A Comparison of Hierarchical Pt@CeO₂/Si-Al₂O₃ and Pd@CeO₂/Si-Al₂O₃

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Abstract

A comparison of catalytic and adsorption properties for Pt@CeO₂/Si-Al₂O₃ (1-wt% Pt and 9-wt% CeO₂) and Pd@CeO₂/Si-Al₂O₃ (1-wt% Pd and 9-wt% CeO₂) core-shell catalysts indicates that the CeO₂ shell is stable for Pd but not for Pt. Following calcination at 773 K, Pt@CeO₂/Si-Al₂O₃ exhibits Water-Gas-Shift (WGS) rates in 3% H₂O and CO that are similar to rates found on conventional Pt/CeO₂, implying that there is good contact between the Pt and CeO₂ phases, even at the relatively low CeO₂ loading. WGS rates on Pt@CeO₂/Si-Al₂O₃ were also reasonably stable with time and unaffected by pre-reduction of the catalyst. By comparison, WGS rates over Pd@CeO₂/Si-Al₂O₃ declined rapidly due to reduction of CeO₂ and were suppressed by pre-reduction of CeO₂. After calcination to 1073 K, large metal particles were observed with Pt@CeO₂/Si-Al₂O₃, but not on Pd@CeO₂/Si-Al₂O₃. Coulometric titration

measurements on these two materials suggest stronger interactions between CeO_2 and Pd and these are likely responsible for the higher stability of the core-shell structure in Pd@CeO_2 compared to Pt@CeO_2 .

Keywords: platinum, ceria, palladium, core-shell catalyst, coulometric titration, water gas shift

1. Introduction

Ceria-supported transition metals often show significantly enhanced catalytic properties, usually because of the reducibility of ceria [1-4]. Because metal-ceria contact is important for promoting catalytic performance, there has been considerable effort at maximizing the interactions between transition metals and ceria [5,6]. For example, a series of recent papers examined the synthesis of hierarchically structured nanoparticles having a Pd, Pt, or Au core surrounded by a thin oxide shell and showed that these materials can have unique catalytic properties [7-14]. Pd@CeO_2 catalysts prepared by these methods showed excellent thermal stability for methane oxidation upon heating to temperatures as high as 1123 K [11]. However, these same Pd@CeO_2 catalysts exhibited very low rates Water-Gas Shift (WGS) [8,9] and methane-steam reforming (MSR) [11] when they were calcined to only 773 K and reduced at 673 K. The Pd@CeO_2 catalysts calcined at 773 K and reduced at 673 K also exhibited low CO adsorption uptakes, which was interpreted as being due to encapsulation of the Pd by reduced ceria [11]. All of these results suggest that there is a very strong interaction between Pd and CeO_2 in the core-shell particles that can stabilize the structure to high calcination temperatures and cause the reduced ceria shell to encapsulate the Pd particles when the CeO_2 is reduced.

However, there are differences in how the various transition metals interact with ceria. For example, with ceria-supported Pd, it has been reported that contact with CeO₂ shifts the reoxidation temperature of Pd, stabilizing the oxide [15]; but, with Pt, it is likely the reduced form of the metal that is in contact with CeO₂ [16]. These differences could potentially have important consequences for the stability of core-shell structures and the activity of the catalysts. Therefore, we set out to determine whether similar strong interactions would occur for Pt and CeO₂ in Pt@CeO₂ catalysts prepared by the same methods. We will show that the interactions between the Pt and CeO₂ appear to be much weaker, to the extent that the CeO₂ shell does not suppress adsorption of CO for catalyst calcined at lower temperatures nor stabilize Pt sintering for higher calcination temperatures.

2. Experimental

2.1 Preparation of the catalysts

Synthesis of the Pt(1-wt%)/CeO₂(9-wt%)/Si-Al₂O₃ and Pd(1-wt%)/CeO₂(9-wt%)/Si-Al₂O₃ catalysts followed previously published procedures [7,9]. The support (Si-Al₂O₃) was made hydrophobic by reacting a commercially available Al₂O₃ (Sasol) with triethoxy(octyl)silane (TEOOS) [10]. To prepare the dispersed core-shell particles, Pt or Pd nanoparticles, dispersed in THF using 11-mercaptoundecanoic acid ligands, were added dropwise to a solution of cerium(IV) tetrakis(decyloxy) under constant stirring. After adding dodecanoic acid (1 mol per Ce) dissolved in THF to disperse the particles, controlled amounts of water were added to hydrolyze the remaining alkoxide groups. Next, the Si-Al₂O₃ was slowly added to the Pt@CeO₂ or Pd@CeO₂ solutions in an amount sufficient to give a final composition of 1-wt% metal and 9-wt% CeO₂. After stirring the slurry overnight, the solvent was removed by

rotary evaporation. The dried powders were calcined in air at 773 K or 1073 K for 6 h using a heating ramp of 3 K/min.

