XAFS Analysis on Reduction Process of Cerium Oxide

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The cerium species have been characterized during the temperature-programmed reduction (TPR) process under H₂ atmosphere by means of the X-ray absorption fine structure (XAFS) spectroscopy and the X-ray diffraction (XRD) method. The in-situ XAFS measurements revealed that the CeO₂ species was finally reduced to Ce₂O₃ at 900 °C with an intermediate state generated in the temperature rage of 550–750 °C. The absorption edge shift of the X-ray absorption near edge structure (XANES) spectra indicated that the non-stoichiometric compound was formed as the intermediate species, and the estimated composition was CeO₁.₆₅. The in-situ XRD measurements during the TPR process showed the shift of the diffraction lines of CeO₂ above 400 °C, indicating the formation of the non-stoichiometric intermediate. The quantitative analysis of the lattice parameter demonstrated that the crystal plane spacing for the (111) plane of the non-stoichiometric intermediate was expanded by about 0.03 Å than the initial CeO₂ phase.

1. Introduction

Cerium oxide is one of important functional materials because of its excellent property for the oxygen release and storage. A solid solution of CeO₂ and ZrO₂ is actually used as a co-catalyst of so-called three-way catalyst (TWC), which has a high performance to convert harmful substances, such as CO, NOₓ, and hydrocarbons (CₙHₙ), into harmless compounds in automotive emissions. The catalytic performance of TWCs was affected by the air-fuel (A/F) ratio of the exhaust gas. For instance, the NOₓ is effectively converted to N₂ under the fuel rich condition, but the detoxification reactions of CₙHₙ and CO are not favorable under such conditions. On the other hand, the conversions of CO and CₙHₙ effectively proceed under the fuel lean condition, although the detoxification of NOₓ does not operate [1]. Therefore, it is necessary to keep the A/F ratio at an ideal value in order for TWCs to get its high performance. Because the adjustment of the A/F ratio using the detection of an oxygen sensor and the mechanical motion of a flow valve for air intake is not sufficient for the dynamic changeover during the actual operation, it is possible to be finely controlled the A/F ratio to the ideal value by the solid solution of CeO₂ and ZrO₂ with the oxygen storage capacity (OSC) in TWCs. It is recognized that the redox reactions of CeO₂ species contributes to the OSC. However, there has been little study concerning the chemical state characterization for the Ce species [2] under the reaction gas atmosphere under elevated temperatures. Therefore, the in-situ analysis of the chemical state is quite important for understanding of the OSC performance of the CeO₂–ZrO₂ co-catalyst. In addition, the knowledge about the chemical state of the Ce species leads a guiding principle to generate new functional materials for oxide ion conductor, which is necessary electrolyte of solid oxide fuel cells with its enhanced performance.

The X-ray absorption fine structure (XAFS) method is a powerful technique for understanding the electronic state and the local structure of a target element in catalyst samples under a gas atmosphere. For example, the chemical state change of the Co and Ni species supported on SiO₂ under H₂ or O₂ atmosphere has been analyzed by the in-situ XAFS measurements [3–5]. In addition to the short-range information obtained by the XAFS method, the crystal structure and its long-range information is derived by the X-ray diffraction (XRD) method. The in-situ XRD measurements provide the crystal structure change during the reaction process. It is also effective for chemical state analysis of CeO₂ under reaction conditions.

The purpose of this study is to clarify the chemical state change of CeO₂ under the temperature-programmed reduction (TPR) conditions. The in-situ XAFS measurements at the Ce L₃ edge have been carried out under diluted H₂ gas atmosphere, and the crystal structure change has been revealed by the in-situ XRD measurements.

2. Experimental

A standard catalyst of CeO₂ distributed by the Catalysis Society of Japan (JRC-CÉO-01) was used as received in this study. The XAFS measurements were performed at BL-3 of the SR Center (Ritsumeikan University) and BL-9A of Photon Factory (High Energy Accelerator Research Organization: KEK) at the Ce L₃ edge in the
transmission mode. The measurement time to get one XAFS spectrum was 1 min, and the XAFS scans were repeated during the TPR process with the interval time of 1 min. The CeO$_2$ sample was diluted by boron nitride (BN), and two samples with the different mixing ratio (CeO$_2$ : BN = 1.4 : 38.6 and 1.4 : 21.9 in weight) were prepared to check the influence of the BN dilution to the reduction properties of CeO$_2$. The sample powder was set in a flow-type in-situ XAFS cell, and was heated from room temperature to 900 ºC with the increase rate of 10 ºC/min under the diluted H$_2$ gas flow (10 vol% balanced by He) with the flow rate of 100 cm$^3$/min.

