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The Water–Gas-Shift Reaction on Pd/Ceria–Praseodymia: The Effect of Redox Thermodynamics

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Abstract Reaction rates for the water–gas-shift (WGS) reaction were measured on catalysts with 1-wt% Pd supported on CeO_2, $Ce_{0.5}Pr_{0.5}O_{2-x}$ and PrO_x in order to determine whether the weakly bound oxygen associated with Pr could enhance reaction rates. However, differential rates in 25 Torr of both CO and H_2O showed that the activity of Pr-containing catalysts were much lower. Measurements of the oxygen content of these samples after reduction in dry H_2 at 873 K, after reoxidation in steam at 873 K, and following exposure of the catalysts to WGS conditions at 873 K demonstrate that ceria is easily reoxidized by steam and remains oxidized under WGS conditions, while the loosely bound oxygen associated with praseodymia or ceria–praseodymia is lost under WGS conditions and cannot be restored by oxidation in steam. These results can be understood by comparing the equilibrium redox properties of the support materials to the typical $P(O_2)$ experienced under WGS conditions.

Keywords Ceria · Praseodymia · Palladium · Oxidation thermodynamics · Water–gas-shift

1 Introduction

Ceria-supported metals have received a great deal of attention in recent years because they can exhibit high activities for the water–gas-shift (WGS) [1–7] and steam-reforming reactions [8–11]. While there is still some debate over the role that ceria plays in these reactions [12, 13], one of the leading proposals is that ceria, because of its ability to cycle between the +3 and +4 oxidation states, donates oxygen to the metal for oxidation of the CO or hydrocarbons and then is re-oxidized by the steam [5]. There are of course variations in the details of this proposal. For example, reaction may occur at the metal-ceria interface so that complete donation of oxygen to the metal is not necessary [14]. In still another variation, CO may be oxidized by OH to form a carboxyl intermediate [15, 16]. However, despite differences in the details, the ability of ceria to undergo oxidation and reduction should be critical in each of these proposals. Indeed, changing the reducibility of ceria has been shown to influence WGS activity in at least one study [5].

Because the redox properties of ceria are important, a significant fraction of work in this area has involved modification of ceria to enhance its reducibility, with the idea of making oxygen transfer to adsorbates on the metal easier. For example, ceria reducibility is reported to be enhanced by decreasing the crystallite size [17, 18] or doping with various other metal cations, such as +3 rare-earth ions (e.g., La^{+3}, Sm^{+3}) [19], Zr^{+4} [20, 21], and Ti^{+4} [22, 23]. While some of these ceria-based catalysts have shown better performance following ceria modification, further improvements are clearly needed, especially for the WGS reaction.

In the present study, we chose to consider modification of ceria by Pr doping. Praseodymia is similar to ceria in that the Pr exists in the +3 and +4 oxidation states in the common oxides [24, 25]. Pr adopts the trivalent oxidation state much more readily than Ce, to the degree that PrO_2 is difficult to form by simple calcination. At least one study has argued that the activity of praseodymia-supported catalysts might be limited by slow re-oxidation kinetics of Pr_2O_3 [26]. However, there is evidence that the problem of

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slow re-oxidation can be solved by forming a solid solution with either ceria–zirconia [27, 28] or ceria [29]. Due to the ease with which praseodymia reduces, praseodymia–ceria–zirconia solutions show promise for low-temperature oxygen storage in automotive catalysts [27, 28]. A recent study from our laboratory indicated that ceria–praseodymia mixtures formed solid solutions that were stable to very high temperatures and that normal calcination conditions were able to completely oxidize Pr to its +4 oxidation state [29]. Finally, temperature programmed desorption showed that $Ce_{0.5}Pr_{0.5}O_2$ released a significant fraction of its oxygen at 750 K. Since this is a similar temperature as that which would be expected for O_2 desorption from PdO [30], transfer of oxygen from the mixed oxide to a precious metal should be nearly iso-energetic.

What we will show in the present study is that there is an optimum reducibility for the oxide support used in WGS. While Pr doping enhances reducibility, it does not enhance WGS activity because the oxygen associated with Pr is too reducible. Thermodynamics does not favor replacement of oxygen in the lattice by reaction with steam.

