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Spatial Distribution of Cerium Valence in Model Planar $Pd/Ce_{0.7}Zr_{0.3}O_2$ Catalysts

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Cerium oxide is one of the most important and well-studied environmental catalyst materials, due to its widespread use in the three-way catalyst (TWC) for automobile exhaust gas treatment. In the present work, we consider the mixed-oxide, $Ce_{0.7}Zr_{0.3}O_2$, which has long been known to provide bulk lattice oxygen for catalytic reactions, though many details regarding the oxygen extraction process remain unclear. Our approach is to employ electron energy loss spectroscopy (EELS) in the spherical aberration (C_S)-corrected scanning transmission electron microscope (STEM) to map the distribution of Ce^{3+} near Pd particles in cross-sectional specimens made from model planar $Pd/Ce_{0.7}Zr_{0.3}O_2$ catalysts [1].

Single-crystal films of $Ce_{0.7}Zr_{0.3}O_2$, of order 100 nm thick, were grown on the (111) surface of yttria-stabilized zirconia (YSZ) substrates by molecular beam epitaxy, and a monolayer of Pd was deposited on their surfaces by thermal evaporation. Additional thermal treatments were used to simulate the fresh and slightly aged catalyst states in the resulting $Pd/Ce_{0.7}Zr_{0.3}O_2$ model planar catalyst, according to previous TPR results [2]. In the fresh sample, reduced in 10% H_2 at 200 °C, well-dispersed Pd metal particles with average diameter of 5-6 nm cover the surface of the $Ce_{0.7}Zr_{0.3}O_2$ film, as shown in Figure 1a. The distance between adjacent Pd particles appears to be 10-15 nm. EELS spectra taken from the surface to the bottom of the film at various points below the Pd particle, shown in Fig. 1b, reveal a laterally uniform variation in cerium valence, ranging from approximately 80% 3+ at the surface to approximately 40% 3+ beyond a few nanometers below, as shown in Figs. 1c and d. Our most interesting results were obtained from a sample in which simulated aging (5 hours at 700 °C in N_2) was used to promote Pd particle coarsening and a corresponding decrease in areal density of Pd particles, creating a distance of about 100 nm between adjacent particles. In this case, we also used a lower reduction temperature, which, in combination with the lower Pd particle areal density, led to non-overlapping reduction zones associated with each Pd particle. (The large, laterally uniform variation in Ce^{3+} fraction was still found, but only near the surface.) The shape of the reduction zone, shown in Figure 2, is apparently not hemispherical, since it extends farther along the surface than below the Pd particle. Similar results obtained from several other Pd particles showed that the horizontal extent of the reduction zone is in the range of 60-100 nm, and the vertical extent is no greater than 10 nm. The example shown in the bottom of Figure 2 exhibits a slightly wider reduction zone than in the top, possibly due to the larger size of the Pd particle. In summary, our STEM and EELS results provide clear

evidence for distinct bulk and surface processes previously thought to be involved in oxygen release during low-temperature hydrogen reduction of $Pd/Ce_{0.7}Zr_{0.3}O_2$ catalysts.

References

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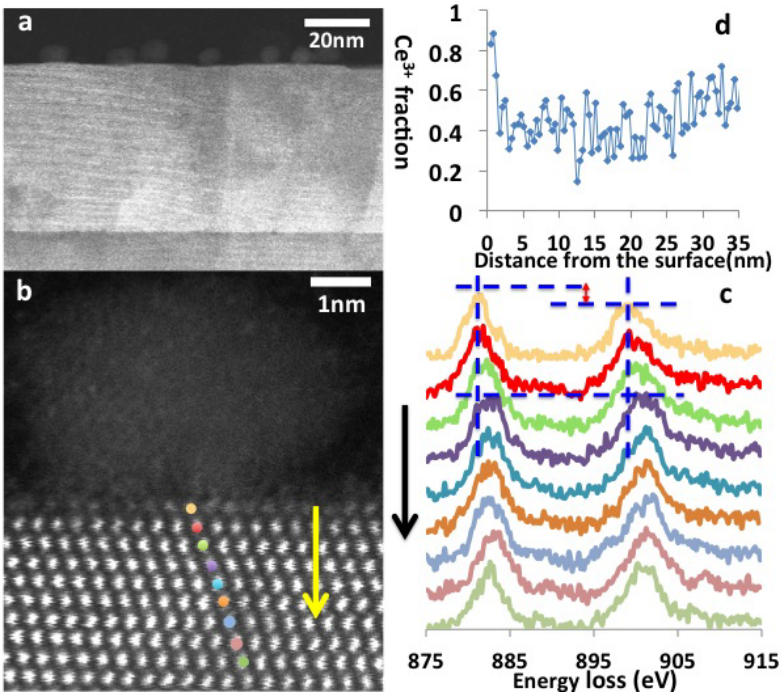

Figure 1. (a) STEM image of a cross section of the fresh catalyst, reduced at 200 °C. (b) Atomic-scale HAADF image of an individual Pd particle and (c) the EELS spectra of Ce taken at the indicated points beneath the particle. (d) The Ce^{3+} fraction derived from an EELS line scan taken from the surface adjacent to a metal particle toward the bulk.

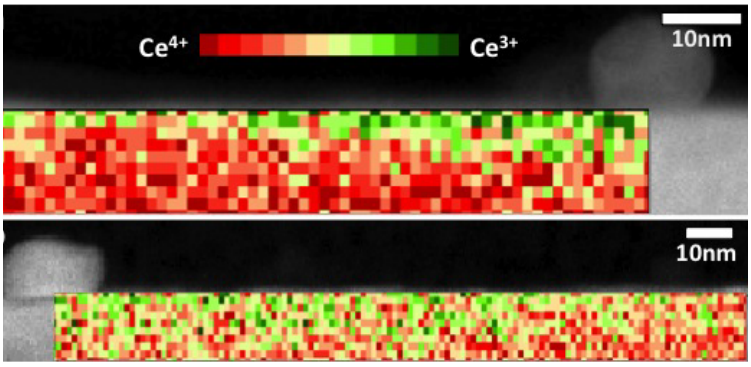

Figure 2. HAADF images of two individual Pd particles with the cerium valence maps from beneath the particles shown superposed.

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