Conventional Pt/Al₂O₃, Pt/CeO₂, Pd/Al₂O₃ and Pd/CeO₂ catalysts with 1-wt% metal were also prepared for comparison purposes by impregnation of Al₂O₃ or CeO₂ with aqueous solutions of Pt(NH₃)₄(NO₃)₂ or (NH₃)₄Pd(NO₃)₂. Prior to being used, the Al₂O₃ was calcined to 1173 K for 24 h. The ceria support was prepared by thermal decomposition of Ce(NO₃)₃·H₂O at 973 K for 6 h with a heating ramp of 3 K/min. The dried powders were calcined in air at 773 K for 6 h using a heating ramp of 3 K/min. The Al₂O₃, Si-Al₂O₃ and CeO₂ supports had BET surface areas of 100, 90 and 35 m²/g, respectively.

2.2 Characterization of the catalysts

Transmission electron microscopy (TEM) images were obtained using a JEOL 2100 microscope, with an accelerating voltage of 200 kV. CO chemisorption measurements were performed using a home-built adsorption apparatus and procedures that have been described in detail elsewhere [17]. To prepare a sample for chemisorption, the calcined sample was exposed to 200 Torr O₂ at 673 K for 2 min and then evacuated. Next, the sample was reduced by exposure to 200 Torr of H₂ at either 423 K or 673 K for 5 min, followed by evacuation. Each pretreatment was repeated three times. CO adsorption uptakes were then determined at room temperature by adding small pulses of CO to the sample until a pressure rise was detected. In this pretreatment procedure, the reduction step is critical in order to avoid the reaction of CO and subsequent adsorption of CO₂ onto the reduced ceria [17].

Coulometric titration is an equilibrium, electrochemical technique for measuring oxidation state as a function of P(O₂) and a more detailed description of the apparatus is given elsewhere [18]. Briefly, 1 g of the calcined sample was placed in an alumina crucible and

inserted inside a yttria-stabilized zirconia (YSZ) tube with Ag electrodes painted on the inside and outside. After heating the sample overnight to 873 K in flowing air with a temperature ramp of 1 K/min, a mixture of 5% O₂, 11% H₂O and 84% Ar was allowed to flow through the YSZ tube, over the sample, for 1 h, after which the tube was sealed at both ends using cajon fittings. Controlled amounts of oxygen were then added or removed from inside the tube by applying current across the electrodes using a Gamry Instruments potentiostat. The quantities of oxygen that were transferred were quantified by integrating the current. The P(O₂) at 873 K were determined from the open-circuit potential across the electrodes, using the Nernst Equation, after the system came to equilibrium. The ability of coulometric titration to accurately quantify both the amount of oxygen that can be removed from the catalyst and the equilibrium conditions at which this reduction occurs has been verified in previous studies with known samples [12,19,20].

The water-gas-shift (WGS) reaction was studied in a 1/4-inch, quartz, tubular reactor using 0.10 g of catalyst. The samples were first oxidized in flowing 20% O₂-He mixtures at 573 K for 30 min. For rate measurements, the reactant partial pressures were fixed at 25 torr CO and 25 torr H₂O and the conversions were kept below 10% to maintain differential conditions. For measuring catalyst stability in the WGS environment, the conversion was measured while holding the catalyst temperature at 623 K in a total flow rate of 120 mL/min. Products were analyzed using an online gas chromatograph (SRI8610C) equipped with a HayeSep Q column and a TCD detector.

3. Results and Discussion

3.1 Catalyst characterization

In previous work on Pd@CeO₂/Si-Al₂O₃ catalysts, TEM results showed that, after calcination at 773 K, the Pd particles were uniformly 2 nm in diameter and surrounded by ceria nanocrystals to form particles that were 6 nm in diameter. This structure was largely maintained even after calcination to temperatures as high as 1123 K. The results for Pt@CeO₂/Si-Al₂O₃ were quite different, as shown in Fig. 1. Following calcination of the sample to 773 K, the TEM images of the Pt@CeO₂/Si-Al₂O₃ in Figure 1A show Pt cores that are again approximately 2 nm in diameter, very close to the starting Pt-MUA nanoparticles [9]. It is not possible to tell if there is a ceria shell surrounding the Pt particles. However, after calcination to 1073 K, TEM images of the Pt@CeO₂/Si-Al₂O₃ exhibit a number of very large particles, some approaching 40 nm, demonstrating that significant sintering occurred (Fig. 1B).

