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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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ABSTRACT

The spatial distribution of cerium valence in H_2-reduced model planar Pd/$Ce_{0.7}Zr_{0.3}O_2$ catalysts was determined by electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM). Spherical reduction zones were found beneath each Pd particle, consistent with a Pd-catalyzed, oxygen anion diffusion-limited bulk oxide reduction process. Evidence was also found for a more extended surface reduction process, possibly associated with hydrogen spillover from the Pd particles.

1. Introduction

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 [1]. In the present work, we consider the mixed oxide, $Ce_{0.7}Zr_{0.3}O_2$, variants of which have largely supplanted pure CeO_2 in this application, where the primary purpose of the oxide is to provide a source of oxygen via a Mars-van Krevelen-type mechanism during oxygen-deficient operation of the TWC, and alternately, an oxygen sink under excess-oxygen conditions [2]. The superiority of $Ce_{0.7}Zr_{0.3}O_2$ over CeO_2 arises from the fact that bulk lattice oxygen can easily be extracted from the mixed oxide, whereas only near-surface oxygen is available from CeO_2 [3]. This allows the mixed oxide to function after loss of much of its surface area, which eventually occurs under the most extreme TWC operating conditions.

While the ready availability of bulk lattice oxygen in $Ce_{0.7}Zr_{0.3}O_2$ is fully appreciated in practice, many details regarding its extraction during a catalytic reduction process remain unknown. It is generally believed that catalytic reaction steps occur on, or in close proximity with, the supported metal particles, such as Pd, implying that oxygen ions necessarily diffuse through the oxide toward metal particles, where they are consumed in the oxidation of molecules such as CO or hydrocarbons. As a consequence, oxygen vacancies are inserted into the oxide lattice, which leads to the corresponding reduction of Ce^{4+} to Ce^{3+}. Based on this simple picture, it seems reasonable that a region containing a high concentration of Ce^{3+} should develop within the mixed oxide around each metal particle.

The objective of our work here is to demonstrate that such regions do, indeed, exist. 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, as described below. We believe that ours is the first spatially detailed observation of this phenomenon.

2. Experimental details

Single-crystal films of $Ce_{0.7}Zr_{0.3}O_2$, of order 100 nm thick, were grown on the (1 1 1) surface of yttria-stabilized zirconia (YSZ) substrates by molecular beam epitaxy, as described in detail elsewhere [4]. Following calcination in dry air at 600 °C for 1 h, 1 monolayer of Pd was evaporated onto the films in ultra-high vacuum, and the samples were again calcined in dry air at 600 °C for 1 h. These samples comprise the model planar Pd/$Ce_{0.7}Zr_{0.3}O_2$ catalyst in its fresh, fully oxidized state, previously shown to consist of nanometer-sized PdO particles dispersed on a (1 1 1) surface of $Ce_{0.7}Zr_{0.3}O_2$ [5].

Additional thermal treatments, based on consideration of temperature-programmed reduction (TPR) measurements from

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conventional high-surface-area Pd/$Ce_{0.7}Zr_{0.3}O_2$ catalysts (Fig. S1, Supplementary material), were performed in a quartz tube furnace. These included a low-temperature (150 or 200 °C) reduction treatment in a flowing gas mixture of 1% H_2 in N_2 for 1 h, followed by cooling to at least 30 °C in the same flowing gas mixture. A high-temperature (700 °C) annealing treatment in flowing N_2 for 5 h was employed to decompose the PdO particles initially present in the fresh catalyst and cause the resulting Pd particles to coarsen in one of the samples. In this case, the sample was again calcined in dry air at 600 °C for 1 h in order to restore it to a fully oxidized state before performing the subsequent reduction treatment.

Cross-sectional TEM specimens of all the samples were prepared by conventional methods, ending with mechanical polishing on diamond lapping media, followed by Ar-ion milling (Gatan PIPS, model 691) at 3 kV, 3° angle of incidence, to electron transparency. A Cs-corrected JEOL JEM-2100F TEM equipped with Gatan 863 Tridium Image Filter (GIF) was used to record the STEM image and EELS spectra simultaneously. EELS reference spectra of the Ce $M_{4,5}$ edge were acquired from a CeO_2–$CePO_4$ composite ceramic sample, in which Ce has a valence 4+ in the oxide and 3+ in the orthophosphate. The characteristic differences in these spectra, shown in Fig. 1, provide the basis for our valence mapping. EELS quantification was based on the second derivative of the original spectra, obtained using the Gatan Digital Micrograph software package, assuming a linear relationship between the peak ratio of the second derivative of M_4 to M_5 and cerium oxidation state. (Additional details regarding Ce EELS are contained in the Supplementary material.)

