

## Investigation of Local Structure of Re Active Site in Re/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> Catalysts by Re-K Edge EXAFS

Re/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> catalysts possess a characteristic activity on methanol partial oxidation reaction to produce methylal (CH<sub>2</sub>(CH<sub>3</sub>O)<sub>2</sub>) selectively [1]. The reaction proceeds under a mild condition and the selectivity is more than 90%. In addition, the lifetime of the Re/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is quite long. In many cases, rhenium forms sublimable oxides such as Re<sub>2</sub>O<sub>7</sub> under the oxidative conditions and cannot be used as oxidation catalysts. Thus, ReO<sub>x</sub>/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, an active and long living rhenium catalyst under oxidative conditions, is quite unusual. This may be due to an unusual local structure of the rhenium species.

To elucidate the structure of the rhenium species, we measured the Re *K*-edge EXAFS of Re/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Re/Al<sub>2</sub>O<sub>3</sub> at SPing-8. As Fe<sub>2</sub>O<sub>3</sub> support absorbs X-rays at the energy range of Re *L*<sub>III</sub>-edge (10 - 11 keV), Re *L*<sub>III</sub>-edge EXAFS is difficult to measure because of its large background. On the other hand, as Fe<sub>2</sub>O<sub>3</sub> support does not absorb X-rays in the energy range of Re *K*-edge (71 - 72 keV), Re *K*-edge EXAFS can be measured with small background. Thus Re *K*-edge EXAFS is a useful technique to elucidate the local structure around Re species in Re/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> catalysts.

Catalyst preparation has been described elsewhere [1]. Re *K*-edge EXAFS spectra of ReO<sub>x</sub>/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and ReO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts with various Re loadings were measured at beamline BL01B1 with the transmission mode at ca. 10 K. The spectra were analyzed by use of the UWXAFS package [2]. After background subtraction, *k*<sup>3</sup> weighted EXAFS functions were Fourier transformed (FT) to the R-space and fitted in this space. The FT *k* range and fitting R-ranges were 40 - 140 nm<sup>-1</sup> and 0.1 - 0.4 nm, respectively.

Backscattering amplitudes and phase shifts were calculated by the FEFF8 code [3]. The line broadening due to the resolution of monochromator and core-hole lifetime was estimated to be 15 eV and was taken into account to calculate the phase and amplitude.

Figure 1 shows an X-ray absorption spectrum of Re(9.2 wt%)/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. EXAFS oscillations were observed in a wide energy range even though the near edge structure was smeared by broadening. Figures 2 show Fourier transformed EXAFS functions of Re/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Re/Al<sub>2</sub>O<sub>3</sub> catalysts together with the result of curve fitting analysis. Phase shift was not corrected in these figures. Table I shows structural parameters obtained by curve fitting analysis for Re/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Re/Al<sub>2</sub>O<sub>3</sub> catalysts. In the EXAFS functions of Re/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, a strong peak of Re-O was observed at 0.175 nm in all Re loadings. In addition, a peak for Re-Fe was observed at 0.382 nm in EXAFS of Re(9.2 wt%)/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. On the contrary, Re-O contribution in the EXAFS of Re/Al<sub>2</sub>O<sub>3</sub> was a convolution of two Re-O bondings, at 0.175 nm and 0.2 nm. In addition,

