_3	0.24	63

* extrapolated from high-temperature data.

Fig 1

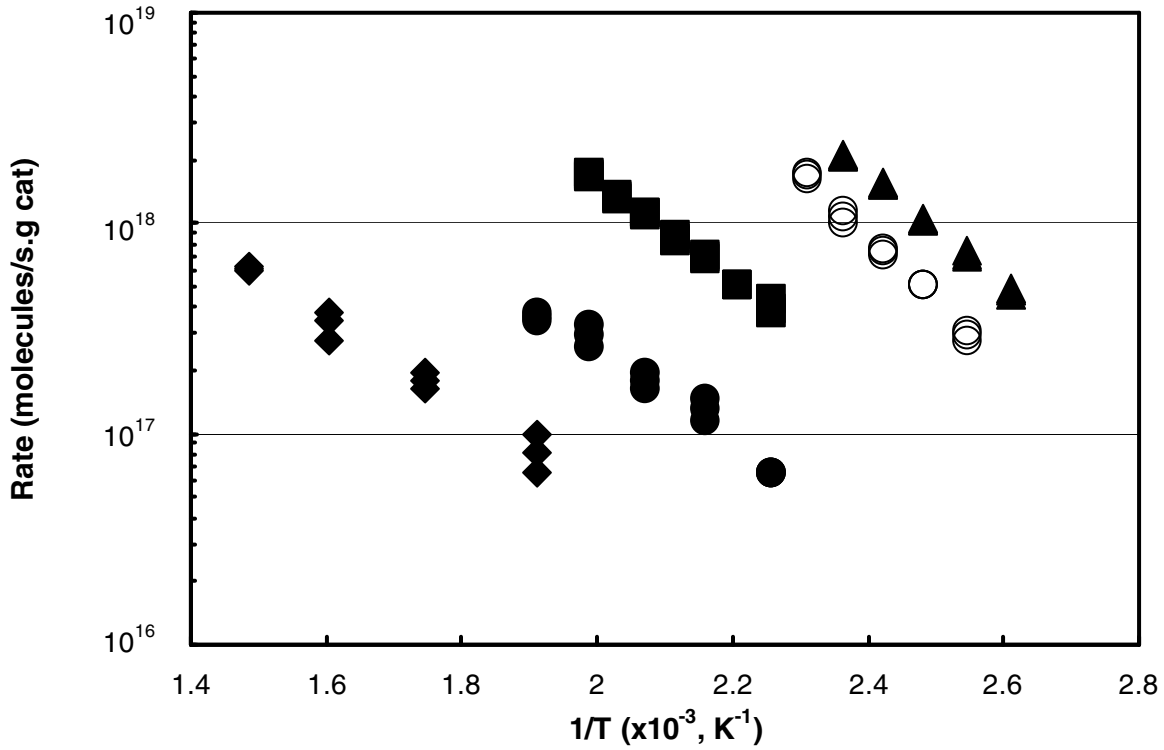
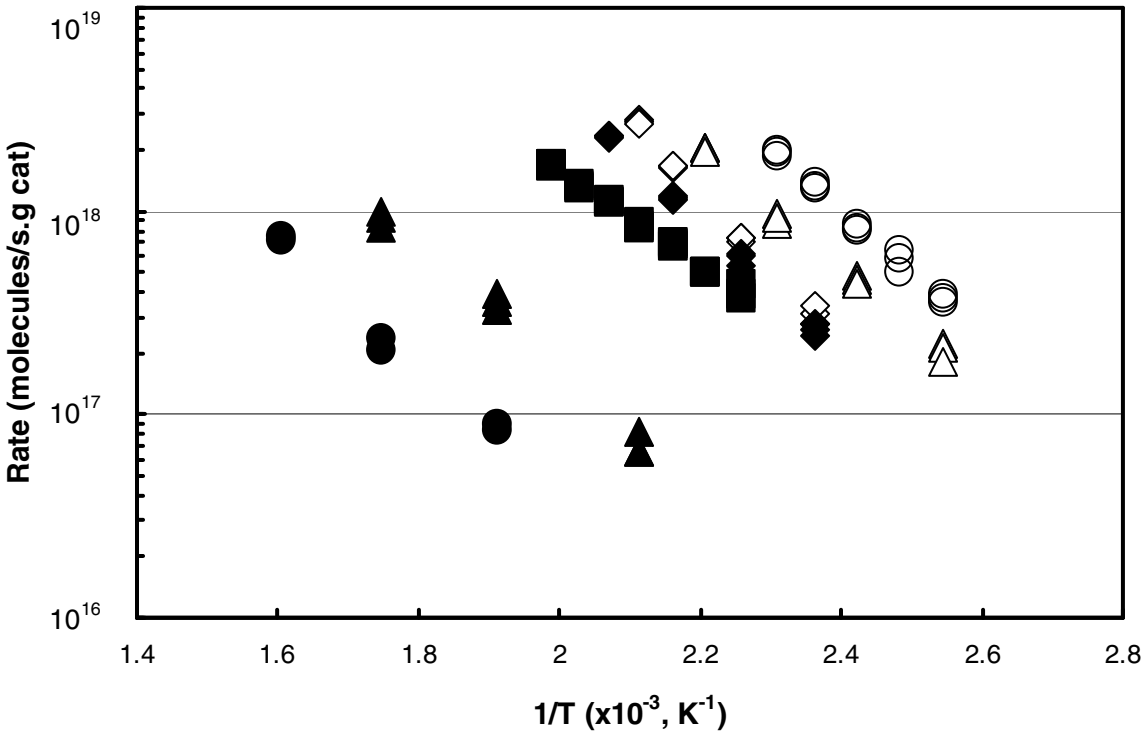

Rate (molecules/s.g cat)
10^19
10^18
10^17
10^16
1.4
1.6
1.8
2
2.2
2.4
2.6
2.8
1/T (x10^-3, K^-1)

Fig. 2


Rate (molecules/s.g cat)
10^19
10^18
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10^16
1.4
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1.8
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1/T (x10^-3, K^-1)