TEM Study of Metal/Support Interaction in Pd/Ce_xZr_{1-x}O_2 Model Auto Catalyst


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Ceria-zirconia mixed oxide holds many advantages to be used as the support for palladium-based automotive three-way catalysts (TWCs) with excellent thermal stability [1]. However, substantial fraction of Pd can be encapsulated by the ceria-zirconia mixed oxides after redox aging at high temperature [2, 3]. Thermal degradation of auto catalysts may be related with the metal-support interaction. To understand more detail of this interaction, model catalyst systems were prepared by deposition of a monolayer Pd onto a (111) Ce_xZr_{1-x}O_2 (CZO)/(111)ZrO_2:Y (YSZ) substrate in ultra high vacuum (UHV). The samples were then calcined in air, reduced in (H_2+CO)/N_2, and finally reoxidized in O_2/N_2. Cross sectional samples were made for analytical transmission electron microscopy (ATEM) investigation after each step in one redox cycle. It was found that the morphology change of the Pd particle is dramatic. Fig. 1(a) shows a cross section view of the Pd/CZO/YSZ model catalyst after reducing treatment. The Pd particles show specific faceted shapes due to the minimization of surface/interface free energy. A large and flat Pd/support interface can be identified. Some materials piled up around the Pd particle and it appears like the Pd particles are located in a crater and partially encapsulated by the substrate. More detailed interfacial microstructure is revealed in a high resolution TEM image, as shown in Fig.1(b). The Moire fringe results from overlapping of the Pd lattice with that of the surrounding materials which has epitaxial relationship with the CZO substrate.

After reoxidization of the reduced sample, the Pd particles will grow, see Fig. 2(a). The chemistry of the Pd and surrounding hillock can be identified by energy dispersion spectroscopy (EDS) of X-ray (Fig. 3). The EDS indicates small composition difference between the hillock and the CZO substrate, and the Ce peaks are strong. Many crater-like hillocks remain on the CZO surface after reoxidization but Pd particles are missing, see Fig. 2(b-c), which indicates a weak bonding between Pd particles and CZO support.

M4/M5 ratio of Ce in electron energy loss spectrum (EELS) was used to estimate the valence state of Ce in the CZO substrate. The ratio is ~1.1 for Ce^{+4} in CeO_2 and ~0.78 for Ce^{+3} in CePO_4. Fig. 4 shows a set of EELS spectra of Ce in CZO film from both the surface and the CZO/YSZ interface regions for the samples before and after reducing. The results indicate that some Ce changes from Ce^{+4} to Ce^{+3} after reducing, and the Ce^{+3}/Ce^{+4} ratio is higher at CZO surface than that at the CZO/YSZ interface.

In summary, redox treatment will affect the metal/oxide interaction and hence the shape and size of the particle. In reducing environment, there is a strong metal/oxide interaction between Pd and CZO, which may involve complex mass and charge transportation around the metal/support interface area. The redox treatment will also affect the properties of support surface, such as valance state of cation.

References:
Figure 1. (a) Cross-sectional TEM image of the reduced Pd/CZO model catalyst. (b) HRTEM image shows partial encapsulation of a Pd particle by the CZO support, which indicates a strong metal/oxide interaction.

Figure 2. (a) Cross-sectional TEM image of the reoxidized Pd/CZO model catalyst. (b)-(c) Morphology and microstructure of the hillock on CZO surface while Pd particle is missing.

Figure 3. EDS spectra of Pd particle (top) and CZO surface hillock (bottom), which are obtained from area 1 and 2 in Figure 2(a) respectively using 1nm-spot size electron beam.

Figure 4. EELS spectra of Ce acquired from CZO/YSZ interface (1, 3) and CZO film surface (2, 4) of the sample before (1, 2) and after reducing (3, 4) treatment.