Encapsulation of Pd particles by ceria–zirconia mixed oxides

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Redox aging above 1000°C of initially high-surface-area (of order 100 m^2/g) cerium-rich ceria–zirconia mixed oxides containing a few wt% Pd results in the loss of most of the surface area and concomitant encapsulation of a substantial fraction of the Pd. The encapsulated Pd exists in the form of metallic particles on the order of 10 nm in diameter held under a large (as much as 3.6 GPa) compressive stress by the mixed oxide. This stress, evidently arising from changes in lattice parameter of the mixed oxide, induced by aging, produces a volume contraction of Pd, which appears as a shift of Pd-peak positions in XRD measurements. Subsequent reduction and reoxidation of the mixed oxide in turn relieves and restores the stress on the Pd particles, which remain metallic throughout, demonstrating that this portion of the Pd is effectively lost for catalytic purposes.

Keywords: particle encapsulation, Pd catalysts, ceria–zirconia mixed oxides

1. Introduction

Encapsulation of metal by support material might reasonably be expected in supported-metal catalysts under conditions where significant loss of support surface area occurs. Such conditions apply to Pd on high-surface-area ceria–zirconia mixed oxides at temperatures of about 1000°C, and, indeed, evidence for encapsulation of Pd particles has been obtained in this case from an unusual effect of the mixed-oxide matrix on Pd-peak positions in X-ray diffraction measurements. It is concluded that a substantial fraction, about one-quarter in a particular instance, of the Pd becomes unavailable for catalysis as a result of the encapsulation.

2. Experimental aspects

A number of supported-Pd catalysts, prepared both in-house and by different commercial suppliers, were examined, and generally similar results were obtained for all ceria–zirconia mixed-oxide compositions made from at least 50 mol% cerium. For illustrative purposes, results are presented here for the often-studied 50–50 composition [1], $Ce_{0.5}Zr_{0.5}O_2$, provided at our request, in powder form, by Johnson Matthey, loaded with 2.25 wt% Pd. Specific surface areas (BET method) and X-ray diffraction (XRD) patterns (using Cu-Kα radiation) were obtained with Micromeritics ASAP 2400 and Scintag X1 instumentation, respectively, following various aging or thermal treatments of the catalyst. Redox aging was performed by 12 h of heating at 1050°C in a flowing gas mixture containing 1 mol% CO/H_2 ($[CO]/[H_2] = 3/1$) alternating every 10 min with 0.5 mol% O_2; the remainder of the mixture consisted of 0.002 mol% SO_2, 10 mol% H_2O, and balance N_2. The redox aging ended with the oxidizing portion of the cycle, followed by 30 min of natural cooling, to about 500°C, under N_2, followed by further natural cooling under air.

3. Results

The specific surface area of the catalyst, 88 m^2/g after calcination at 600°C for 12 h, fell dramatically to only 2.8 m^2/g after redox aging.

The XRD pattern of the catalyst after 600°C calcination reveals only peaks from the mixed oxide, which roughly exhibits a fluorite-type structure [2]. After redox aging, the pattern more nearly reflects the expected tetragonal structure of the mixed oxide, and weak diffraction features due to Pd appear, as shown in figure 1a [2]. A slower scan over the region of the (111) Pd peak after redox aging is shown in figure 2a. Unexpectedly, there are two peaks present, one near 40.1°, the normal position, another near 40.6°. The broader, weaker feature near 41.9° is the (110) PdO peak [2].

Calcination of the redox-aged catalyst at 700°C for 2 h (leading to a state subsequently termed "oxidized") resulted in elimination of the (111) Pd peak near 40.1°, as shown in figure 2b. Subsequent reduction of the catalyst, performed by heating at 500°C for 0.5 h in 1 mol% H_2 (balance N_2), eliminated the (110) PdO peak and replaced the peak near 40.6° with the (111) Pd peak near 40.1°, as shown in figure 2c. An additional effect of reduction on the overall diffraction pattern, shown in figure 1b, is the shift of the mixed-oxide peaks to smaller scattering angles. All of these changes, as reflected in XRD, relative to any of the states formed directly after the redox aging, were found to be reversible upon application of appropriate thermal treatments. For example, the patterns in figures 2a or 2b could be reproduced after

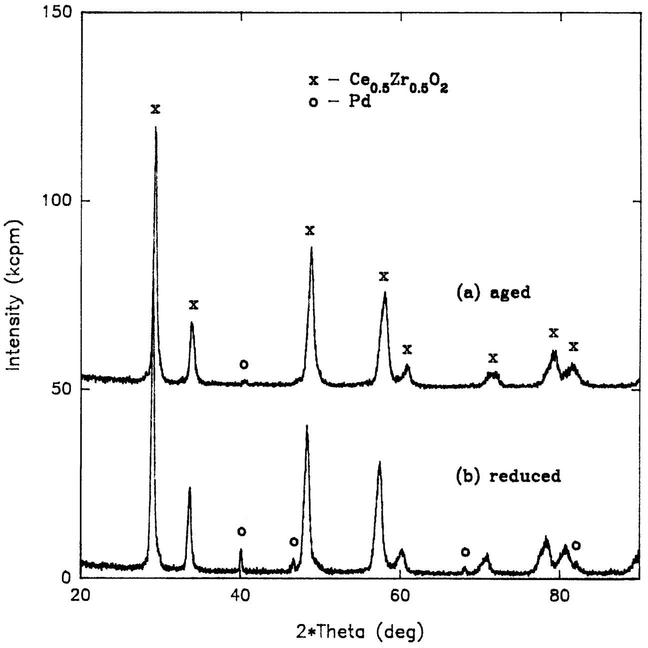

Figure 1. Broad-scan XRD patterns of the catalyst after redox aging (a) and subsequent calcination and reductions steps (b).

subjecting the reduced catalyst to the last half cycle of the redox aging procedure or the 700°C calcination treatment, respectively.