The CO chemisorption data in Table 1 support the above conclusions. For reference, conventional 1-wt% Pt/Al₂O₃ and Pt/CeO₂ catalysts had dispersions of 41 and 43% after calcination to 773 K and reduction at 673 K. Following calcination at 773 K, the Pt@CeO₂/Si-Al₂O₃ samples had a Pt dispersion between 19 and 21%, essentially independent of the reduction temperature. This is in sharp contrast to what we observed with Pd@CeO₂/Si-Al₂O₃, for which the apparent dispersion depended on the reduction temperature [11], decreasing from 24% after reduction at 423 K to 5% after reduction at 673 K. (Note: This loss in dispersion is reversed by mild oxidation, followed by reduction at 423 K.) With Pd@CeO₂/Si-Al₂O₃, it was previously argued that reduction of the ceria nanocrystals that make up the shell caused the oxide to “close up” around the metal particles and block adsorption. The difference between Pd@CeO₂/Si-Al₂O₃ and Pt@CeO₂/Si-Al₂O₃ is consistent with stronger attractive interactions between the Pd and CeO₂ stabilizing the core-shell structure.

As measured by CO adsorption, heating of Pt@CeO₂/Si-Al₂O₃ to 1073 K caused the Pt dispersion to fall to 6 %, in agreement with the large growth in metal particle size found by TEM. It is noteworthy that the high-temperature treatment had very little effect on the dispersion of Pd@CeO₂/Si-Al₂O₃ [11]. This is again consistent with the core-shell structure stabilizing the Pd particle size but not the Pt particle size.

3.2 WGS activity

The Pt@CeO₂/Si-Al₂O₃ catalyst was tested for the WGS reaction (Fig. 2) and compared to the analogous Pd system (Fig. 3). As reported in many previous investigations, WGS rates on Pt/CeO₂ are significantly higher than those observed over Pt/Al₂O₃ [18,21,22]. WGS rates over the Pt@CeO₂/Si-Al₂O₃ calcined at 773 K were nearly identical to those measured on Pt/CeO₂, implying that Pt and CeO₂ phases must still be in contact with each other on the hierarchical catalyst, even with the relatively low CeO₂ loading of 9-wt%. When the Pt@CeO₂/Si-Al₂O₃ catalyst was calcined to 1073 K, the rates were much lower, in agreement with the loss in metal dispersion and the likely separation of Pt and CeO₂ phases.

Of greater interest is the comparison of Pt@CeO₂/Si-Al₂O₃ and Pd@CeO₂/Si-Al₂O₃ stabilities in the WGS reaction, shown in Figure 3. As reported previously [8,9], Pd@CeO₂/Si-Al₂O₃ catalysts calcined at 773 K deactivate rapidly in the WGS environment due to reduction of the ceria, which in turn causes a loss in the CO adsorption uptakes on Pd, probably due to the ceria shell closing up around the Pd [23]. This is shown in Figure 3 by the decrease in conversion from larger than 25% to less than 15% over the period of only 1 h. The reduction of the ceria shell takes place even in the relatively oxidizing environment of the WGS reaction [24]. By comparison, the CO conversions during the WGS reaction over Pt@CeO₂/Si-Al₂O₃ were much

higher and more stable, consistent with the much smaller effect of reduction on CO adsorption capacity, reported in Table 1.

