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REDOX BEHAVIOR BELOW 1000K OF Pt-IMPREGNATED CeO_2-ZrO_2 SOLID SOLUTIONS: AN IN-SITU NEUTRON DIFFRACTION STUDY

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ABSTRACT

The $Ce^{3+} \leftrightarrow Ce^{4+}$ redox process in automotive three-way catalysts such as Ce-ZrO_2/Pt provides an essential mechanism to oxygen storage/release under dynamic air-to-fuel ratio cycling. Such a function requires a metal-support interaction which is not completely understood. We have carried out an *in-situ* neutron powder diffraction study to monitor the crystal structures (a mixture of a major tetragonal and a minor monoclinic phase) of 10mol% Ce-doped ZrO_2 with and without Pt (1wt%) impregnation under oxidizing and reducing conditions over the temperature range of 25°-700° C. The samples were heated first in flowing 2%O_2/Ar from room temperature to 400° C and then in 1%CO/Ar to about 700° C. A discontinued increase of the tetragonal unit-cell volume, a decrease of tetragonality (c/a), and a change of color from light yellow to gray when changing from oxidizing to reducing atmosphere were observed only in the sample containing Pt. This result supports the model which assumes the formation of oxygen vacancies initially near the Pt atoms. As more Ce ions are reduced from 4+ to 3+ oxidation states at high temperatures, oxygen vacancies migrate to the bulk of the oxide particles.

INTRODUCTION

The present study is motivated by the need of better support materials for noble metals in the three-way catalytic converters for automotive exhaust gas control, but it is also relevant to a wide variety of applications such as oxygen sensor technology and petroleum reforming. The catalytic systems of interest are noble metals (e. g., Pt) dispersed on cerium doped zirconia fine powders. The exact role of ceria in the promotion of simultaneous NO reduction and CO oxidation under dynamic air-to-fuel cycling of the engine is still not understood. The microstructure of the CeO_2-ZrO_2 solid solutions, and the formation of oxygen vacancies in the crystalline lattice in conjunction with the redox process of the Ce ions are thought to be the important factors.[1] Recently we have carried out a series of studies of high-surface-area rare-earth modified zirconia powders using the method of neutron scattering. The microstructure in terms of primary-particle size, surface area, porosity and fractal aggregates of the oxide supports have been characterized by small-angle scattering.[2] The global crystal phases and the nature of short-range oxygen defects in $Ln_{0.1}Zr_{0.9}O_{2-x}$ (Ln = La, Ce and Nd) were investigated by neutron powder diffraction.[3] In the case of La(III)- and Nd(III)-doped ZrO_2, a real-space correlation function, obtained from a Fourier transform of the filtered residual diffuse scattering, showed evidence of static, oxygen vacancy-induced atomic displacements along the pseudocubic <111> and other directions. No such defects were found in Ce-ZrO_2 because Ce has the same oxidation state (4+) as Zr in the solid solution.

It is well know that high-surface-area ceria may undergo reduction/oxidation cycles according to the reaction $2CeO_2 \leftrightarrow Ce_2O_3 + 1/2O_2$ whereby the Ce valence oscillates between the 4+ and 3+ states. Temperature programmed reduction experiments on pure ceria in hydrogen revealed two reduction peaks at about 500° and 800° C corresponding to reduction of Ce ions on the surface and in the bulk, respectively.[1, 4] Magnetic susceptibility measurements of heat-treated ceria under CO showed a similar result.[5] It is also found that adding alkaline earth and transition-metal oxides to CeO_2 enhances the thermal stability of ceria against sintering at high temperatures. Dispersion of platinum group metals on ceria-containing oxide powders dramatically increases the oxygen storage/release capability of ceria in the simultaneous conversion of CO and NOx to CO_2 (oxidation) and N_2 (reduction). The interaction of platinum with ceria may be rationalized by a model which involves associative adsorption of CO on Pt/CeO_2 followed by a reaction to produce CO_2 and an oxygen vacancy.[1] During this process oxygen is released and Ce 4+ → 3+ transition occurs. Since the difference in the ionic radius of Ce^{4+} (0.80 Å) and Ce^{3+} (1.01 Å) is substantial, a change of the lattice cell volume of the oxide is expected if the transition involves Ce ions in the bulk. In this paper we present the results of an in-situ neutron diffraction study of the redox behavior of a 10 mol% CeO_2-ZrO_2 solid solution with and without Pt over the temperature range of 25°-700° C under an oxidizing or reducing atmosphere.