2 Experimental Techniques

Three catalyst supports were used in this study: ceria, praseodymia, and a 50% ceria–praseodymia solid solution. The pure ceria and praseodymia were prepared by thermal decomposition of $Ce(NO_3)_3 \cdot 6H_2O$ (99.5%, Alfa Aesar) and $Pr(NO_3)_3 \cdot xH_2O$ (99.9%, Alfa Aesar). The $Ce_{0.5}Pr_{0.5}O_{2-x}$ mixed oxide was synthesized using the Pechini method, as described elsewhere [29]. Stoichiometric quantities of $Ce(NO_3)$ and $Pr(NO_3)$ were dissolved in distilled water together with citric acid ($\geq$99.5%, Aldrich) to form a solution with a 2:1 citric-acid:metal-ion ratio. The solution was stirred vigorously for 1 h at room temperature, dried by mild heating, and then calcined in air at 723 K for 5 h to produce the mixed oxide. Evidence that this synthesis procedure forms a ceria–praseodymia solid solution is given elsewhere [29].

Pd (1-wt%) was added to each of the oxides by wet impregnation of a 5-wt%, aqueous solution of $(NH_3)_4Pd(NO_3)_2$ (99.9% metals basis, Alfa Aesar). After drying, each of the samples was again calcined at 723 K for 5 h to decompose the nitrate and ammonium ions. Surface areas of each of the catalysts were determined by N_2 BET isotherms, with the results summarized in Table 1. The Pr-containing catalysts exhibited somewhat lower areas compared to Pd/ceria. The dispersions of Pd on the three catalysts are also listed in Table 1. These were determined by CO chemisorption at room temperature, on samples that had been pre-reduced in H_2, according to procedures described elsewhere [31].

Table 1 Properties of catalysts studied

Sample	Surface area (m^2/g)	Pd dispersion (%)
1-wt% Pd/CeO_2	67	31
1-wt% Pd/$Ce_{0.5}Pr_{0.5}O_{2-x}$	42	13
1-wt% Pd/Pr_6O_{11}	35	7

Samples were calcined in air at 723 K. BET measurements were performed after reaction rate measurements

Water–gas-shift reaction rates were measured in a tubular reactor with between 0.1 and 0.2 g of sample. All rate measurements were collected with partial pressures for CO and H_2O of 25 Torr each. Water was introduced to the reactor by saturation of a He carrier gas flowing through a de-ionized water saturator, and the partial pressures of CO, H_2O, and He were controlled by adjusting the relative flow rates of each component. The conversions of CO and H_2O were kept below 10% so that differential conditions could be assumed. 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.

The oxidation state of the catalysts under reaction conditions was determined using a flow-titration/temperature-programmed-oxidation (TPO) system that is described in more detail elsewhere [32]. In these experiments, 0.5 g of a catalyst sample were placed in a tubular reactor, exposed to various environments, and then purged with dry He for 0.5 h. The oxidation states of the catalysts were then determined by re-oxidizing the samples in flowing air (21% O_2 and 79% N_2 at 4.0 mL/min) while monitoring the effluent gasses using a quadrupole mass spectrometer. Oxygen consumption was determined by comparing the lag in the O_2 signal compared to that of the N_2 signal.

3 Results and Discussion

The steady-state WGS rates in 25 Torr CO and H_2O are shown in Fig. 1 as a function of temperature for each of the three catalysts studied. To ensure that steady-state was achieved, the conversion corresponding to each rate measurement was obtained several times over the period of an hour. The rates for the Pd/CeO_2 catalyst were similar to those reported previously [5]; however, the WGS rates on the Pd/PrO_x and Pd/$Ce_{0.5}Pr_{0.5}O_{2-x}$ catalysts were almost an order of magnitude lower. There was no significant difference between Pd/PrO_x and Pd/$Ce_{0.5}Pr_{0.5}O_{2-x}$. The activation energy over the Pd/CeO_2 catalyst, 39 kJ/mol, was slightly lower than that over the Pr-containing materials, 57 and 61 kJ/mol, but earlier studies on doped-ceria catalysts have not shown a strong correlation between

