

## Electron Microscopy Characterization of Pd-Ce Interaction on $\alpha$ -Al<sub>2</sub>O<sub>3</sub> Support

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The reforming reaction of CH<sub>4</sub> with CO<sub>2</sub> has motivated numerous studies in search of active and selective catalysts. The endothermic character of this reaction requires a high reaction temperature to obtain acceptable conversion levels. The high operating temperature produces the sintering of metallic particles, and deactivation of the catalyst by the formation and accumulation of carbonaceous deposits. The use of CeO<sub>x</sub> in a Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst reduces the formation of carbonaceous deposits [1,2]. Understanding the role of Ce in the reforming reaction demands a direct visualization of the Ce distribution and a local study of the initial Pd oxidation state.

The CeO<sub>x</sub>-Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst was obtained in two stages. First, the Pd was incorporated to an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Rhone Poulenc, BET area = 10 m<sup>2</sup>/g) by successive impregnation of acetyl acetate of Pd in toluene (3.0 x 10<sup>-3</sup> g Pd/ml) until the content of Pd rose to 1 wt%. Second, the Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst was kept in contact with an aqueous solution of Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> until the content of Ce reached 0.47 wt%. Several microscopes were used at 200 kV at room temperature for elemental mapping, Z-contrast imaging and electron energy-loss spectroscopy (EELS).

Figure 1 shows a zero loss image and the corresponding Ce elemental map. The map clearly shows that Ce is located in the same region of the sample where Pd is present. Figure 2 shows a Z-contrast image of the catalyst, in which a Pd nanoparticle (NP) coexisting with an alumina crystal is clearly observed. EEL spectra were acquired from the positions indicated in the image in order to determine the local oxidation state of Pd. Ce-L<sub>2,3</sub> and Pd-M edges are shown in Figures 2 and 3. Reference spectra for bulk Pd and PdO are included [3] in Figure 3.

The results suggest that the Pd NPs are not oxidized and Ce distributes around the Pd NPs but does not cover the surfaces of the Pd NPs and locates at the Pd interface with the substrate. This is consistent with the small loss of catalytic activity observed after 35 hours reaction and the XPS results obtained for catalysts with similar Ce content observed previously [4].

[1] K. Nagaoka, K. Aika, Bull. Chem. Soc. Jpn., 74 (2001) 1841.

[2] P.G. Schulz et al., Ind. Eng. Chem. Res., 44 (2005) 9020.

[3] C.C.Ahn and L.L.Krivanek, EELS Atlas, ASU Center for Solid State Science, Tempe, AZ; Gatan Inc., Warrendale, PA (1983).

[4] C. E. Gigola et al., Appl. Surf. Sci., 254 (2007) 325

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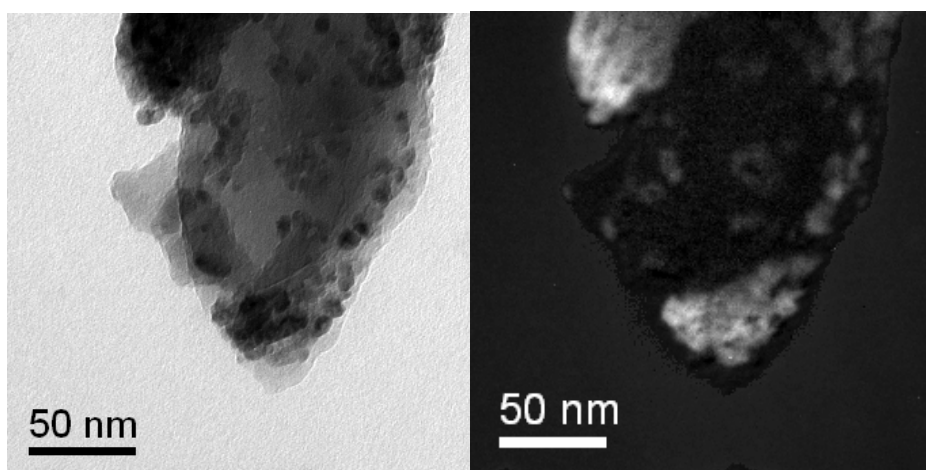


Figure 1. Zero loss filtered image (left) and the corresponding Ce elemental map (right).