EXPERIMENTAL DETAILS

The $Ce_{0.1}Zr_{0.9}O_2$ powders, with and without impregnated Pt (1 wt%), were prepared by a coprecipitation method as described elsewhere previously.[6] The fresh powders that were subjected to heating in air for 3-5h showed a BET surface area of ~26 m^2/g and an average particle size of ~21 nm.[2]

The neutron diffraction experiments were carried out using the Special Environment Powder Diffractometer at the Intense Pulsed Neutron Source of Argonne National Laboratory. A powder was compacted to form pellets (cross-sectional diameter of 11 mm) which were stacked to form a column of about 50 mm tall inside the sample tube of a furnace. A flowing-gas (~100-150 ml/min) sample environment was maintained throughout the experiments at all temperatures. The data were collected by detectors situated at mean scattering angles of ±90° for which a resolution of $\Delta d/d = 0.54\%$ can be achieved (d is the atomic plane spacing). By virtue of the highly collimated neutron entrance and exit beams in conjunction with a 90°-scattering geometry, the detectors admit solely Bragg-scattering intensity from the sample. The sample temperature, monitored by thermocouples above and below the sample, were controlled at a selected temperature to within 15°C in all runs. The diffraction data were collected every hour in the following manner for both samples: heating from 25° to 400° C in flowing 2%O_2/Ar gas followed by continued heating from 400° to 700°C in flowing 1%CO/Ar gas. The temperature was stepped at an interview of 50° C and a 20-min wait prior to the data collection was allowed for thermal equilibration at each temperature. At 400°, 500°, 600° and 700° C multiple 1h-data sets were collected. The data were analyzed by the Rietveld refinement technique using the Generalized Structural Analysis System (GSAS) computer code.[7]

RESULTS AND DISCUSSION

Pure ZrO_2 has three polymorphs: a cubic fluorite structure (space group Fm3m) above 2640 K, a tetragonal structure ($P4_2/nmc$) between 1400 and 2640 K, and a monoclinic structure ($P2_1/c$) below 1400 K. The tetragonal and cubic phases over a wide range of temperatures can be stabilized by a small amount of rare-earth solutes. The exact crystal phases and microstructure of rare-earth modified zirconia powders, however, may vary depending on the rare-earth dopant and the processing route.[8] The present samples, regardless of the presence of Pt metal, compose of a major tetragonal phase (74±2 mol%) and a minor monoclinic phase (26±4 mol%). The relative phase fraction did not change with respect to temperature. Fig. 1 shows a diffraction pattern for Ce-ZrO_2/Pt at 400° C in a flowing CO/Ar environment. The general features in the intensity profile are typical to all runs. In particular, the broad peaks and non-Gaussian line shapes indicate the small crystalline grain size and the presence of microstructure. A detailed analysis of the diffraction data of Ce-, La- and Nd-doped zirconia powders has been given in another publication.[3] Contributions to the intensity profiles from the dispersed Pt particles in the Ce-ZrO_2/Pt sample or oxygen-vacancy defects in the reduced samples are too small to be analyzed quantitatively by the Rietveld refinements. All the refinements were made using a nominal sample stoichiometry of $Ce_{0.1}Zr_{0.9}O_2$.

