XAFS ANALYSIS OF THE LOCAL STRUCTURE OF CeO_2-ZrO_2 MIXED OXIDES

Oxygen storage/release capacity (OSC) is one of the important functions required of automobile three-way catalysts (TWCs) in order to efficiently remove harmful compounds such as hydrocarbons, CO and NOx in automotive exhaust gases [1]. In the TWCs, CeO_2 is widely used as a promoter due to its high OSC according to the reversible reaction ($2\ CeO_2 \leftrightarrow Ce_2O_3 + 1/2\ O_2$). However, the OSC performance and the durability of pure CeO_2 are still inadequate for practical use. Recently, our laboratory discovered that the addition of ZrO_2 to CeO_2 would enhance the OSC over that of pure CeO_2 as well as improve the thermal stability [2]. Thereafter, a considerable number of studies on the physical properties and structures of CeO_2-ZrO_2 have been made by many research groups (e.g. [3]). We have improved the OSC of CeO_2-ZrO_2 by modification of the preparation methods (Fig. 1). CZ55-1, CZ55-2 and CZ55-3 have identical composition ratio (Ce/Zr =1), yet they were prepared using different methodologies. Although the CeO_2-ZrO_2 has been widely utilized for commercial catalysts, the key factor in improving OSC is not clearly understood. The purpose of this study is to clarify the relationship between the OSC and the structure of CeO_2-ZrO_2. We investigated the local structure around both of Ce and Zr of these CeO_2-ZrO_2 by XAFS and clarified the cation-cation (cation = Ce, Zr) network at atomic level [4].

Although several groups have reported XAFS analyses on CeO_2-ZrO_2, all of them have utilized Ce L_3-edge (5.7 keV) XAFS [5] while there have been no studies employing Ce K-edge (40.5 keV) XAFS. The usable data region of Ce L_3-edge EXAFS is limited to ca. 3 - 9 $Å^{-1}$ in electron wave number (k) because of the presence of Ce L_2-edge (6.2 keV). Since Ce and Zr contributions to EXAFS signals are remarkable in the high-k part, the XAFS measurement of the Ce K-edge with a wide k-range is necessary in order to obtain the precise information

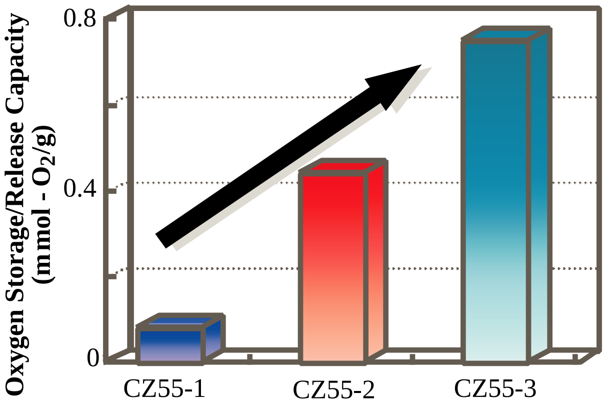


Fig. 1. Improvement of the oxygen storage/release capacity (OSC) of CeO_2-ZrO_2 with the same composition ratio (Ce/Zr =1). The OSC was estimated at 773 K. These samples were prepared by the following methods. CZ55-1 was prepared by the precipitation process using CeO_2 powder and zirconyl nitrate solution. CZ55-2 was prepared by the coprecipitation process using cerium nitrate and zirconyl nitrate solutions. CZ55-3 was synthesized by the heating CZ55-2 at 1473 K under reductive condition.

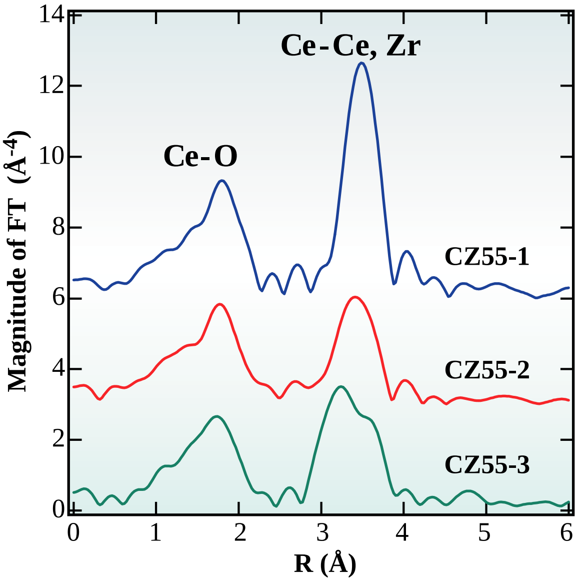


Fig. 2. Fourier-transformed $k^3\chi$ data from Ce K-edge EXAFS.

on Ce-Ce and Ce-Zr bonding. The high-energy X-ray at SPring-8 makes it possible to record XAFS spectra with an excellent signal-to-noise ratio at the *K*-edges of heavy elements [6].

Ce *K*-edge (40.5 keV) and Zr *K*-edge (18.0 keV) XAFS spectra were measured at **BL01B1** and **BL16B2**. Measurements were carried out using a Si (311) double crystal monochromator in a transmission mode at room temperature. The detailed procedure of data reduction have been described elsewhere [7]. Fourier transformations (FTs) were performed on Ce and Zr *K*-edges EXAFS spectra in about 3.0 - 17.0 Å^{-1} region.