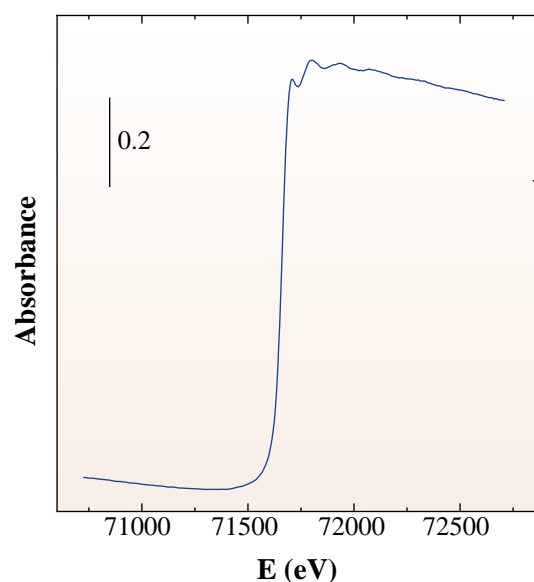


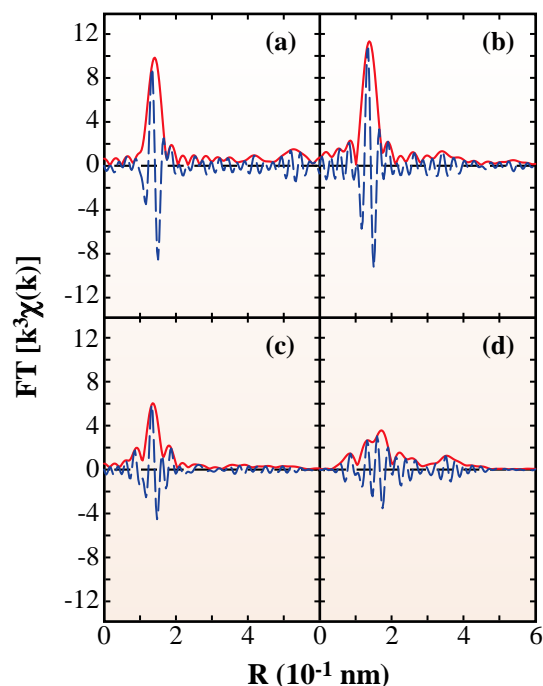
Fig. 1. Re *K*-edge X-ray absorption spectrum of Re (9.2 wt%)/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

several peaks corresponding to  $\text{ReO}_2$  were observed in EXAFS of  $\text{Re}(9.2 \text{ wt}\%)/\text{Al}_2\text{O}_3$ . A Re  $K$ -edge EXAFS analysis revealed that tetrahedral  $\text{ReO}_4$  structure was stabilized by forming Re-Fe binary oxide on  $\gamma\text{-Fe}_2\text{O}_3$  support. The  $\text{ReO}_4$  structure is unstable on the  $\text{Al}_2\text{O}_3$  surface and converts to  $\text{ReO}_2$ . Figure 3 shows the proposed structure of an Re-Fe binary oxide formed on  $\text{Re}/\gamma\text{-Fe}_2\text{O}_3$  catalyst. The  $\text{ReO}_4$  structure bound to Fe ion and the formation of sublimable  $\text{Re}_2\text{O}_7$  was prohibited. A Re  $K$ -edge EXAFS study revealed that active  $\text{ReO}_4$  species were stabilized by forming Re-Fe binary oxide on the  $\gamma\text{-Fe}_2\text{O}_3$  surface.

**Table I.** Structural parameters of supported Re catalysts delivered by curve fitting analysis of Re  $K$ -edge EXAFS.

Sample ( $\Delta E_0/\text{eV}$ , $R_f(\%)$ )	shell	CN <sup>(a)</sup>	R <sup>(b)</sup> /0.1 nm	$\sigma^2$ <sup>(c)</sup> /10 <sup>-5</sup> nm <sup>2</sup>
Re (1.7wt%)/ $\gamma\text{-Fe}_2\text{O}_3$ (0, 1.0)	Re-O	4	1.75	3
Re (9.2wt%)/ $\gamma\text{-Fe}_2\text{O}_3$ (-5, 0.9)	Re-O	4	1.75	3
	Re-Fe	1	3.82	20
Re (2.0wt%)/ $\text{Al}_2\text{O}_3$ (0, 0.8)	Re-O	4	1.75	3
	Re-O	1	1.95	1
Re (9.2wt%)/ $\text{Al}_2\text{O}_3$ (7, 2.7)	Re-O	1	1.76	1
	Re-O	3	2.00	4

(a) coordination number  
(b) interatomic distance  
(c) Debye-Waller factor



**Fig. 2.** Fourier transformed Re  $K$ -edge EXAFS functions ( $k^3 \chi(k)$ ) of  $\text{Re}(1.7\text{wt}\%)/\gamma\text{-Fe}_2\text{O}_3$  (a),  $\text{Re}(9.2\text{wt}\%)/\gamma\text{-Fe}_2\text{O}_3$  (b),  $\text{Re}(2.0\text{wt}\%)/\text{Al}_2\text{O}_3$  (c), and  $\text{Re}(9.2\text{wt}\%)/\text{Al}_2\text{O}_3$  (d). Red and blue lines represent observed and calculated EXAFS functions, respectively.

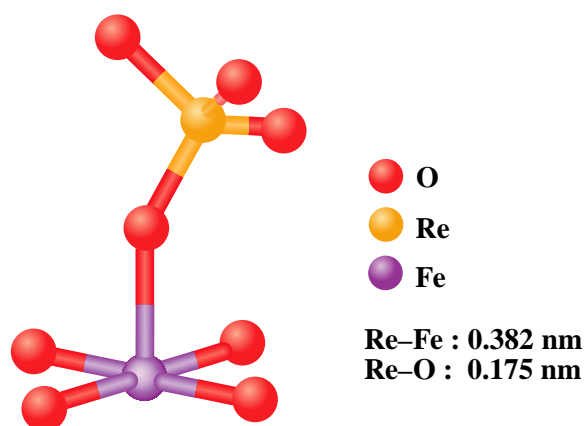
T. Shido, F. Nakagawa and Y. Iwasawa

The University of Tokyo

E-mail: shido@chem.s.u-tokyo.ac.jp

## References

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**Fig. 3.** Proposed structure of Re active site on  $\text{Re}/\gamma\text{-Fe}_2\text{O}_3$  catalysts.