

## EXAFS analysis of activity site for glycerol hydrogenolysis reaction

Shuichi KOSO\*<sup>1</sup>, Akira Shimao<sup>1</sup>, Tomohisa Miyazawa<sup>1</sup>Kazu OKUMURA<sup>2</sup>, Kimio KUNIMORI<sup>1</sup>, Keiichi TOMISHIGE<sup>1</sup><sup>1</sup>Institute of Materials Science, Univ. of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan<sup>2</sup>Department of Materials Science, Tottori Univ., Koyama-cho, Minami, Tottori 680-8552, Japan**Introduction**

Utilization of biomass as a renewable raw material will gain importance in the industrial production of chemical substances for sustainability and as a substitute for petroleum for energy production. Terminal-diols, which have a linear carbon-carbon chain and carbons at both edges with the OH group have been used as monomers for production of polyesters and polyurethanes. Attempts have been carried out for the production of terminal-diols from renewable resources. Recently, our group has found that the Rh–ReO<sub>x</sub>/SiO<sub>2</sub> catalyst shows high activity for glycerol hydrogenolysis, and the catalyst is effective for synthesis of 1,3-propanediol. In this study, we attempt to know the catalyst's fine structures. That is why we carried out extended X-ray absorption fine structure (EXAFS) as a characterization.

**Experimental**

Rh–ReO<sub>x</sub>/SiO<sub>2</sub> catalyst was prepared using the sequential (two-step) impregnation method. Firstly RhCl<sub>3</sub>·3H<sub>2</sub>O aq. was impregnated to SiO<sub>2</sub> and dried catalyst at 383 K for 12 h. Secondary, NH<sub>4</sub>ReO<sub>4</sub> aq. was impregnated Rh/SiO<sub>2</sub> catalyst and then after dried at 383 K for 12 h, calcined at 773 K in air for 3 h. The resultant catalyst is denoted as Re/Rh. The catalyst was pressed into self-supporting 7 mm-diameter wafers under atmosphere, followed by the treatment, with H<sub>2</sub> at 393 K for 1 h in the cell. We also measured the EXAFS of the catalysts after the reaction of glycerol. After the reaction, the H<sub>2</sub> pressure was decreased to some extent and the autoclave was opened in a glove box filled with nitrogen. The used catalysts, after separation, were transferred again to the measurement cell. Re L<sub>3</sub>-edge EXAFS spectra was measured by transmission mode at room temperature. After back ground subtraction, k<sup>3</sup> weighted EXAFS functions were Fourier transformed into R space and the one or two-shell fitting were analyzed by curve fitting.

**Results and Discussion**

Figure 1 shows Fourier transform of Re L<sub>3</sub>-edge EXAFS oscillations of various catalysts after H<sub>2</sub> reduction. The FT of Re powder and NH<sub>4</sub>ReO<sub>4</sub> is also shown as a reference for Re–Re and Re–O, respectively. For both catalysts, peaks between 0.15 and 0.30 nm were observed in the FT; they are assignable to the Re–O and Re–Rh

bond. Table 1 lists their curve fitting results. From the result of Fourier transform of k<sup>3</sup>-weighted Re L<sub>3</sub>-edge EXAFS of Rh–ReO<sub>x</sub>/SiO<sub>2</sub>, samples after H<sub>2</sub> reduction and after the glycerol hydrogenolysis reaction sample are suggested almost same conditions. The catalyst in the glycerol hydrogenolysis reaction is reduced by H<sub>2</sub> gas in the autoclave. From the Re–Rh bond which was observed in the EXAFS of Rh–ReO<sub>x</sub>/SiO<sub>2</sub>, Re and Rh atoms are relatively near and interacts between Re and Rh. In addition, the two Re–O bonds were also observed in the Rh–ReO<sub>x</sub>/SiO<sub>2</sub>. From this result, it was suggested that Re was not reduced completely in the reaction.

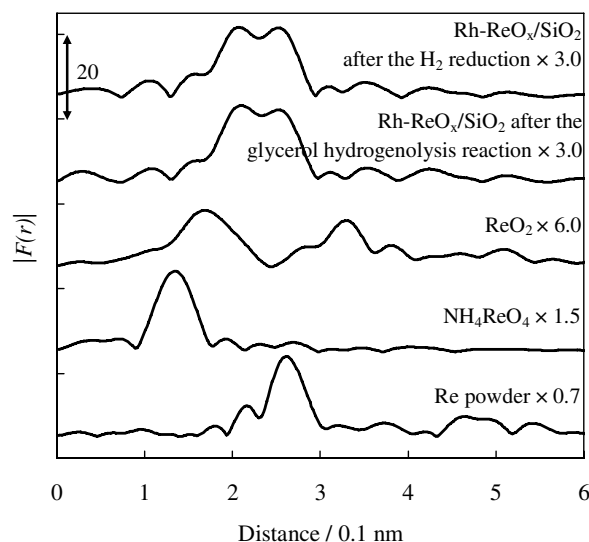


Fig.1 Results of Fourier transform of k<sup>3</sup>-weighted Re L<sub>3</sub>-edge EXAFS oscillation of Rh–ReO<sub>x</sub>/SiO<sub>2</sub> after the H<sub>2</sub> reduction and glycerol hydrogenolysis reaction. The results of ReO<sub>2</sub>, NH<sub>4</sub>ReO<sub>4</sub> and Re powder are also shown as a reference.

Table 1 Curve fitting of Re L<sub>3</sub>-edge EXAFS of various catalysts.

Catalyst	Pretreatment	Shells	CN	R / 10 <sup>-1</sup> nm
Rh–ReO <sub>x</sub> /SiO <sub>2</sub> <sup>a</sup>	reduction	Re–Rh	2.6±0.6	2.65±0.007
		Re–O	1.1±0.3	2.06±0.034
		Re–O	2.0±0.9	2.31±0.013
Rh–ReO <sub>x</sub> /SiO <sub>2</sub> <sup>a</sup>	after the glycerol reaction	Re–Rh	2.8±0.9	2.67±0.007
		Re–O	1.2±0.7	2.07±0.010
		Re–O	2.1±1.3	2.29±0.010
ReO <sub>2</sub>	-	Re–O	2.0	1.73
NH <sub>4</sub> ReO <sub>4</sub>	-	Re–O	4.0	1.74
Re powder	-	Re–Re	12	2.75

<sup>a</sup> Re/Rh = 1/2

\* s-sk\_0513@ims.tsukuba.ac.jp