

Ce L_{III}-edge XANES Study on Valence of alumina-supported cerium oxide

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Introduction

Cerium atom in oxides usually exists as Ce(III) or Ce(IV) and the ratio of them can be determined quantitatively by XANES spectroscopy. In the previous study, we examined series of silica-supported cerium oxide samples and concluded that Ce atoms would mainly exist as Ce(III) when they are highly dispersed on silica support.¹

In the present study, series of alumina-supported cerium oxide samples were examined by Ce L_{III}-edge XANES spectroscopy in order to obtain the ratio of Ce(III) and Ce(IV), and also to compare them to the silica-supported ceria system.

Experimental

Alumina-supported ceria samples were prepared by impregnation method. Alumina was a reference catalyst donated from the Catalysis Society of Japan, JRC-ALO-8, which specific surface area was 163 m²g⁻¹. Alumina support were impregnated with an aqueous solution of cerium nitrate (Kishida), dried at 383 K in an oven overnight and calcined at 773 K in a flow of dry air for 5 h. CeO₂ and Ce(NO₃)₃ sample was commercially obtained and employed as reference compounds.

The Ce L_{III}-edge XANES measurement was performed at room temperature in transmission mode (Ce > 1 mol%) and fluorescence mode (Ce < 1 mol%) at the BL-9A station of KEK-PF, Tsukuba, Japan, with a Si(111) double-crystal monochromator. Before recording XANES spectra, the sample was pretreated with 100 Torr oxygen for 1 h at 773 K, followed by evacuation for 1 h at 773 K. Then the sample was sealed with a polyethelene film in a dry atmosphere.

DR UV-vis spectra were recorded at room temperature on a JASCO V-570 equipped with an integrating sphere covered with BaSO₄. Before recording a UV-vis spectrum, the sample was pretreated like the one before recording the XANES spectra. Thus, the sample was transferred to the optical cell without exposure to atmosphere by using a specially designed in-situ cell.

Results and discussion

For analysis of XANES spectra, Ce(NO₃)₃ is used as Ce(III) reference and CeO₂ is used as Ce(IV) reference. XANES spectra of samples with low loading of Ce on alumina support showed the dominant peak of Ce(III), while high loading samples showed peaks similar to CeO₂. It is suggested that in the sample of low loading, Ce would be highly dispersed on the support and mainly exist as Ce(III), while the Ce would mainly exist as Ce(IV) cation like as CeO₂ at high loading samples.

The results from XANES spectra are in agreement with those from DR UV-Vis spectra. High loading samples exhibited a large band, where the absorption edge shifted to shorter wavelength than that for CeO₂ as results of quantum size effect, suggesting that the Ce species in high loading samples would be nano-sized CeO₂ particles. Samples with low loading of Ce exhibited an absorption band at 265 nm, which was assignable to Ce(III) species.¹ These similar trends were also found in silica-supported ceria samples.¹ Even though in many cases Ce⁴⁺ would be dominantly exist due to its stability, we confirm here that the formation of Ce³⁺ is possible specially at low loading of Ce, as also reported in some literatures.^{2,4}

The deconvolution of XANES spectra was carried out according to the method in the previous study.¹ Fig 1 showed the comparison of Ce(III) ratio between silica-supported ceria samples and alumina-supported ceria samples. Among samples with the same loading of Ce (< 0.1 mol%), alumina-supported ceria samples showed higher Ce(III) ratio than silica-supported ceria samples did. The stabilization of Ce³⁺ may be related to the strong interaction between ceria and alumina, which lead the formation of CeAlO₃.^{2,3}

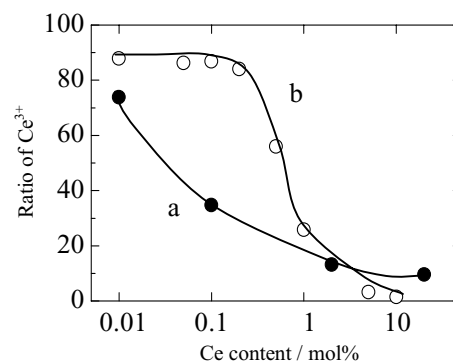


Fig 1. The plot of Ce³⁺ ratio versus Ce content. The samples are a) the Ce/SiO₂ and b) Ce/Al₂O₃. The ratio was determined by curve fitting analysis of Ce L_{III}-edge XANES. The data on silica-supported ceria samples were from ref. 1.

References

- [1] H. Yoshida et al., Mater. Trans., **45** (2004) 2062.
- [2] J. Z. Shyu et al., J. Phys. Chem., **92** (1988) 4964.
- [3] A. Piras et al., Appl. Catal. B., **28** (2000) L77.
- [4] G. K. DasMohapatra, Mater. Lett., **35** (1998) 120.

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