The in-situ XRD measurements during the TPR process of CeO$_2$ were carried out with the Ultima-IV diffractometer (Rigaku, Japan) using the Cu Kα line (1.5418 Å). The CeO$_2$ powder was heated up to 600 ºC under the diluted H$_2$ gas flow (10 vol% balanced by He) with the flow rate of 100 cm$^3$/min. The diffraction intensity was recorded over the 2θ range between 25° and 50°. The crystal plane spacing, $d$, was calculated by the Bragg equation.

3. Results and Discussion

The X-ray absorption near edge structure (XANES) spectral change of CeO$_2$ during the TPR process is shown in Fig. 1. The initial spectrum of CeO$_2$ has a double white-line peak at 5726.0 eV and 5732.8 eV, and its absorbance was declined together with the temperature increase. In addition, the absorption edge energy was shifted to the lower side. Finally, the absorption edge and the white line energy were almost in agreement with those of cerium(III) nitrate, but were not perfectly consistent, indicating that the reduction of Ce(IV) was not perfectly proceeded under the current reaction conditions.

The X-ray absorbance at the white line peak of cerium(III) nitrate (5721.6 eV) and at the second peak of CeO$_2$ (5732.6 eV) are plotted in Fig. 2 as a function of temperature for two CeO$_2$ samples diluted by BN with the different mixing ratio. Figure 2 clearly demonstrated that the reduction of CeO$_2$ was started at 300 ºC and the conversion was temporarily stopped at the temperature range of 550–750 ºC. At much higher temperature than 750 ºC, a further reduction was progressed. Because the absorbance change was not terminated at 900 ºC, it was concluded that the reduction to Ce(III) was not completed at 900 ºC. This is a reason why the X-ray energies at the absorption edge and the white line were not matched to those of cerium(III) nitrate as mentioned above. Figure 2 clearly demonstrated that the observed changes for two samples were consistent, thus it was clarified that the reduction temperature of CeO$_2$ was independent to the dilution ratio by BN. The observed data only for the sample with the mixing ration (CeO$_2$ : BN) of 1.4 : 38.6 will be used in the following discussion.

It is well known that the absorption edge energy is a good measure to evaluate the average oxidation state of the Ce element. The observed XANES change during the TPR process was precisely analyzed to estimate the average composition of

![Fig. 1](image1.png)  
**Fig. 1** XANES change during the TPR process from room temperature to 900 ºC. The reference XANES spectra of Ce(NO$_3$)$_3$·6H$_2$O and CeO$_2$ are given for comparison.

![Fig. 2](image2.png)  
**Fig. 2** The change of X-ray absorbance at 5732.6 eV (circles) and 5721.6 eV (squares) for two CeO$_2$ samples diluted by BN with the different mixing ratio of CeO$_2$ : BN = 1.4 : 38.6 (red and blue) and 1.4 : 21.9 (green and black) in weight.
CeO$_2$ on the basis of the average oxidation state of Ce. The absorption edge energy, $E_0$, in this study was set to the X-ray energy at where the absorbance was a half value of the absorbance for the XANES spectrum at 5732.8 eV (the second peak of the double white line) measured at room temperature. The temperature change of $E_0$ and its differential curve are given in Fig. 3.

![Fig. 3](image_url)  
**Fig. 3** The change of $E_0$ (circles) and its differential curve (squares) as a function of temperature during the TPR process.

Two maxima are observed in the differential curve, thus the reduction from CeO$_2$ to finally Ce(III) is concluded to be composed of two steps via an intermediate state. This is consistent with the observed change shown in Fig. 2. The first step is initiated at 300 °C, and the intermediate species is found to form as a transient state at the temperature range of 550–750 °C. Because the $E_0$ value of cerium(III) nitrate is 5717.8 eV, the reached $E_0$ value at 900 °C clearly demonstrates the incomplete reduction by the current TPR process. The $E_0$ value of the intermediate species is located between the values of CeO$_2$ (5720.6 eV) and Ce(III) (5717.8 eV), indicating that the intermediate species takes the non-stoichiometric composition, CeO$_x$ (1.50 < $x$ < 2).

