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Atomic displacement parameters and structural disorder of oxygen ions in the $Ce_xZr_{1-x}O_2$ solid solutions ($0.12 \leq x \leq 1.0$): Possible factors of high catalytic activity of ceria-zirconia catalysts

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Introduction

Ceria-zirconia ($Ce_xZr_{1-x}O_2$) catalysts are widely used in the cleaning of exhaust gases from automobiles. The development of improved catalysts requires a better understanding of crystal structure and oxygen-ion diffusion in ceria-zirconia materials. Here we report a high-angular-resolution synchrotron x-ray powder diffraction study of $Ce_{1-x}Zr_xO_2$ (x=0.12, 0.4, 0.5, 0.6, 0.7, 0.8 and 1.0) to clarify the structural origin of greater catalytic activity of this material. (M. Yashima and T. Wakita, "Atomic displacement parameters and structural disorder of oxygen ions in the $Ce_xZr_{1-x}O_2$ solid solutions ($0.12 \leqslant x \leqslant 1.0$): Possible factors of high catalytic activity of ceria-zirconia catalysts", ***Appl. Phys. Lett.***, **94**, [14] 171902 (3 pages) (2009).).

Experiments

High-angular-resolution synchrotron x-ray powder diffraction analyses ($\delta d/d$ = 0.0022%, where d and δd are the lattice spacing and peak width, respectively) were performed using the multiple-detector system installed at the BL-4B$_2$ beam line of the Photon Factory operated by the High Energy Accelerator Research Organization (KEK), Japan. A monochromatized 1.20645(5) Å x-ray beam was utilized. The crystal structure was refined by the Rietveld method with a computer program RIETAN-2000. Electron-density distribution was studied by a maximum-entropy method (MEM).

Results and discussion

As shown in Fig. 1, the isotropic atomic displacement parameter of the oxygen atoms U(O) in tetragonal $Ce_{1-x}Zr_xO_2$ and cubic CeO_2 was larger than that of Ce and Zr atoms U(Ce, Zr) in the whole compositional range of $0.12 \leqslant x \leqslant 1.0$. The $Ce_{0.5}Zr_{0.5}O_2$ composition has the highest U(O) value in the $Ce_xZr_{1-x}O_2$ solid solutions (x=0.12, 0.4, 0.6, 0.7, 0.8 and 1.0), suggesting higher bulk diffusivity of the oxygen ions in $Ce_{0.5}Zr_{0.5}O_2$ compared with those at other compositions. Figures 2(a), 2(b) and 2(c) show the electron density contour maps on the (100) and (110) planes of tetragonal $Ce_xZr_{1-x}O_2$ (x=0.12 and 0.5) and cubic CeO_2, respectively. The results reveal that the oxygen ions in $Ce_{0.5}Zr_{0.5}O_2$ are spread over a wide area compared with $Ce_xZr_{1-x}O_2$ (x=0.12 and 1.0), which suggest higher bulk diffusivity of the oxygen ions in $Ce_{0.5}Zr_{0.5}O_2$. The greater U(O) and large spatial distribution of oxygen ions in $Ce_{0.5}Zr_{0.5}O_2$ are possible factors of its higher catalytic activity.

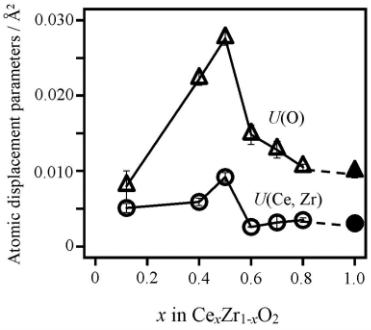

Fig. 1. Composition dependence of isotropic atomic displacement parameters of Ce and Zr atoms U(Ce, Zr) and O atoms U(O) in tetragonal $Ce_xZr_{1-x}O_2$ solid solutions and cubic CeO_2 (x=0.12-1).

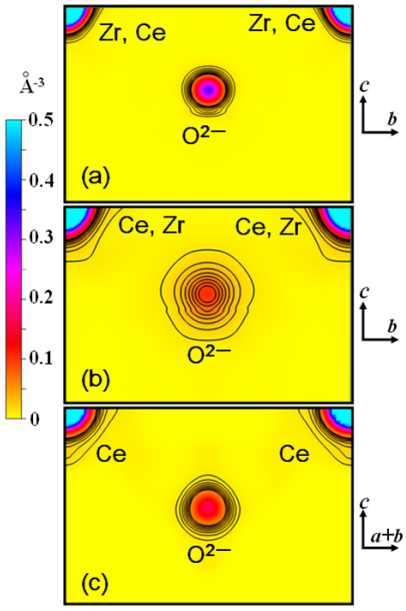

Fig. 2. Parts of electron density distributions on the (100) planes of (a) $Ce_{0.12}Zr_{0.88}O_2$ and (b) $Ce_{0.5}Zr_{0.5}O_2$. (c) A part of electron density distribution on the (110) plane of CeO_2 with black contours in the range from 4.0 to 20.0 Å^{-3} (2.0 Å^{-3} step) at 299 K ($1/2 \leqslant z \leqslant 1$).

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