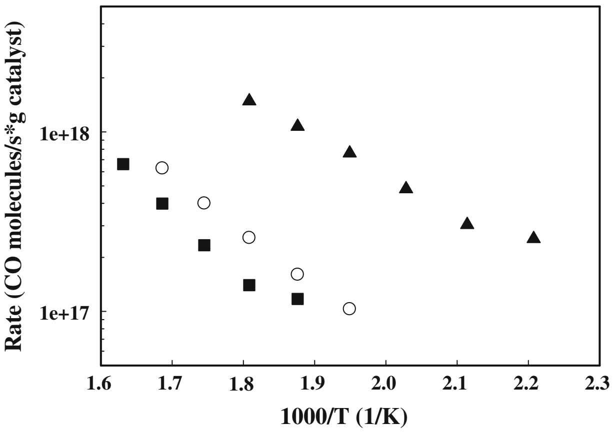

Fig. 1 The differential reaction rates for the WGS reaction over 1-wt% Pd supported on: ▲ CeO_2, ○ $Ce_{0.5}Pr_{0.5}O_{2-x}$, and ■ PrO_x

activation energy and activity [23]. Some of the increased activity can be associated with the higher surface area and better Pd dispersion of the Pd/CeO_2 catalyst, as shown in Table 1; but the activity differences are larger than that of the surface areas.

A noticeable difference between catalysts was that the activities of the Pr-containing materials changed with time following the initial calcination. This is shown in Fig. 2 for the $Pd/Ce_{0.5}Pr_{0.5}O_{2-x}$ sample for conversions measured at 423 K. The initial conversion was high, comparable to that measured over the Pd/CeO_2, but the conversion decreased steadily with time over the period of an hour. Once this lower activity state was reached, high activities could only be restored by oxidizing the catalyst in air. While we considered the possibility that deactivation could be due to carbonate formation, it should be noted that the surface of Pd/CeO_2 is also covered with carbonates under the WGS conditions used here [4] and we did not observe similar changes in the activity of that catalyst.

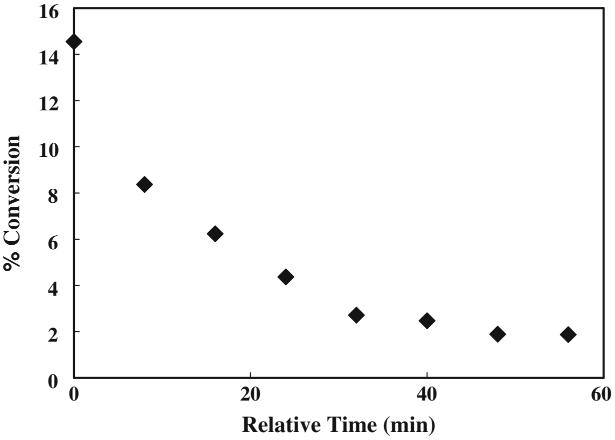

Fig. 2 Evolution of CO conversion during the WGS reaction at 423 K over an air-calcined, 1-wt% $Pd/Ce_{0.5}Pr_{0.5}O_{2-x}$ catalyst

To understand the differences between the three catalysts in this study, we performed flow-titration measurements to determine the oxidation state on the samples in various atmospheres. The measurements were performed at 873 K for two reasons. First, the higher temperatures increased oxidation and reduction kinetics and ensured access to bulk oxygen. Second, the oxidation states of ceria, praseodymia, and the ceria–praseodymia mixed oxide are known, at least approximately, at 873 K in air [29]. This is a necessary requirement in order to calculate the initial oxidation state of the sample from the oxygen consumption. While the O:M ratio for ceria will be close to 2, the O:M ratios for PrO_x and $Ce_{0.5}Pr_{0.5}O_{2-x}$ are expected to be approximately 1.77 and 1.90, respectively, under these conditions. In particular, 873 K is well above the temperature at which $Ce_{0.5}Pr_{0.5}O_2$ converts to $Ce_{0.5}Pr_{0.5}O_{1.9}$ in temperature programmed desorption [29], so that the most weakly bound oxygen will not be populated and complicate the analysis.

