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 H_2 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 CeO_2 species was finally reduced to Ce_2O_3 at 900 ºC with an intermediate state generated in the temperature rage of 550–750 ºC. 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 $CeO_{1.65}$. The *in-situ* XRD measurements during the TPR process showed the shift of the diffraction lines of CeO_2 above 400 ºC, 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 CeO_2 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 CeO_2 and ZrO_2 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, NO_x, and hydrocarbons (C_mH_n), 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 NO_x is effectively converted to N_2 under the fuel rich condition, but the detoxification reactions of C_mH_n and CO are not favorable under such conditions. On the other hand, the conversions of CO and C_mH_n effectively proceed under the fuel lean condition, although the detoxification of NO_x 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 CeO_2 and ZrO_2 with the oxygen storage capacity (OSC) in TWCs. It is recognized that the redox reactions of CeO_2 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 CeO_2–ZrO_2 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 SiO_2 under H_2 or O_2 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 CeO_2 under reaction conditions.

The purpose of this study is to clarify the chemical state change of CeO_2 under the temperature-programmed reduction (TPR) conditions. The *in-situ* XAFS measurements at the Ce L_{III} edge have been carried out under diluted H_2 gas atmosphere, and the crystal structure change has been revealed by the *in-situ* XRD measurements.

2. Experimental

A standard catalyst of CeO_2 distributed by the Catalysis Society of Japan (JRC-CEO-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 L_{III} 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.

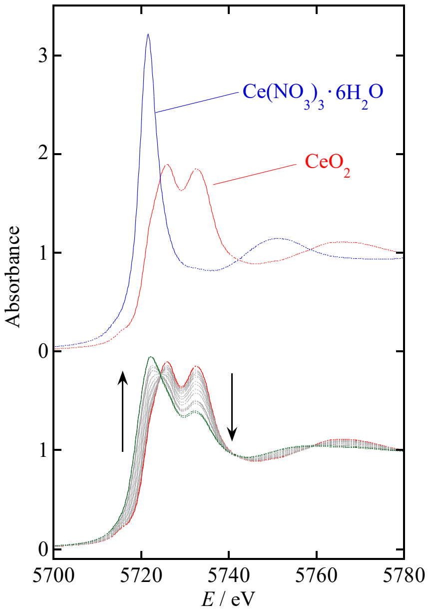

Fig. 1 XANES change during the TPR process from room temperature to 900 ºC. The reference XANES spectra of $Ce(NO_3)_3•6H_2O$ and CeO_2 are given for comparison.

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

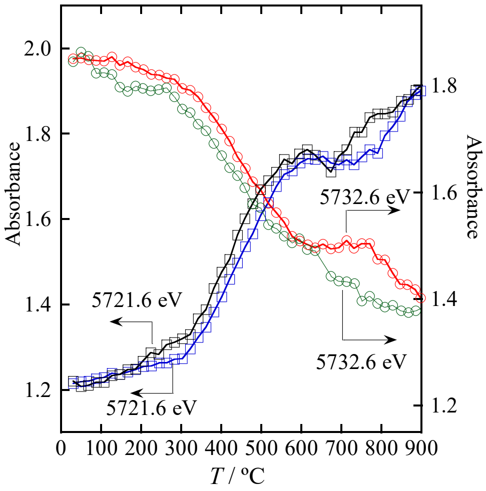

Fig. 2 The change of X-ray absorbance at 5732.6 eV (circles) and 5721.6 eV (squares) for two CeO_2 samples diluted by BN with the different mixing ratio of CeO_2 : BN = 1.4 : 38.6 (red and blue) and 1.4 : 21.9 (green and black) in weight.

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.

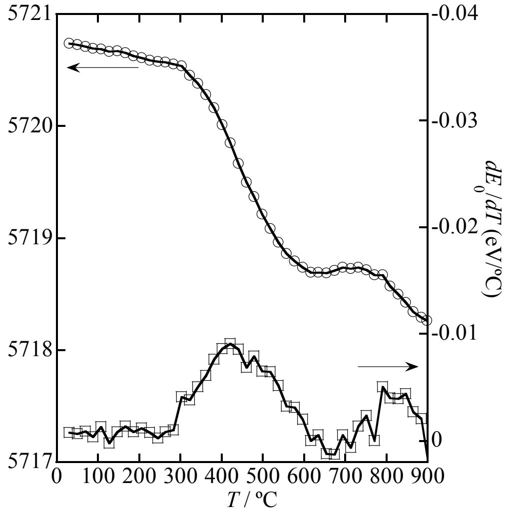

Fig. 3 The change of E_0 (circles) and its differential curve (squares) as a function of temperature during the TPR process.

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.

$$\mathrm{CeO_2} \rightleftharpoons \mathrm{CeO_{1.65}} \rightleftharpoons \mathrm{CeO_{1.50}} \qquad (1)$$

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.

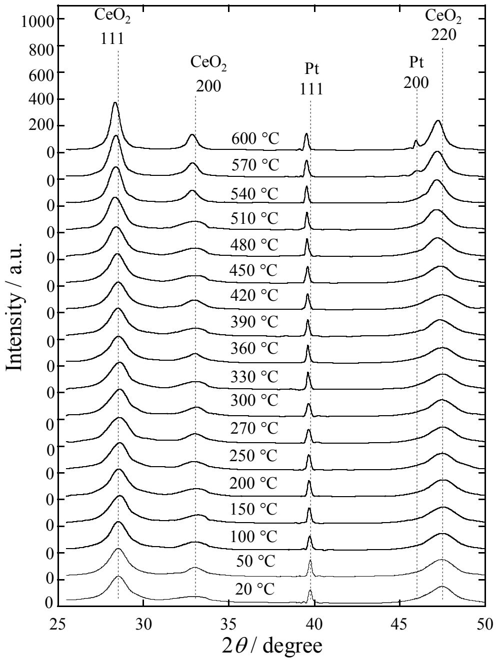

Fig. 4 The change of XRD pattern of CeO_2 during the TPR process. The diffraction lines of sample holder made of Pt were also observed.

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) plain. 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.

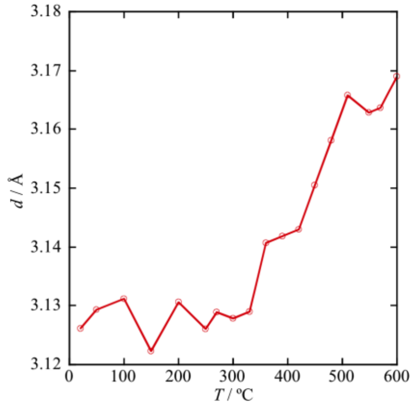

Fig. 5 Temperature change of the crystal plane spacing of the (111) place during the TPR process.

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_2O_3) under the H_2 atmosphere. The absorption edge shifts revealed that the reduction of CeO_2 started at 300 ºC and the non-stoichiometric $CeO_{1.65}$ phase was generated in the temperature range of 550–750 ºC 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.

Acknowledgement

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