

Chemical State Analysis of Cerium Oxide under H₂ atmosphere by Means of XAFS-XRD Simultaneous Measurement

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1 Introduction

Cerium oxide is one of the important functional materials for exhaust gas purification because of its excellent property for the oxygen storage and release [1]. It is important for understanding this property to analyse the chemical state conversion and crystal structure change of the Ce species under reaction conditions. The XAFS technique is a powerful tool for chemical state analysis, and it provides the short-range information. On the other hand, the long-range information is available using the XRD technique. Therefore, the XAFS-XRD simultaneous measurement of CeO₂ under the reaction condition leads to clarify the chemical conversion during the oxygen storage/release process. The purpose of this research is to evaluate the chemical state and crystal structure change of CeO₂ during the temperature-programmed reduction (TPR) process.

2 Experiment

The *in-situ* XAFS-XRD simultaneous measurements of standard CeO₂ were performed at BL-15A1 of Photon Factory (KEK). The CeO₂ powder diluted by BN was heated from room temperature to 1020 °C under H₂ atmosphere. The XAFS measurements were performed by the transmission mode over the range from 5500 to 6150 eV. After the XAFS measurement, the X-ray energy was set to be 6150 eV for the XRD measurement. The intensity of diffraction X-rays was recorded by the PILATUS 100K.

3 Results and Discussion

The lower energy shift was observed for the Ce L_{III}-edge during the TPR process, and the final edge energy became almost comparable to that of the Ce(III) species. In addition, the diffraction line derived from Ce₂O₃ was appeared at 1020 °C. These results indicated that CeO₂ reduced to Ce₂O₃. The absorption edge energy (E_0) and the XRD angle (2θ) are plotted in Figure 1 as a function of temperature. It was found that the reduction of CeO₂ proceeded at two temperature range, 390-570 °C and 780-1020 °C.

The intermediate state was found to generate in the temperature range from 570 to 780 °C, and there was no XRD lines of Ce₂O₃. It means that the intermediate state disagrees with the mixture of CeO₂ and Ce₂O₃, and it is thus assigned to the non-stoichiometric compound represented by CeO_{*x*} (1.50 < *x* < 2). The value of *x* was estimated to be 1.73 according to the E_0 shift. The spacing of (111) plane of CeO_{1.73} is *ca.* 0.03 Å larger than that of

CeO₂. The formation of the non-stoichiometric CeO_{1.73} phase expands the plane spacing because of the partial reduction of the Ce sites.

The present *in-situ* XAFS-XRD simultaneous measurement revealed that the reduction process of CeO₂ was expressed as eq. 1.



This study provides the formation conditions of the CeO_{1.73} phase with the O atom defects during the TPR process.

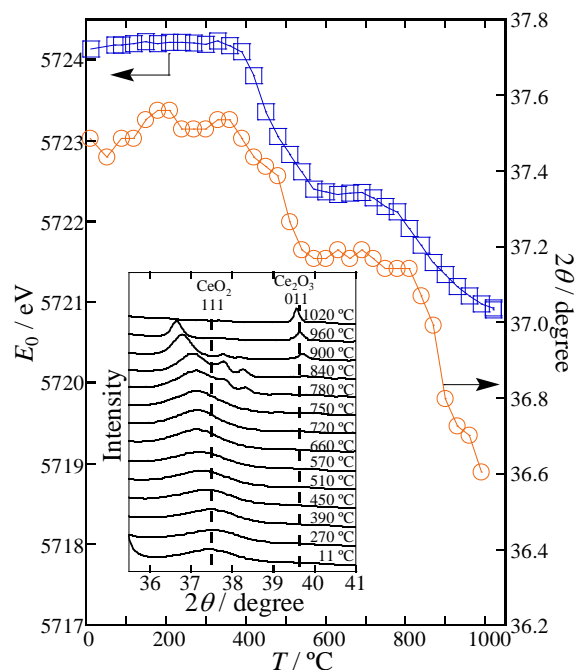


Figure 1. The shifts of absorption edge energy (E_0) and diffraction line angle (2θ angle of CeO₂ 111 reflection) during the TPR process of CeO₂. The XRD patterns at some temperatures were inserted.

References

[1] J. Kašper, P. Fornasiero, and M. Graziani, *Catal. Today*, **50**, 285 (1999).

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