

XAFS analysis on the unusual promoting effects of ceria

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INTRODUCTION

Ceria(CeO_2) is one of characteristic supports which has surface area of more than $60 \text{ m}^2 \text{ g}^{-1}$. It easily operates oxidation-reduction cycles. We recently observed that Ru/ CeO_2 has revealed an unusual catalysis for the reaction between C_3H_6 and N_2O . A XAFS analysis of Ru(K-edge) has been done to clarify the interaction between Ru and CeO_2 .

EXPERIMENTAL

$\text{Ce}(\text{OH})_3$ was precipitated from aqueous $\text{Ce}(\text{NO}_3)_3$ with NaOH at pH of about 11. The filtrate while it is wet, was dispersed in deionized water. A known amount of RuCl_3 was added followed by introducing HCHO under stirring at 90°C for 1 h. Then 3 N-NaOH was added to the mixture until the pH of the solution was about 11. The solid portion was filtered and washed with deionized water followed by drying at 80°C overnight and calcination at 500°C for 3 h in air. Two samples were prepared: (1) 18 wt% $\text{RuO}_2/\text{CeO}_2$ was reduced with H_2 at 200°C for 2 h, and (2) this was reoxidized at 300°C for 1 h. X-ray absorption spectra were obtained with the Beam Line 10B (Ru K-edge) station by a transmission mode.

RESULTS AND DISCUSSION

Fig. 1A shows the normalized Ru K-edge XANES spectra of Ru(0)(metal), Ru(III)(NO_3)₃ and Ru(IV) O_2 as standard samples. As the valence of Ru increases, the energy of Ru K-edge was shifted to higher energy. As shown in Fig. 1B, Ru of the original $\text{RuO}_2/\text{CeO}_2$ exists in RuO_2 , and Ru on CeO_2 after treated with H_2 is in a modestly reduced state, but not in the zero valence. Ruthenium must be bonded to CeO_2 via Ru-O-Ce. When the reduced Ru/ CeO_2 was oxidized in oxygen, all of Ru didn't return to $\text{RuO}_2/\text{CeO}_2$; the oxidized and reduced Ru species coexist. Judging from the relationship between valence of Ru and K-edge energy shift in Fig. 1(A), half of Ru is estimated to be oxidized. This means that the

oxidized Ru is highly dispersed on the surface of CeO_2 . The still reduced Ru species are in the bulk.

The synergistic effects of oxidation–reduction couples of Ru species and oxygen release-storage properties of CeO_2 showed an unusual reaction between C_3H_6 and N_2O to give C_2H_4 .

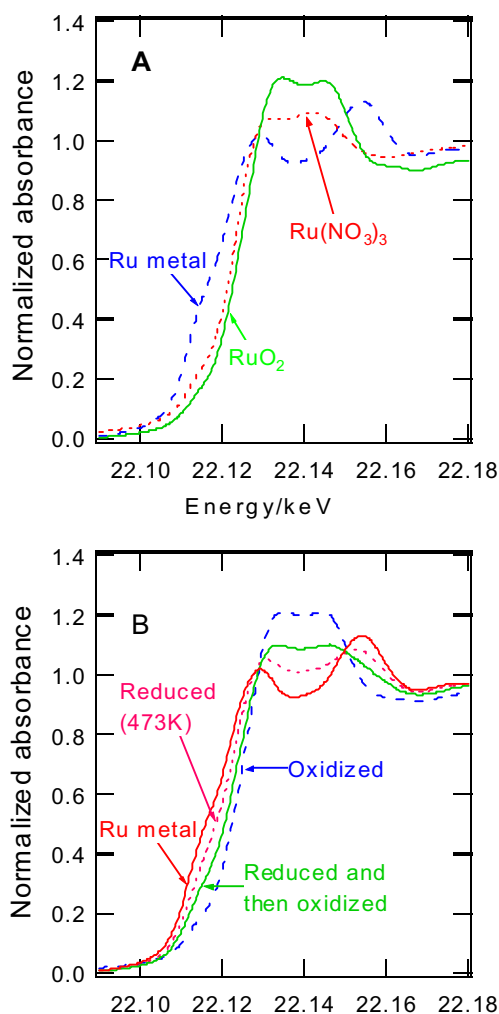


Fig. 1 Normalized XANES spectra of Ru (K edge).
A: standard samples, B: 18wt% Ru/ CeO_2 .

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