It has been shown that high-temperature calcination of ceria dramatically changes its reducibility [25] and that this in turn changes its ability to promote the WGS reaction over ceria-supported Pt and Pd catalysts [3]. Because the reducibility of the catalyst appears to be so important for the WGS reaction, we performed Coulometric Titration experiments on the various catalysts to better understand their redox properties. Results for conventional Pt and Pd catalysts are reported in Figure 4, with Figure 4A showing data for alumina-supported Pt and Pd and Figure 4B data for Pd/CeO₂. All of the catalysts used for the data in this figure were prepared by impregnation of the metal salts, followed by calcination in flowing air at 773 K. As discussed in the Experimental section, the catalysts were then exposed to flowing mixture of 5% O₂, 11% H₂O and 84% Ar at 873 K prior to taking the Coulometric Titration data and the titration experiments themselves were performed at 873 K. Figure 4A demonstrates that very little (<10 $\mu\text{mol/g}$) oxygen could be removed from the 1-wt% Pt/Al₂O₃ catalyst, implying that the Pt remained in a reduced state in the flowing gas mixture. Results for the 1-wt% Pd/Al₂O₃ have been reported previously [12]. Approximately 95 $\mu\text{mol/g}$ of oxygen atoms are removed in a narrow range of O₂ pressures, between 10^{-3} and 10^{-5} atm. The amount of oxygen agrees well with reduction of PdO to Pd and the reduction occurs near the $P(\text{O}_2)$ that would be predicted based on Pd-PdO equilibrium pressure at this temperature, 2.0×10^{-3} atm [26]. With 1-wt% Pd/CeO₂, Figure 4B, one can again see removal of approximately 100 $\mu\text{mol/g}$ of oxygen near 10^{-3} atm corresponding to the Pd-PdO transition; however, additional reduction occurs at lower $P(\text{O}_2)$ due to the removal of oxygen from the CeO₂ support. It is noteworthy that the PdO and CeO₂ reduce in distinctly different $P(\text{O}_2)$ ranges.

Data for the Pt@CeO₂/Si-Al₂O₃ and Pd@CeO₂/Si-Al₂O₃ core-shell catalysts are given in Figure 5, with Figure 5A showing results for the samples calcined at 773 K and Figure 5B showing results for the samples calcined at 1073 K. Considering first the Pd@CeO₂/Si-Al₂O₃ samples, the sample calcined at 773 K exhibits removal of ~100 $\mu\text{mol/g}$ of oxygen near 10^{-5} atm, the expected amount and the expected $P(\text{O}_2)$ for the PdO-Pd transition. An additional ~220 $\mu\text{mol/g}$ of oxygen is removed from the CeO₂ at lower $P(\text{O}_2)$. Considering that this sample had only 9-wt% CeO₂, the O:Ce ratio at this point is estimated to be approximately 1.6. It is interesting to note that this reduction of CeO₂ is much more extensive, and occurs at significantly higher $P(\text{O}_2)$, than that found for the CeO₂ in the conventional Pd/CeO₂ catalyst. This is likely due to the fact that the redox properties of CeO₂ are strongly dependent on crystallite size and pretreatment conditions [11,24].

The isotherm for the Pd@CeO₂/Si-Al₂O₃ calcined to 1073 K is significantly different. Similar to what some of us reported earlier for Pd@ZrO₂/Si-Al₂O₃ [12], there is no well-defined transition corresponding to a PdO-Pd transition. Reduction of the Pd@CeO₂/Si-Al₂O₃ occurred gradually with decreasing $P(\text{O}_2)$. Since spectroscopic data showed that the Pd in these catalysts is easily oxidized to PdO [23], the results in Figure 4B imply that the PdO and CeO₂ reduction occur together. The high-temperature calcination, which has previously been demonstrated to enhance the catalytic properties of Pd@CeO₂/Si-Al₂O₃, is shown to promote a stronger interaction between PdO and CeO₂ even in the redox isotherm.

Interactions between Pt and CeO₂ in the Pt@CeO₂/Si-Al₂O₃ catalysts were less apparent. Although the redox isotherm for the Pt@CeO₂/Si-Al₂O₃ catalyst calcined at 773 K is very similar to that of the redox isotherm for Pd@CeO₂/Si-Al₂O₃ with the PdO-Pd transition removed, this only implies that reduction of CeO₂ is identical in both catalysts. For both Pd@CeO₂/Si-Al₂O₃

and Pt@CeO₂/Si-Al₂O₃, when calcined at 773 K, the redox properties of the ceria component do not appear to be strongly affected by interactions with the precious metal. Following calcination to 1073 K, reduction of Pt@CeO₂/Si-Al₂O₃ is different from that of Pd@CeO₂/Si-Al₂O₃. Reduction of the Pt catalyst does not begin until $\sim 10^{-15}$ atm, a similar $P(O_2)$ to that which would occur with normal ceria nanocrystals. There is no evidence for contact between the Pt and the CeO₂ phases.