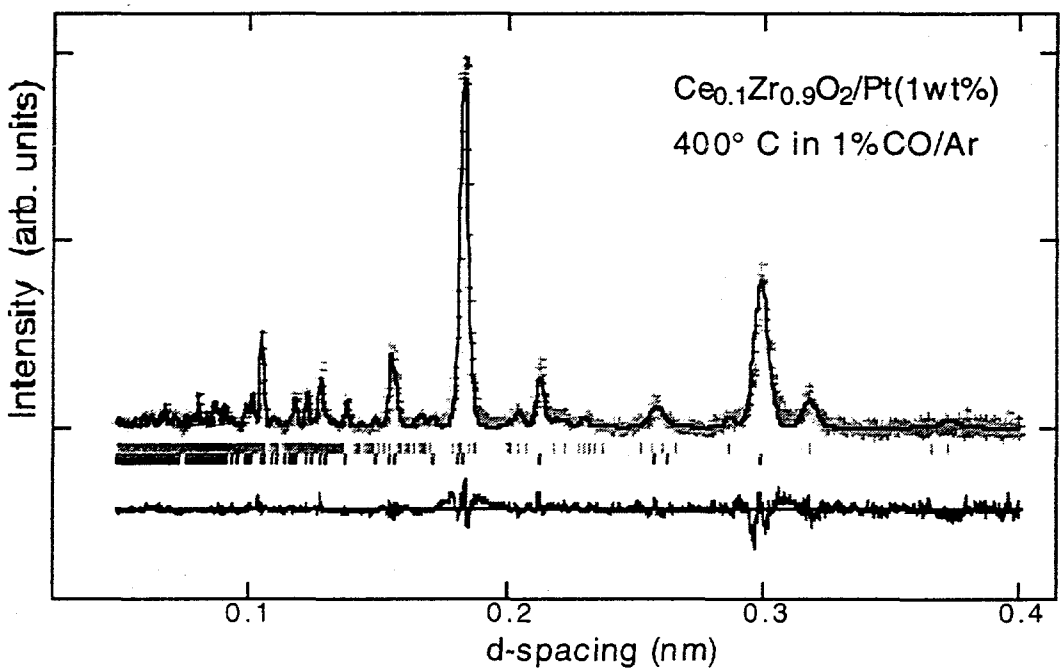

Figure 1. Rietveld profile fit in the 0.04-0.4 nm region of d-spacing for the $Ce_{0.1}Zr_{0.9}O_2$ powder impregnated with 1 wt% of Pt metal at 400° C under a flowing 1%Co/Ar gas environment. The symbols are the observed, background subtracted intensities. The solid line represents the calculated crystalline intensities. The tick marks indicate the positions of the Bragg reflections of the monoclinic (top row) and tetragonal (bottow row) phases. The difference between the observed and calculated intensities is shown at the bottom of the figure.

Fig. 2 shows the lattice parameters of the tetragonal phase of Ce-ZrO_2 and Ce-ZrO_2/Pt as a function of temperature and sample environment. In the case of Ce-ZrO_2 (Fig. 2a) both a and c increase linearly with increasing temperature regardless of the oxidizing atmosphere below 400° C or the reducing atmosphere above 400° C. The small differences in the lattice parameters at 400° C arose from systematic errors in the experiment because the run with O_2/Ar was conducted at a different time from that with CO/Ar. In the case of Ce-ZrO_2/Pt the two runs were conducted in sequence without removing the sample. After the completion of heating the Ce-ZrO_2/Pt sample up to 400° C under O_2/Ar, the sample environment was evacuated and then CO/Ar gas was fed into the furnace tube. Fig. 2b clearly shows an increase of the basal plane lattice parameter a at 400° C after CO/Ar gas was introduced into the system. The lattice parameter c, on the other hand, show little or no increase over the 6h period at 400° C under flowing CO/Ar. An examination of the tetragonality (c/a) of the lattice showed that under oxidizing conditions c/a increased (from 1.018 to 1.019) with temperature from 25° to 400° C for both samples. Under reducing conditions c/a decreased with increasing temperature for both samples, but the decrease was larger for the Ce-ZrO_2/Pt sample.

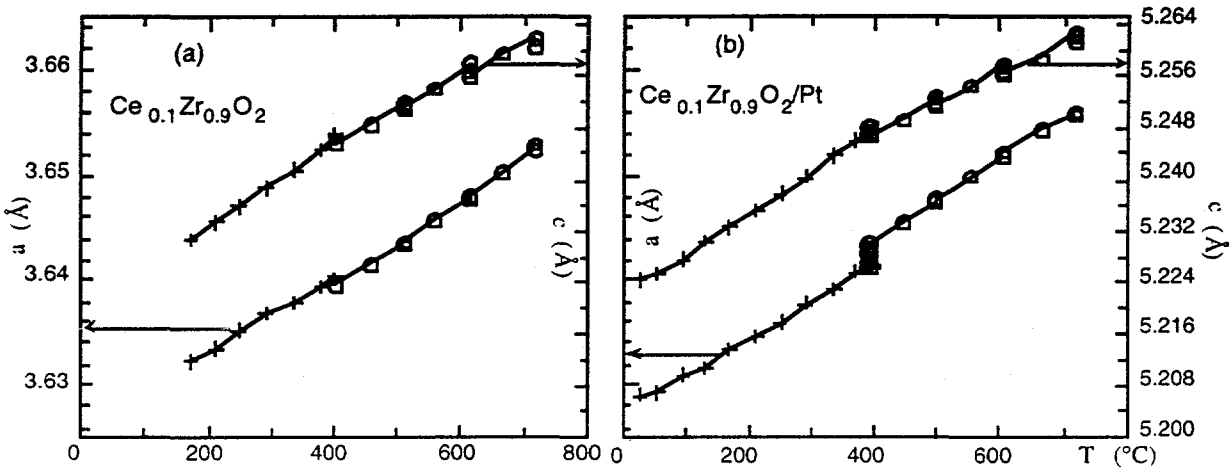

Figure 2. The lattice parameters of tetragonal $Ce_{0.1}Zr_{0.9}O_2$ (a) and $Ce_{0.1}Zr_{0.9}O_2$/Pt (b) versus temperature. The samples were first heated in 2%O_2/Ar (+) and then switched to 1%CO/Ar and continued heating to 700° C (o). Each data point represents 1h data collection.