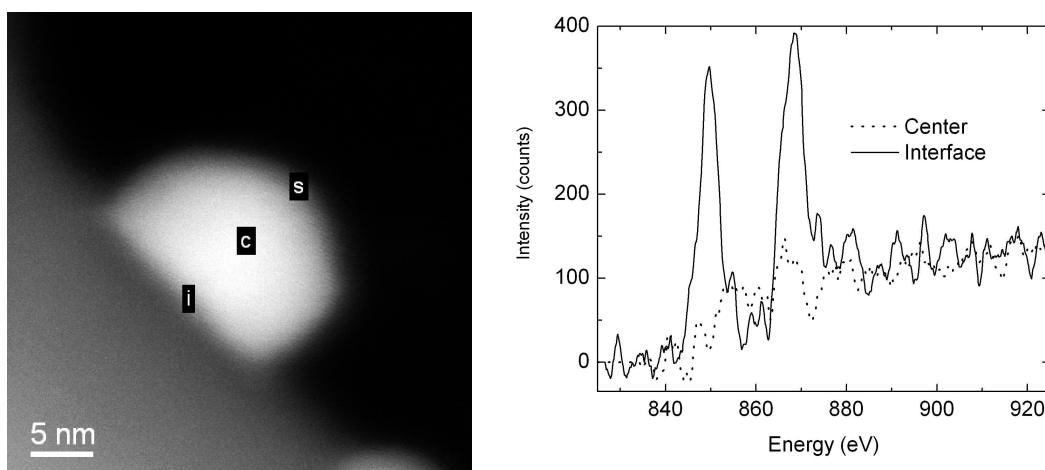


Figure 2. Z-contrast image showing the positions of EEL spectra acquired from a Pd particle (left). EEL spectra of Ce-L<sub>2,3</sub> edge of the single Pd NP acquired from the regions marked (right).

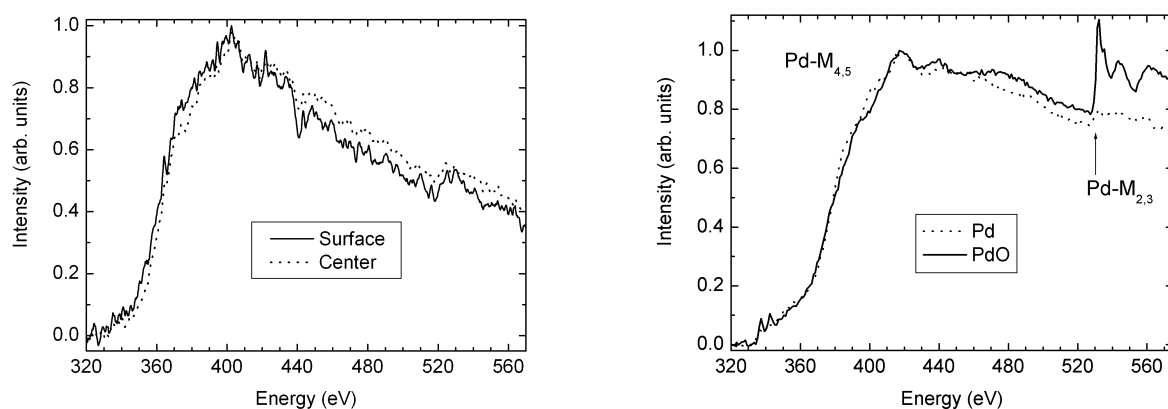


Figure 3. EEL spectra of a single Pd NP showing Pd-M<sub>4,5</sub> (~335 eV) and Pd-M<sub>3</sub> (~520 eV) edges and O-K (532 eV) edge (left). Reference spectra for bulk Pd and PdO (right).