3. Results and discussion

We begin with results from a fresh sample that has been reduced at 200 °C. As shown in Fig. 2a, 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, which is 50–60 nm thick. The distance between adjacent Pd particles appears to be 10–15 nm, but this is actually an underestimate since the TEM specimen itself has a finite thickness, 25–30 nm at the surface in this case (based on attenuation of the zero-loss EELS peak). EELS spectra taken at various points below the Pd particle shown in Fig. 2b, displayed in Fig. 2c, reveal a systematic variation in cerium valence, ranging from approximately 80% 3+ at the surface to approximately 40% 3+ a few nanometers below. In fact, this same variation in Ce^{3+} fraction at the surface, together with a relatively constant value of 40–50% throughout the rest of the film, was generally found in all line scans taken perpendicular to the surface of this sample, as shown in Fig. 2d.

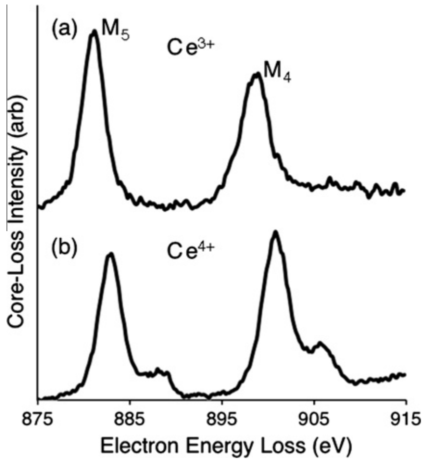

Fig. 1. EELS spectra for the Ce $M_{4,5}$ edge from (a) $CePO_4$ (Ce^{3+}) and (b) CeO_2 (Ce^{4+}).

It is important to emphasize that no Ce^{3+} was found anywhere, including at the surface, in identically treated samples without Pd, as shown in Fig. 3. This simply reflects the catalytic role played by Pd in the low-temperature reduction of $Ce_{0.7}Zr_{0.3}O_2$ (Supplementary material). It also establishes that sample reduction due to electron beam exposure, a known effect that we were able to induce at much higher beam exposures, was not occurring under our experimental observation conditions. (Furthermore, we found no evidence of any reduction of Ce^{4+} due to electron beam exposure in fully oxidized samples containing Pd.)

Our most interesting results were obtained from a sample in which simulated aging (5 h at 700 °C in N_2) was used to promote Pd particle coarsening and a corresponding decrease in areal density of Pd particles, as shown in Fig. 4a. 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. An example is shown in Fig. 4b. The shape of the reduction zone 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 60–90 nm, and the vertical extent is no greater than 10 nm. We also found that the large systematic variation in Ce^{3+} fraction still appears near the surface, even far away from Pd particles, as shown in Fig. 4c.

At the most basic level, our results demonstrate that Pd-catalyzed H_2 reduction of $Ce_{0.7}Zr_{0.3}O_2$ can be studied by STEM/EELS, using cross-sectional samples of model planar catalysts. Clearly, the success of this demonstration hinges on preservation of the reduced state of the mixed oxide during TEM specimen preparation. To that point, X-ray diffraction has previously shown that re-oxidation of reduced Pd/$Ce_{0.7}Zr_{0.3}O_2$ powder catalysts does not occur spontaneously upon exposure of the catalysts to normal ambient conditions (Supplementary material). Further, temperature-programmed oxidation experiments have recently confirmed that this process is thermally activated, with a strong dependence on mixed oxide crystallinity [6]. We conclude that the state of our model planar catalyst, following the low-temperature reduction treatment, is a meta-stable one.

TPR measurements performed on high-surface-area $Ce_{0.7}Zr_{0.3}O_2$ powder show that (1) bulk reduction of this mixed oxide occurs, with most of the lattice oxygen extracted under H_2 reduction conditions between 400 and 600 °C, and (2) there is little effect of oxide surface area on this process (Fig. S1a, Supplementary material). Further, most of this lattice oxygen can be removed at much lower temperature, below 100 °C, through the catalytic influence of supported Pd particles, separated by approximately 10 nm. The majority of this oxygen remains extractable below a somewhat higher reduction temperature, 200 °C, even when the supported Pd particles are separated by a much larger distance, 100 nm (Fig. S1b, Supplementary material). Evidently, oxygen anion diffusion plays an important role in the overall lattice oxygen removal process.

These results appear to be borne out by the EELS results from the fresh model planar Pd/$Ce_{0.7}Zr_{0.3}O_2$ catalyst, shown in Fig. 2, and the Pd-free sample, shown in Fig. 3. That is, the degree and extent of reduction of the $Ce_{0.7}Zr_{0.3}O_2$ film in the catalyst is both large and uniform, as expected in-plane, due to the close spacing of the Pd particles along the surface (of order 10 nm), and in the perpendicular direction, due to the choice of reduction temperature (200 °C) relative to film thickness (50–60 nm). The larger degree of reduction observed within a few nm of the surface is tentatively ascribed to the presence of surface hydroxyl species (*vide infra*). For the sample without Pd, no reduction occurs because the temperature is too low.

By judiciously increasing the separation between Pd particles (of order 100 nm) while lowering the reduction temperature