The unit-cell volumes of the tetragonal and monoclinic phases for Ce-ZrO_2 and Ce-ZrO_2/Pt are shown in Fig. 3. There is an volume increase of ~0.25% only in the Ce-ZrO_2/Pt sample under reducing condition. The effect of the redox of Ce on the monoclinic phase is less clear, perhaps due to the relatively large uncertainties in the refinement of this minor phase. No obvious increase of the lattice volume attributable to the reducing environment is evident from the data. From the Rietveld refinements the volume of the monoclinic phase for the Ce-ZrO_2/Pt sample is slightly larger (~0.15%) than that for the Ce-ZrO_2 sample throughout the whole temperature range. The origin of this difference is not yet understood. More measurements of Ce-ZrO_2 solid solutions over a wide range of compositions have been planned for the future.

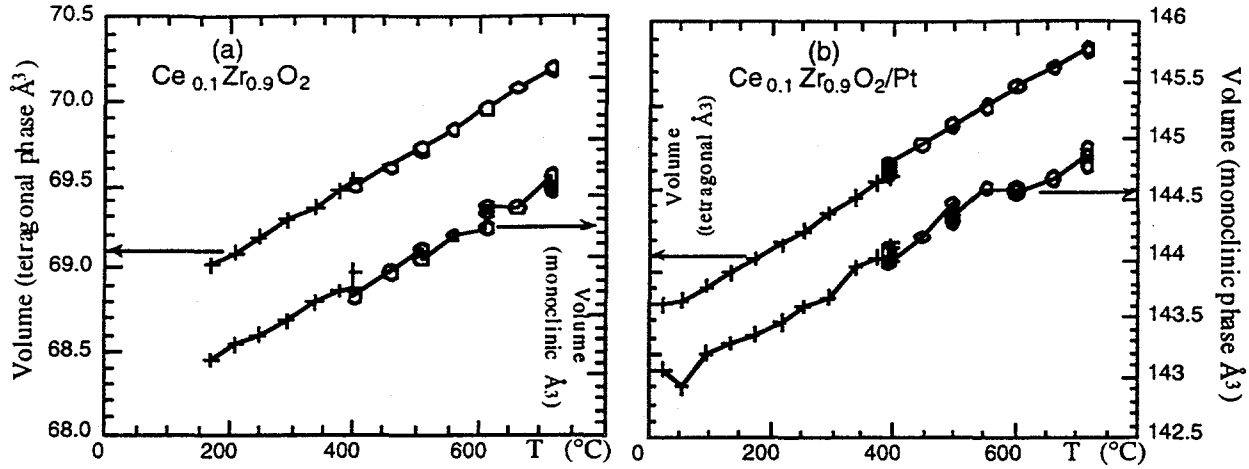

Figure 3. The unit-cell volumes of the tetragonal and monoclinic phases of $Ce_{0.1}Zr_{0.9}O_2$ (a) and $Ce_{0.1}Zr_{0.9}O_2$/Pt (b) versus temperature. The samples were first heated in 2%O_2/Ar (+) and then switched to 1%CO/Ar and continued heating to 700° C (o). Each data point represents 1h data collection.

CONCLUSION

The lattice parameters of the tetragonal and monoclinic phases of $Ce_{0.1}Zr_{0.9}O_2$ with and without Pt impregnation increase linearly with increasing temperature over the 25°-700° C range. From Fig. 1 the thermal expansion coefficients for the tetragonal phase at ~300° C are $\alpha_a = 9.5 \times 10^{-6}$ /°C and $\alpha_c = 13.1 \times 10^{-6}$ /°C. These values are comparable with those reported for Sc, In or Yb stabilized zirconia.[9] Switching from an oxidizing atmosphere for 25°-400°C to a reducing one for 400°-700° C in heating the Ce-ZrO_2 sample does not induce an anomaly in the thermal expansion. Since the observed d-spacing reflects the long-range order structure in the crystalline grains, the lack of anomaly implies that the reduction of Ce ions, if any, occurs mainly on the surfaces the oxide particles. If Ce-ZrO_2 is impregnated with Pt metal, on the other hand, an increase of the axial lattice parameter (c) of the tetragonal phase when switching from oxidizing to reducing conditions was observed. Consequently, the tetragonality decreases. This suggests a gradual (over several hours) conversion of the 4+ to 3+ state of the Ce ions. This process probably occurs initially in the interfacial region between the oxide and Pt particles and then migrates to the bulk of the oxide lattice. This phenomenon can also be seen visually from the change of color (from light yellow before to gray after reduction) only for the Pt-impregnated sample. The original color can be recovered by heating the gray sample under an O_2-rich atmosphere. The origin for the color change in zirconia resulted from heat treatments was a subject of debate previously.[10-12] In the present case, it is undoubtedly caused by the redox process of Ce ions.

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