

Ce L_{III}-edge XANES Study on Valence of Highly Dispersed Ceria Supported in Silica

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Introduction

In silica matrix, Ce atom may exist as Ce (III) or Ce (IV), depends on the Ce concentration and preparation method. These species show each UV absorption band. However, unfortunately, the assignment of the absorption band for each species has not been determined yet and some literatures show the variations of the assignment.¹⁻²

Ce L_{III}-edge XANES spectroscopy has been proposed as a useful method for the quantitative determination of the ratio of Ce(III) and Ce(IV), since both species exhibit each distinguishable absorption peaks.³ In the present study, a series of SiO₂-CeO₂ samples were studied by Ce L_{III}-edge XANES through a curve fitting analysis in order to know the ratio of Ce(III) and Ce(IV) and assignment of the UV absorption band for these species on silica.

Experimental

Amorphous silica (SiO₂, powder) was prepared from Si(OEt)₄ by sol-gel method followed by calcination in a flow of air at 773 K for 5 h. Silica-supported cerium oxide samples, Ce/SiO₂, were prepared by impregnation an aqueous solutions of Ce(NO₃)₃ and heated to dryness. Then, the obtained powder was dried at 383 K for 12 h in an oven and calcined at 773 K in a flow of 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 r.t. in transmission/fluorescence mode at the BL-9A (and BL-7C for some samples) of KEK-PF with a Si(111) double-crystal monochromator. Before measurement, the sample was treated with 60 Torr of oxygen at 773 K for 1 h, followed by evacuation at 773 K for 1 h and sealed with polyethylene film in dry atmosphere.

Diffuse reflectance UV-vis spectra were recorded at room temperature on a JASCO V-57. Before recording a UV-vis spectrum, the sample was treated with 100 Torr of oxygen at 773 K for 1 h, followed by evacuation at 773 K for 1 h. Thus, the sample was transferred to the optical cell without exposure to atmosphere by using a specially designed in-situ cell.

Results and discussion

As shown in Fig. 1, the samples containing smaller amount of Ce showed Ce(III) peak dominantly with Ce(IV) peak as minor, while the samples of high content

exhibited similar spectra to that of CeO₂. The ratio of Ce(III) in the Ce/SiO₂ samples has been determined quantitatively by curve fitting analysis of XANES.⁴

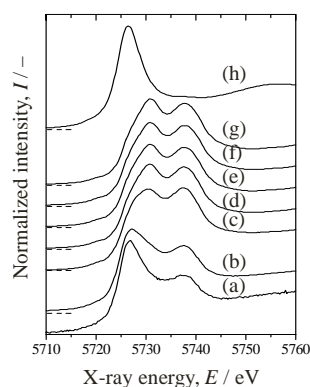


Fig. 1 Normalized Ce L_{III}-edge XANES of the Ce/SiO₂ samples containing (a) 0.01, (b) 0.1, (c) 2, (d) 4, (e) 8 and (f) 20 mol % of Ce, with reference compounds (g) CeO₂ for Ce(IV) and (h) Ce(NO₃)₃ for Ce(III).

The UV absorption band of the Ce/SiO₂(0.01) sample seems closed to be symmetric (Fig. 2a), suggesting almost one kind of species is there. Since the major species on this sample was elucidated to be Ce(III) oxide species, it is proposed that the absorption band at 265 nm is assignable to Ce(III) oxide species that would be highly dispersed on silica.

On the other hand, Ce(IV) species as major species in CeO₂ nano-particles dispersed on silica exhibited similar absorption to that of the bulk CeO₂ (Fig. 2d and 2e). The Ce/SiO₂(2) sample showed two shoulders at 265 nm and 300 nm (Fig. 4c). The former at 265 nm would be assignable to Ce(III), and the latter at 300 nm would be assignable to Ce(IV) in CeO₂ nano-particle.

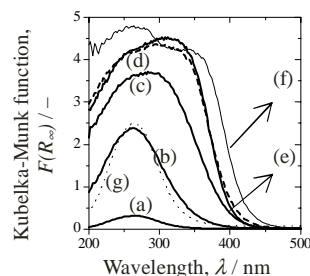


Fig. 2 Diffuse reflectance UV-visible absorption spectra of the Ce/SiO₂ samples containing (a) 0.01, (b) 0.1, (c) 2, (d) 4 and (e, broken line) 20 mol % of Ce, and (f, thin line) CeO₂. The spectrum (g, dotted line) was obtained from curve (a) multiplied by 8.

References

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