The FTs of the Ce *K*-edge EXAFS spectra are presented in Fig. 2. The position and amplitude of the Ce-O peaks for CZ55-1, CZ55-2 and CZ55-3 are slightly different from each other. The CZ55-2 and CZ55-3 exhibit lower Ce-cation (cation = Ce, Zr) peak intensities than that of CZ55-1. Additionally the Ce-cation peak of CZ55-3 appears to have split in two. The FTs of the Zr *K*-edge EXAFS spectra are shown in Fig. 3. Here, the shape of FTs for CZ55-1, CZ55-2 and CZ55-3 are obviously different. According to the results mentioned above, it is thus suggested that the OSC exhibits a significant correlation with the local structure around Ce and Zr. A quantitative curve-fitting analysis was performed for cation-cation shells in FTs to clarify this network. First, the Ce-cation shell for CZ55-1 was fitted with a single Ce-Ce shell, while the Zr-cation shell was also fitted with a single Zr-Zr shell. Thus, CZ55-1 consists of pure CeO_2 and ZrO_2 existing simultaneously (Fig. 4 (a)). Secondly, in the case of CZ55-2, not only Ce-Ce (Zr-Zr) but also Ce-Zr (Zr-Ce) shells were required to obtain an appropriate fit for the cation-cation shell at the Ce (Zr) *K*-edge. The Ce-cation shell was fitted with Ce-Ce (coordination number; CN = 8.0) and Ce-Zr (CN = 3.6) shells. The CN of the Ce-Ce shell is larger than that of the Ce-Zr shell. Likewise the CN of the Zr-Zr (CN = 3.0) was not equal to that of the Zr-Ce (CN = 4.0). This indicates that the CeO_2-ZrO_2 solid solution in CZ55-2 forms, but Ce rich domain and Zr rich one still remain

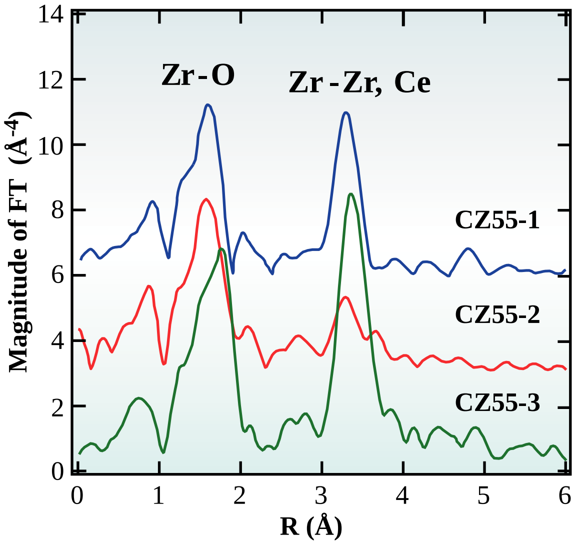
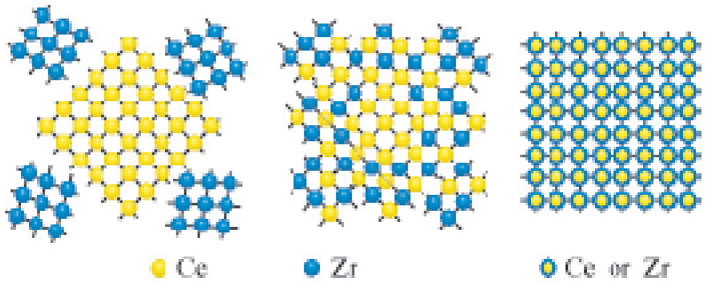


Fig. 3. Fourier-transformed $k^3\chi$ data from Zr K-edge EXAFS.



(a) **CZ55-1** (b) **CZ55-2** (c) **CZ55-3**

Fig. 4. Model illustration of the cation-cation network for the CeO_2-ZrO_2 samples with the same chemical composition (Ce/Zr = 1). CZ55-1 consists of pure CeO_2 and ZrO_2. Ce rich domain and Zr rich one in CZ55-2 still remain. $Ce_{0.5}Zr_{0.5}O_2$ solid solution in CZ55-3 forms homogeneously at the atomic level.

(Fig. 4 (b)). Finally, the Ce-cation shell for CZ55-3 was fitted with Ce-Ce (CN = 6.0) and Ce-Zr (CN = 6.0) shells. The Zr-cation shell also was fitted with Zr-Zr (CN = 6.0) and Zr-Ce (CN = 6.0) shells. The evaluated values correspond with the Ce/Zr composition ratio = 1 of the sample. It is clear that the $Ce_{0.5}Zr_{0.5}O_2$ solid solution in CZ55-3 forms homogeneously at atomic level (Fig. 4 (c)). We conclude from these results that the OSC increases with enhanced homogeneity of the CeO_2-ZrO_2 solid solution at the atomic level.

Thus the relationship between the OSC and the cation-cation network of CeO_2-ZrO_2 has been elucidated, however, the mechanism of the OSC improvement is not yet completely understood. We consider that the configuration of the oxygen around Zr and Ce is modified by enhancing the homogeneity of CeO_2-ZrO_2 solid solution at atomic level. This modification should generate additional active oxygen for the OSC improvement. In order to study this possibility we plan to investigate the oxygen storage/release behavior of homogeneous CeO_2-ZrO_2 solid solution by XAFS and clarify the configuration of oxygen.

Through this research, we have determined an important rule that catalyst design at the atomic level is necessary in order to develop high performance catalysts of practical use.

Yasutaka Nagai[a], Takashi Yamamoto[b] and Tsunehiro Tanaka [b]

(a) Toyota Central R&D Labs., Inc.
(b) Kyoto University

E-mail: e1062@mosk.tytlabs.co.jp

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