

EXAFS analysis for structure of active site for glycerol hydrogenolysis

Yasushi AMADA*¹, Shuichi KOSO¹Kazu OKUMURA², Yoshinao NAKAGAWA¹ and Keiichi TOMISHIGE^{1,3}¹Department of Applied Chemistry, Tohoku University, Sendai, Miyagi 980-8579, Japan²Department of Materials Science, Tottori University, Minami, Tottori 680-8552, Japan³Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan**Introduction**

The grouping importance in the production of non-petroleum chemicals for a substitute for petroleum and sustainability has led to the development for the transformation of non food biomass. A target of the non-petroleum chemicals is oxygenates such as terminal-diols. Terminal-diols will be used as monomers for the production of polyesters and polyurethanes. It has been recently reported that modification of Rh/SiO₂ with Re species is effective for the hydrogenolysis of glycerol, although the selectivity to 1,3-propanediol is not so high. In this research, we carried out the characterization of modification of Ir/SiO₂ with Re species which shows high activity in the hydrogenolysis of glycerol to 1,3-propanediol. The maximum yield of 1,3-propanediol over Ir-ReO_x/SiO₂ catalyst is 38% at 36 h.

Experimental

Supported Ir-ReO_x catalyst was prepared using the sequential impregnation method. First, H₂IrCl₆ aq was impregnated to SiO₂ and dried catalyst at 383 K for 12 h. Secondary, NH₄ReO₄ aq was impregnated Ir/SiO₂ catalyst and then after dried at 383 K for 12 h, calcined at 773 K in air for 3 h and reduced at 473 K in H₂ for 1 h. The reference compounds such NH₄ReO₄ and Re powder were pressed into self-supporting 7 mm-diameter wafers under atmosphere. The EXAFS analysis of Ir-ReO_x/SiO₂ catalysts was used after the reaction of glycerol. The glycerol hydrogenolysis reaction was performed using the autoclave. Therefore, after the reaction, H₂ 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 L₃-edge EXAFS spectra were measured by transmission mode at room temperature. After background subtraction, k³ weighted EXAFS functions were Fourier transformed into R space and the one or two-shell fitting were analyzed by curve fitting.

Results and Discussion

Fig. 1 shows the Fourier transform (FT) of Re L₃-edge EXAFS oscillations of Ir-ReO_x/SiO₂ after the glycerol hydrogenolysis reaction. The FT of NH₄ReO₄ and Re powder are shown as a reference for Re-O bond and Re-Re bond, respectively. Theoretical functions for the Re-Ir bond were calculated using the FEFF8.2 program. For Ir-ReO_x/SiO₂, a peak between 0.14 and 0.32 nm was

observed in the FT; they are assignable to the Re-O and Re-Ir (or -Re) bond. In the EXAFS analysis, it is impossible to distinguish between Ir and Re as a backscattering atom theoretically. Table 1 lists their curve fitting results. The curve fitting analysis indicates the presence of the Re-O and Re-Ir (or -Re) bonds with bond distance of 0.202–0.203 and 0.268 nm, respectively.

The presence of the Re-O bond indicates that Re species is not fully reduced to the metallic state. The CN of the Re-Ir (or -Re) bond was almost constant among the Ir-ReO_x/SiO₂ catalysts with various Re contents. This suggests that local structures of Re were not dependent on the added Re amount.

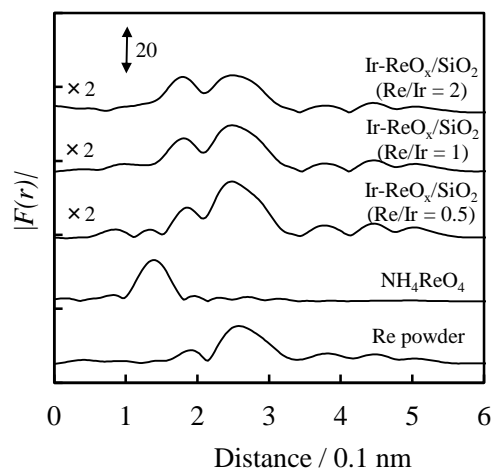


Fig. 1 Results of Fourier transform of k^3 -weighted Re L₃-edge EXAFS oscillation of Ir-ReO_x/SiO₂ after the glycerol hydrogenolysis reaction, NH₄ReO₄ and Re powder. The results of NH₄ReO₄ and Re powder are also shown as a reference.

Table 1 Curve fitting of Re L₃-edge EXAFS of Ir-ReO_x/SiO₂.

Catalyst	Re/Ir	Shells	CN ^a	R / 10 ⁻¹ nm
Ir-ReO _x /SiO ₂	0.5	Re-O	1.1 ± 0.8	2.03 ± 0.07
		Re-Ir (or -Re)	5.9 ± 0.8	2.68 ± 0.01
Ir-ReO _x /SiO ₂	1	Re-O	1.4 ± 0.5	2.02 ± 0.03
		Re-Ir (or -Re)	6.2 ± 0.9	2.68 ± 0.01
Ir-ReO _x /SiO ₂	2	Re-O	1.7 ± 0.5	2.03 ± 0.03
		Re-Ir (or -Re)	6.1 ± 1.1	2.68 ± 0.01
NH ₄ ReO ₄	-	Re=O	4.0	1.74
Re powder	-	Re-Re	12.0	2.74

^aCoordination number. ^bBond distance. Ir: 4 wt%, Re/Ir = 0.5–2. Fourier filtering range: 0.129–0.316 nm.

* yasushi.amada@gmail.com