The results from the flow-titration measurements are shown as a bar graph in Fig. 3. For the Pd/ceria catalyst, reduction in dry, flowing H_2 led to significant reduction, requiring 1,450 μmol of O/g of catalyst for reoxidation. Oxidation of the 1-wt% Pd to PdO could account for 100 μmol of O/g but the majority of the oxygen was obviously consumed by the ceria. For comparison, oxidation of Ce_2O_3 to CeO_2 would require approximately 2,900 μmol of O/g. Interestingly, Pd/ceria is not significantly reduced under WGS conditions at 873 K. Following 0.5 h of reaction in 25 Torr each of CO and H_2O, only 390 μmol of O/g were taken up by the catalyst. The obvious interpretation is that H_2O and CO_2 are more effective in oxidizing the sample than H_2 and CO are in reducing it. To

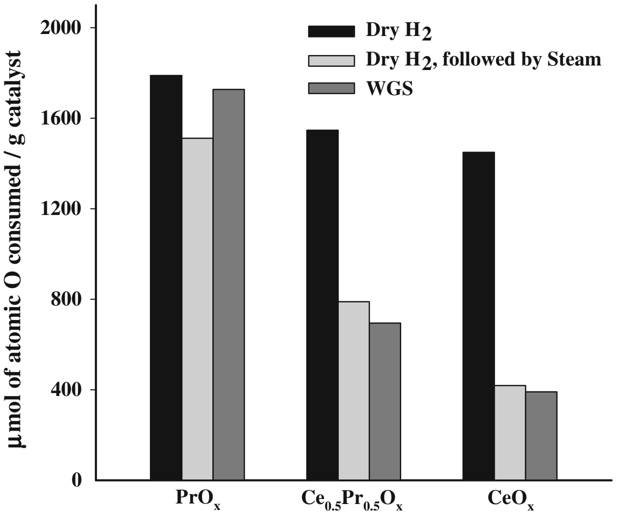

Fig. 3 Oxygen consumption by the various supported-Pd catalysts following reduction by pure H_2 gas at 873 K, subsequent partial oxidation by 76 Torr H_2O at 873 K, and following exposure to WGS conditions at 873 K

test this idea, we reduced the Pd/ceria catalyst in dry H_2, then passed 76 Torr H_2O (in He) over the catalyst for 0.5 h before measuring the amount of oxygen that could be consumed by the catalyst. As expected, the catalyst was significantly re-oxidized by the steam, requiring only 420 μmol of O/g to complete the re-oxidation process in air.

The results for the Pd/praseodymia catalyst were dramatically different. Praseodymia is reasonably easy to reduce to Pr_2O_3 and is expected to form $PrO_{1.77}$ in air at 873 K [29], a change of approximately 1,600 μmol of O/g. In good agreement with this, 1,790 μmol of O/g were required to re-oxidize the sample following reduction in dry H_2. While this result is similar to that obtained on Pd/ceria, the O_2 required to re-oxide Pd/praseodymia was virtually unaffected by passing 76 Torr H_2O over the sample (1,510 μmol of O/g was taken up by the sample following the steam treatment.) and the WGS environment was found to be similarly reducing (1,730 μmol of O/g). The results over the ceria–praseodymia, mixed-oxide catalyst were between that observed on the pure oxides. The oxygen consumption was 1,550 μmol of O/g following reduction in dry H_2, 790 μmol of O/g following re-oxidation by H_2O, and 700 μmol of O/g after exposure to the WGS environment.

Based on these data, the decline in the WGS rates with time over the Pd/$Ce_{0.5}Pr_{0.5}O_{2-x}$ catalyst in Fig. 2 is easy to understand. Following calcination in air, this catalyst contains a significant amount of oxygen that is slowly consumed by the CO under WGS conditions. Because this oxygen cannot be replaced by steam, the conversion of CO declines with time.

