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A comparison of hierarchical Pt@CeO_2/Si–Al_2O_3 and Pd@CeO_2/Si–Al_2O_3

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A comparison of catalytic and adsorption properties for Pt@CeO_2/Si–Al_2O_3 (1-wt% Pt and 9-wt% CeO_2) and Pd@CeO_2/Si–Al_2O_3 (1-wt% Pd and 9-wt% CeO_2) core–shell catalysts indicates that the CeO_2 shell is stable for Pd but not for Pt. Following calcination at 773 K, Pt@CeO_2/Si–Al_2O_3 exhibits water–gas-shift (WGS) rates in 3% H_2O and CO that are similar to rates found on conventional Pt/CeO_2, implying that there is good contact between the Pt and CeO_2 phases, even at the relatively low CeO_2 loading. WGS rates on Pt@CeO_2/Si–Al_2O_3 were also reasonably stable with time and unaffected by pre-reduction of the catalyst. By comparison, WGS rates over Pd@CeO_2/Si–Al_2O_3 declined rapidly due to reduction of CeO_2 and were suppressed by pre-reduction of CeO_2. After calcination to 1073 K, large metal particles were observed with Pt@CeO_2/Si–Al_2O_3, but not on Pd@CeO_2/Si–Al_2O_3. 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 Pd@CeO_2.

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 for 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 CeO_2 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 CeO_2 [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 CeO_2 in Pt@CeO_2 catalysts prepared by the same methods. We will show that the interactions between the Pt and CeO_2 appear to be much weaker, to the extent that the CeO_2 shell does not suppress adsorption of CO for catalyst calcined at lower temperatures nor stabilize Pt sintering for higher calcination temperatures.

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2. Experimental

2.1. Preparation of the catalysts

Synthesis of the Pt (1-wt%)@CeO_2 (9-wt%)/Si–Al_2O_3 and Pd (1-wt%)@CeO_2 (9-wt%)/Si–Al_2O_3 catalysts followed previously published procedures [7,9]. The support (Si–Al_2O_3) was made hydrophobic by reacting a commercially available Al_2O_3 (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(decyloxide) 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–Al_2O_3 was slowly added to the Pt@CeO_2 or Pd@CeO_2 solutions in an amount sufficient to give a final composition of 1-wt% metal and 9-wt% CeO_2. 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/Al_2O_3, Pt/CeO_2, Pd/Al_2O_3 and Pd/CeO_2 catalysts with 1-wt% metal were also prepared for comparison purposes by impregnation of Al_2O_3 or CeO_2 with aqueous solutions of $Pt(NH_3)_4(NO_3)_2$ or $(NH_3)_4Pd(NO_3)_2$. Prior to being used, the Al_2O_3 was calcined to 1173 K for 24 h. The ceria support was prepared by thermal decomposition of $Ce(NO_3)_3 \cdot H_2O$ 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 Al_2O_3, Si–Al_2O_3 and CeO_2 supports had BET surface areas of 100, 90 and 35 m^2/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 O_2 at 673 K for 2 min and then evacuated. Next, the sample was reduced by exposure to 200 Torr of H_2 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 CO_2 onto the reduced ceria [17].

Coulometric titration is an equilibrium, electrochemical technique for measuring oxidation state as a function of $P(O_2)$ 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% O_2, 11% H_2O 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 $P(O_2)$ 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 ¼-in., quartz, tubular reactor using 0.10 g of catalyst. The samples were first oxidized in flowing 20% O_2–He mixtures at 573 K for 30 min. For rate measurements, the reactant partial pressures were fixed at 25 Torr CO and 25 Torr H_2O 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@CeO_2/Si–Al_2O_3 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@CeO_2/Si–Al_2O_3 were quite different, as shown in Fig. 1. Following calcination of the sample to 773 K, the TEM images of the Pt@CeO_2/Si–Al_2O_3 in Fig. 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@CeO_2/Si–Al_2O_3 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/Al_2O_3 and Pt/CeO_2 catalysts had dispersions of 41 and 43% after calcination to 773 K and reduction at 673 K. Following calcination at 773 K, the Pt@CeO_2/Si–Al_2O_3 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@CeO_2/Si–Al_2O_3, 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@CeO_2/Si–Al_2O_3, 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@CeO_2/Si–Al_2O_3 and Pt@CeO_2/Si–Al_2O_3 is consistent with stronger attractive interactions between the Pd and CeO_2 stabilizing the core–shell structure.

As measured by CO adsorption, heating of Pt@CeO_2/Si–Al_2O_3 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@CeO_2/Si–Al_2O_3 [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@CeO_2/Si–Al_2O_3 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/CeO_2 are significantly higher than those observed over Pt/Al_2O_3 [18,21,22]. WGS rates over the Pt@CeO_2/Si–Al_2O_3 calcined at 773 K were nearly identical to those measured on Pt/CeO_2, implying that Pt and CeO_2