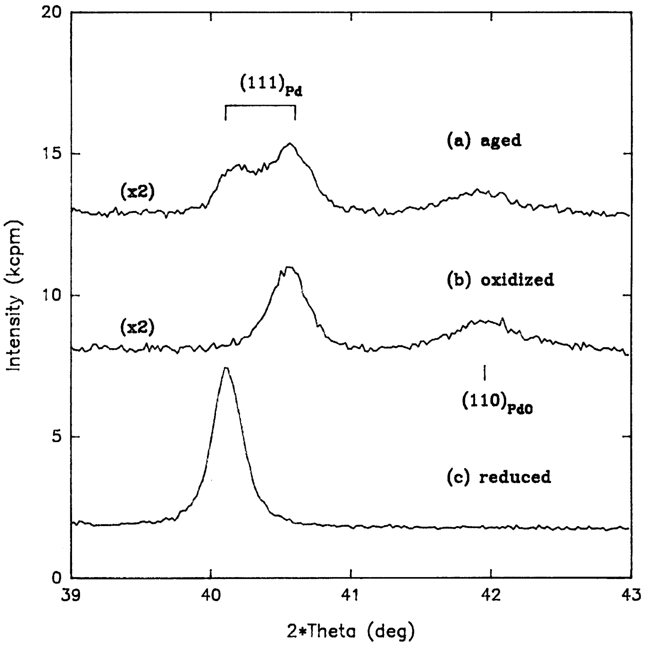

Figure 2. Narrow-scan XRD patterns of the catalyst after redox aging (a), subsequent calcination (b), and finally, reduction (c). The normal position of the (111) Pd peak is 40.1°. The broad feature at 41.9° is the (110) PdO peak.

4. Discussion

The unexpected peak near 40.6° in figure 2a corresponds to the (111) peak of Pd which has been compressed by about 1% in linear dimension or by about 3% in volume. (A corresponding shift of the (220) Pd peak, from near 68.1° to near 68.9°, supports this interpretation of a uniform compression of the fcc lattice.) Such an effect is not consistent with incorporation of interstitial atoms, such as carbon or hydrogen, which cause expansion of the Pd lattice [3]. Similarly, it is not consistent with the replacement of some of the Pd atoms by Ce or Zr since these are larger than Pd. It would be consistent with diffraction from the intermetallic Pd_3Fe, but this possibility was ruled out by chemical analysis.

Assuming that the shift of the Pd peaks is indeed due to a compression of the Pd lattice, it is necessary to account for the origin of the applied stress. A natural explanation is provided by the change in lattice parameter of the mixed oxide due to variation in oxygen stoichiometry over the redox cycle. The magnitude of such a change may be roughly gauged by comparing figures 1a and 1b: following reduction, the increased concentration of Ce^{3+} cations (which are about 10% larger than Ce^{4+} cations) in the ceria–zirconia mixed oxide causes an increase of 0.8% in lattice constant relative to that in the mixed oxide after redox aging. A possible scenario under the redox-aging conditions could thus be as follows: (1) Pd (which is metallic at 1050°C, even under 0.5 mol% O_2) sinters into particles (several tens of nanometers in diameter, judging by the diffraction-peak linewidth), (2) ceria–zirconia alternately expands and contracts under the reducing and oxidizing portions of the cycle as it, too, undergoes sintering, (3) Pd particles gradually become encapsulated by the mixed oxide, which would fully contact the particles, applying no stress when reduced, but a compressive stress when oxidized.

A remarkable aspect of this situation is the magnitude of the residual stress, roughly 3.6 GPa, assuming that the Pd particles are characterized by the usual Pd Young's modulus of 120 GPa [4]. (The stress level could be even higher at 1050°C if the coefficient of thermal expansion of the mixed oxide is much less than that of Pd.) Although large, such a stress is certainly plausible. Assuming a strength of order one-tenth the Young's modulus [5], the related material, ThO_2, would support as much as 10 GPa of stress, for example [6]. (Application of this theoretical-strength estimate would seem appropriate in view of the very small length scale involved.)

From a practical point of view, it is interesting to determine what portion of the Pd in the catalyst is contributing to the XRD pattern. A simulated diffraction pattern, generated by the Scintag software using the nominal composition of the catalyst, provides some confidence that all of the Pd is being observed. Further evidence comes from TGA measurements, which indicate that only about 1.6 wt% Pd undergoes oxidation to PdO, consistent with the fraction deduced from the XRD measurements. It is possible to conclude, then, that this phenomenon of Pd encapsulation in ceria–zirconia mixed oxides represents a significant deactivation mode for such catalysts operating under conditions where substantial loss of surface area occurs.

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