

XAFS Analysis of FeO<sub>x</sub> promoted Ir/SiO<sub>2</sub> CatalystsKyoko K. Bando<sup>1,\*</sup>, Nobuyuki Ichikuni<sup>2</sup>, and Ji-Qing Lu<sup>3</sup><sup>1</sup>National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan<sup>2</sup>Chiba University, Inage-ku, Chiba 263-8522, Japan<sup>3</sup>Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China

### 1 Introduction

Selective hydrogenation of  $\alpha$ ,  $\beta$ -unsaturated aldehyde to  $\alpha$ ,  $\beta$ -unsaturated alcohol is one of the key reactions for synthesis of various fine chemicals [1]. However, it is hard to overcome the problems like low selectivity and severe deactivation of catalysts [2]. Recently Lu et al has developed a new catalyst which is composed of FeO<sub>x</sub>-promoted Ir/SiO<sub>2</sub>, which showed excellent activity and stability. It was also found that the catalytic performance varied depending on the preparation procedure, even though the composition of the catalysts was the same. In this work, we conducted XAFS analysis of these catalysts to find out the structural difference between them and to elucidate the key factor which determines the catalytic performance.

### 2 Experiment

FeO<sub>x</sub> promoted Ir/SiO<sub>2</sub> catalysts were prepared using an impregnation method. The nominal content of Ir was 3 wt. %. The catalysts were designated as 3Ir-xFe/SiO<sub>2</sub>, with x referring to the content of Fe in the catalyst.

The catalyst was ground to fine power and put in a glass reactor which is equipped with a XAFS cell. The catalyst was treated at 573 K for 1 h under a flow of hydrogen (99.99%, 50 ml/min). After the treatment, the sample was kept in H<sub>2</sub> at ambient temperature. For the XAFS measurements, the sample in the reactor was transferred to the XAFS cell part without exposure to the air. Ir L<sub>III</sub>-edge spectra were obtained in a transmittance mode. Fe K-edge spectrum for 3Ir-3.5Fe/SiO<sub>2</sub> was measured under the same conditions. For 0.1Fe/SiO<sub>2</sub> and 3Ir-0.1Fe/SiO<sub>2</sub>, Fe K-edge XAFS spectra were obtained in a fluorescence mode. Analysis of the spectra was conducted with a data processing software (Rex2000, Rigaku Co.).

### 3 Results and Discussion

Among catalysts with various composition, 3Ir-0.1Fe/SiO<sub>2</sub> showed the highest efficiency for selective hydrogenation of  $\alpha$ ,  $\beta$ -unsaturated aldehyde to  $\alpha$ ,  $\beta$ -unsaturated alcohol. It had high stability for the reaction as well.

Figure 1 shows Fourier transform spectra of Ir L<sub>III</sub>-edge EXAFS ( $k^3\chi(k)$ ). Since Ir-Ir scattering attributed to Ir metallic clusters were observed for all the samples, it is concluded that most of the Ir atoms were in a metallic state.

On the hand, as shown in Fig.2, the adsorption edge of Fe K-edge XAFS was higher in photon energy compared to that of Fe foil, indicating that Fe species were in oxidized state even after reduction. It is also found that Fe species in 3Ir-0.1Fe/SiO<sub>2</sub> were highly dispersed as small clusters, whereas, those in 3Ir-3.5Fe/SiO<sub>2</sub> formed particles which exhibited peaks assigned to the second and third nearest neighbor atoms in the Fourier transform of EXAFS ( $k^3\chi(k)$ , not shown in this report). It is suggested that the active sites at the interface of Ir metal particles and FeO<sub>x</sub> fine particles were responsible for the high performance.

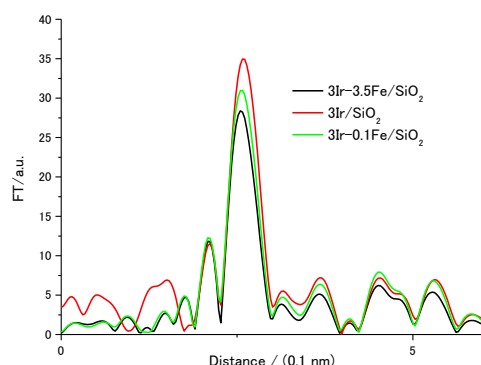


Fig.1 Fourier transform of Ir L<sub>III</sub>-edge EXAFS ( $k^3\chi(k)$ ) observed for reduced catalysts.

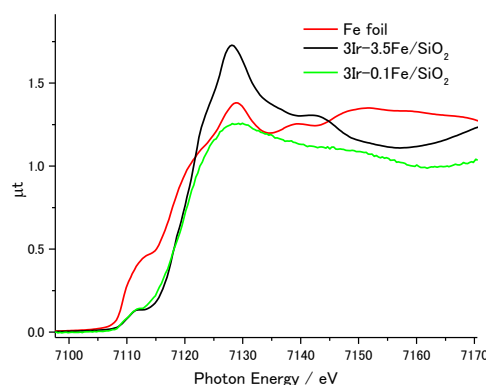


Fig.2 Fe K-edge XANES observed for reduced catalysts

### References

- [1] P. Clause, *Top. Catal.*, **5**, 51-62 (1998).  
 [2] P. Maki-Arvela, et al., *Appl. Catal. A: General*, **292**, 1-49 (2005)

\* kk.bando@aist.go.jp