TEM investigation of Pd/CeO_2, $Pd/Ce_{0.7}Zr_{0.3}O_2$, and Pd/ZrO_2 model catalyst systems

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Introduction

Metal-support interactions play a significant role in many heterogeneous catalyst systems, sometimes affecting catalytic performance dramatically [1,2]. Cross sectional transmission electron microscopy (TEM) has proven to be a useful tool for investigating such interactions, for example, by providing a visual image of a supported metal particle cross section which may be used to calculate the thermodynamic properties of the interface [3]. In the present work, we apply cross-sectional TEM to the study of model catalyst systems of interest in automotive exhaust-gas catalysis, specifically, Pd supported on oxides used for oxygen storage.

Materials and Methods

Thin CeO_2 and $Ce_{0.7}Zr_{0.3}O_2$ (CZO) films were grown epitaxially onto the (111) surface of yttrium-stabilized zirconia, (YSZ), using pulsed laser deposition (PLD), and a monolayer-equivalent of Pd was deposited at room temperature onto the film surfaces, as well as the bare YSZ surface, under ultra-high vacuum (UHV). After deposition, each piece was calcined for 1 hour at 600°C and subjected to two reduction cycles, 1% $(H_2+CO)/N_2$ at 200°C for 20 minutes followed by 5 hours at 700°C, followed by cooling to 50° C under N_2.

Results and Discussion

A low magnification TEM image of Pd particles on the surface of the CeO_2 film is shown in Figure 1. HRTEM images of Pd particles on the surfaces of CeO_2, CZO, and YSZ are shown in Figure 2. In all cases, the average Pd particle size is approximately 10 nm. A prominent morphological characteristic of the CZO sample, previously reported [4], is that the ceria-zirconia support tends to migrate toward Pd particles and wet them (Figure 1b). However this behavior is not observed in the Pd/CeO_2 (or the Pd/YSZ) sample(s). Although the previous work emphasized the role of Ce in driving this interaction, these results indicate that pure CeO_2 is not as likely to undergo migration and wetting as CZO. These results may be explained in part by the fact that ceria-zirconia mixed oxides (containing between 20-50% mole fraction zirconia) have been shown to have a high oxygen storage capacity[5], which indicates that CZO is the most reducible support examined here.

Significance

This work expands on previous work and reveals additional subtleties involved in ceria-based support migration and particle wetting. Hopefully, the work will also provide experimental input needed to further evaluate thermodynamic properties of small particles on oxide surfaces.

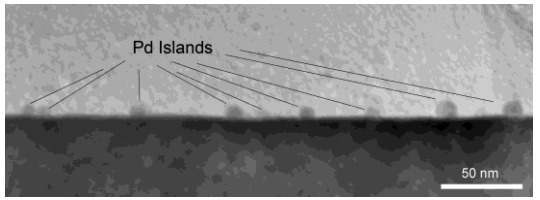
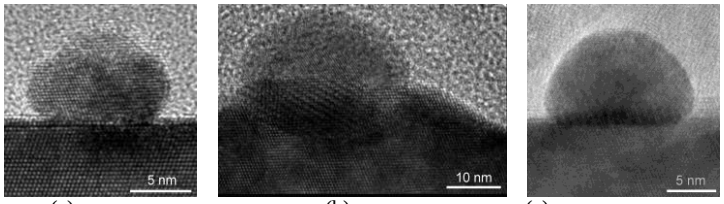


Figure 1. TEM images of Pd particles on the surface of the CeO_2 film.



(a) (b) (c)

Figure 2. HRTEM images of Pd particles on the (a) YSZ, (b) CZO, and (c) CeO_2surfaces.

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