The value of $x$ for the intermediate species was estimated by assuming the linear relationship between $E_0$ and $x$, and was determined to be 1.65 at the temperature range of 550–750 °C. The present in-situ XAFS investigation revealed that the reduction process of CeO$_2$ was described as eq. 1.

$$\text{CeO}_2 \xrightarrow{300^\circ C} \text{CeO}_{1.65} \xrightarrow{550–750^\circ C} \text{CeO}_{1.50}$$  \hspace{1cm} (1)

The in-situ XRD measurement for the TPR process was carried out to analyze the crystal structure of the intermediate non-stoichiometric phase of CeO$_{1.65}$ in the temperature range lower than 600 °C. The highest temperature was limited by the instrumental restriction. The observed XRD patterns are shown in Fig. 4. At all temperatures, two diffraction lines derived from the used Pt holder were observed at 39.8° (111) and 46.2° (200). The slight lower shift of the (111) line is in agreement with the expectation from the thermal expansion of the Pt lattice. The diffraction lines assigned to CeO$_2$ were observed at 28.5° (111), 33.1° (200), and 47.4° (220). These lines also shifted to the lower angle as the temperature increased. Because it was confirmed that the chemical state of CeO$_2$ was kept at lower than 300 °C (see Figs. 2 and 3), the baseline of the angle shift was estimated at this temperature range, and the baseline was subtracted from all diffraction angles. Furthermore, Fig. 4 demonstrated that the diffraction pattern at 600 °C was identical to that of CeO$_2$ at room temperature, indicating that the crystal structure of CeO$_2$ was maintained in the CeO$_{1.65}$ phase.

![Fig. 4](image_url)  
**Fig. 4** The change of XRD pattern of CeO$_2$ during the TPR process. The diffraction lines of sample holder made of Pt were also observed.

The value of crystal plane spacing $d$ was calculated by the Bragg equation using the baseline corrected diffraction angles. The temperature change of $d$ for the (111) plane of CeO$_2$ is illustrated in Fig. 5. The increase of $d$ from 3.127 Å to 3.169 Å was observed in the temperature range from 350 °C to 500 °C, which was consistent with the conversion temperature from CeO$_2$ to CeO$_{1.65}$ as shown in Figs.
2 and 3. The present in-situ XRD experiment has clarified that the crystal plane spacing of CeO$_{1.65}$ is ca. 0.04 Å larger than that of CeO$_2$ (111) plane. The TPR treatment of CeO$_2$ to form the CeO$_{1.65}$ phase produced the O atom defects due to the extraction by H$_2$. The average oxidation number of Ce was reduced from 4 to 3.3, and thus the crystal lattice was reasonably expanded due to the reduction of the Ce sites. Such the lattice expanded and the O atom defected CeO$_{1.65}$ phase is considered to show a good OSC performance and to become a good oxide ion conductor.

4. Conclusions

In this study, the chemical state of the Ce species was investigated by the in-situ XAFS and in-situ XRD measurements for CeO$_2$ during the TPR process. It was revealed that there was an intermediate phase in the reduction process from CeO$_2$ to CeO$_{1.50}$ (Ce$_2$O$_3$) under the H$_2$ atmosphere. The absorption edge shifts revealed that the reduction of CeO$_2$ started at 300 °C and the non-stoichiometric CeO$_{1.65}$ phase was generated in the temperature range of 550–750 °C as an intermediate state. The corresponding phase change from CeO$_2$ to CeO$_{1.65}$ was observed by the in-situ XRD measurement at the consistent temperature range with the in-situ XAFS measurements. The temperature dependent angle shift of the diffraction line successfully revealed the lattice expansion of ca. 0.04 Å for the CeO$_{1.65}$ phase. These results provide the sufficient evidences for the formation of the lattice expanded and the O atom defected CeO$_{1.65}$ phase during the TPR process.

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References