What the isotherm data suggests about Pt@CeO₂/Si-Al₂O₃ is that interactions between the Pt and CeO₂ phases are relatively weak. This explains why the catalyst behaves similarly to what might be expected for a conventional, impregnated catalyst. For the catalyst calcined at 773 K, there remains contact between the Pt and the ceria that is responsible for enhanced WGS rates above that which are found for Pt/Al₂O₃. However, there is no special attraction which would cause CeO₂ to “cover” the Pt following reduction of the CeO₂, as was found with the Pd@CeO₂/Si-Al₂O₃ catalyst. There is also no stabilization of the catalyst after sintering at high temperatures. Calcination to higher temperatures in the Pt@CeO₂ catalyst simply causes sintering and segregation of the Pt and CeO₂ phases.

This does raise the question concerning why contact between Pd and CeO₂ is so different and the Pd@CeO₂ structures so much more stable. It has been reported that Pd reacts with specific sites on CeO₂ [27], which suggests some kind of chemical-bonding interaction between Pd and CeO₂. Furthermore, DFT studies have shown that Pt has the tendency to bind to both cerium and oxygen defect sites [28]. The differences between Pt-ceria and Pd-ceria interactions may be related to the ease with which Pd can be oxidized. However, the reasons behind the differences are not completely understood and this is still an open area of investigation.

Even though CeO₂-supported metals have been applied to automotive, emissions-control catalysis for many years, there is clearly much to be learned about the nature of interactions between metals and reducible oxides. Given the importance of these materials to real applications, additional studies are required.

4. Conclusion

Hierarchically structured, Pt@CeO₂/Si-Al₂O₃ and Pd@CeO₂/Si-Al₂O₃ catalysts are shown to have very different behaviors. Stronger interactions between CeO₂ and Pd help to stabilize a core-shell structure, but this structure is unstable for Pt. For catalysts calcined at 773 K, reduction of CeO₂ can lead to encapsulation of Pd for Pd@CeO₂/Si-Al₂O₃ catalysts but similar behavior is not observed with Pt@CeO₂/Si-Al₂O₃. Strong interactions also help to maintain the core-shell structure at high temperatures with Pd@CeO₂/Si-Al₂O₃, but this is again not observed with Pt.

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TABLES

Table 1 Pt and Pd dispersions (%) measured by CO adsorption uptakes at room temperature for samples after various pre-treatment conditions.

Catalysts	Reduction at 423 K	Particle size (nm)	Reduction at 673 K	Particle size (nm)
Pt/Al ₂ O ₃ – 773 K	34	3	41	3
Pt/CeO ₂ – 773 K	36	3	43	3
Pt@CeO ₂ /Si-Al ₂ O ₃ – 773 K	21	5	19	6
Pt@CeO ₂ /Si-Al ₂ O ₃ – 1073 K	2	54	6	18
Pd@CeO ₂ /Si-Al ₂ O ₃ – 773 K	24	5	5	22
Pd@CeO ₂ /Si-Al ₂ O ₃ – 1073 K	21	5	18	6

FIGURES

Fig. 1 Representative transmission electron microscopy (TEM) images of Pt@CeO₂/Si-Al₂O₃ samples calcined at (A) 773 K and (B) 1073 K in air. Arrows indicate Pt particles.

Fig. 2 Differential reaction rates for the water gas shift (WGS) reaction over (a) Pt/Al₂O₃-773K, (b) Pt/CeO₂-773K, (c) Pt@CeO₂/Si-Al₂O₃-773K and (d) Pt@CeO₂/Si-Al₂O₃-1073K. The samples were pretreated by oxidation in 20% O₂-He mixture at 573 K for 30 min prior to rate measurements. The reactant partial pressures were fixed at 25 torr CO and 25 torr H₂O.

Fig. 3 CO conversion in the WGS reaction as a function of time at 623 K over the Pt@CeO₂/Si-Al₂O₃-773 K (■) and Pd@CeO₂/Si-Al₂O₃-773 K (○) catalysts. The reactant partial pressures were fixed at 25 torr CO and 25 torr H₂O.

Fig. 4 Redox isotherms for (A) 1-wt% Pt/ Al_2O_3 (■) and 1-wt% Pd/ Al_2O_3 (◇), and (B) 1-wt% Pd/ CeO_2 (◆). The samples were initially calcined in air at 773 K. Measurements were conducted at 873 K, starting from the oxidized state.

Fig. 5 Redox isotherms for 1-wt%Pt@CeO₂/Si-Al₂O₃ (■) and 1-wt%Pd@CeO₂/Si-Al₂O₃ (◇) calcined at (A) 773 K and (B) 1073 K. The samples were initially calcined in air at 773 K. Measurements were conducted at 873 K, starting from the oxidized state.