It is instructive to consider the previously reported oxygen isotherms for each of the oxide supports, shown in Fig. 4 for a temperature of 973 K [29, 33]. This plot shows the equilibrium O:M ratio as a function of $P(O_2)$ for bulk CeO_2, PrO_x, $Ce_{0.5}Pr_{0.5}O_{2-x}$ samples that had been calcined to high temperatures to avoid surface effects. Because the flux of molecules to a surface is negligible below approximately 10^{-10} atm, the equilibrium $P(O_2)$ in this figure are established by either the H_2:H_2O or CO:CO_2 ratio, with the samples being simultaneously reduced by H_2 (CO) and oxidized by H_2O (CO_2) [34]. The shaded grid in this plot is the approximate environment experienced by the catalysts under WGS conditions. Temperature will, of course, shift the equilibrium isotherms in a manner that can be calculated from the reaction enthalpies. It should also be recognized that the equilibrium conditions for surface phases can be different that of the bulk [33]. Still, these data explain the results in Fig. 3 very well. Based on the equilibrium data, ceria is expected to be almost completely oxidized under WGS conditions, praseodymia is expected to be completely reduced, and ceria–praseodymia mixed oxides will be between the two extremes, with the loosely bound oxygen associated with the addition of praseodymia being unpopulated in the solid solution.

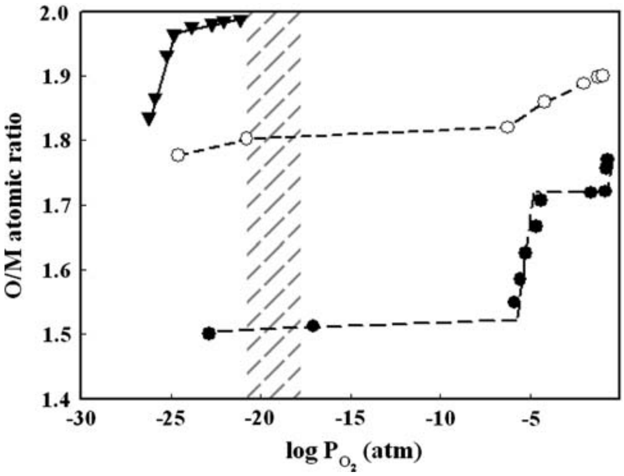

Fig. 4 Equilibrium oxygen to metal-ion (Ce + Pr) ratios for the $Ce_yPr_{1-y}O_{2-x}$ sample as a function of $P(O_2)$ at 973 K. The y values in the samples are as follows: ▲ $y = 1$, ○ $y = 0.5$, and ● $y = 0$. The O:M ratio for $Ce_{0.5}Pr_{0.5}O_{2-x}$ was assumed to be approximately 1.90 at 0.21 atm [29]. WGS operating conditions are *shaded*

The equilibrium data also help to explain the effect of treating the samples with steam. If one assumes that the H_2:H_2O ratio reaches equilibrium during oxidation of a sample by flowing steam over it, the partial pressure of H_2 will be very low if the equilibrium $P(O_2)$ is too high. For reference, the H_2:H_2O ratio approaches unity under WGS conditions. Restoration of the loosely-bound oxygen associated with praseodymia occurs at $P(O_2)$ many orders of magnitude higher than the $P(O_2)$ associated with WGS, implying that the conversion of steam flowing over the sample will be low and that very large amounts of steam and long flow times will be required to oxidize the sample.

After considering the equilibrium data, the only real surprise in the catalytic data is that the Pd/$Ce_{0.5}Pr_{0.5}O_{2-x}$ catalyst exhibited catalytic activity closer to that of Pd/PrO_x than to Pd/CeO_2, even though the oxidation results and the equilibrium data would have suggested that it would have properties between that of ceria and praseodymia. This may indicate that the Pr^{+3} ions form preferentially at the surface of the catalyst. Indeed, calculations with ceria clusters have suggested that +3 ions should form at the surface first in order to maximize Coulombic interactions [35]. Whether this could be changed by different synthesis conditions is unclear.

The lessons learned from WGS measurements over these catalysts almost certainly apply to other catalysts as well. While kinetic properties must certainly dominate in the end, there is an optimum reducibility that should lead to the most active catalysts. Oxides that hold oxygen too weakly will be just as ineffective as oxides that hold oxygen too tightly. In looking for the best oxides as supports for WGS catalysts, there is a relatively narrow range of thermodynamic properties that will be most effective.

4 Conclusions

Water–gas-shift studies on Pd supported over ceria–praseodymia mixed oxides reveal the importance of selecting an oxide support with optimal redox properties. While the addition of Pr to ceria leads to weakly bound oxygen that can be used to oxidize CO, this oxygen cannot be replaced by oxidation with steam. The optimal oxide supports for WGS will have thermodynamic properties that allow them to be oxidized by steam.

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