EXAFS analysis of activity site for glycerol hydrogenolysis reaction

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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/SiO_2 with Re species is selective for the hydrogenolysis of glycerol, although it has a problem in the catalyst stability. In this research, we carried out the characterization of modification of Rh/SiO_2 with Mo species which shows high activity in the hydrogenolysis of glycerol to 1,3-propanediol. In the reaction, $Rh-MoO_x/SiO_2$'s activity is little lower than $Rh-ReO_x/SiO_2$'s one. However, unlike $Rh-ReO_x/SiO_2$, $Rh-MoO_x/SiO_2$ can reuse in the reaction.

Experimental

Supported $Rh–MoO_x$ catalyst was prepared using the sequential (two-step) impregnation method. Firstly $RhCl_3·3H_2O$ aq. was impregnated to SiO_2 and dried catalyst at 383 K for 12 h. Secondary, $(NH_4)_6Mo_7O_{12}•4H_2O$ aq. was impregnated Rh/SiO_2 catalyst and then after dried at 383 K for 12 h, calcined at 773 K in air for 3 h. The catalyst was pressed into self-supporting 7 mm-diameter wafers under atmosphere, followed by the treatment, with H_2 at 393 K for 1 h in the cell. We also measured the EXAFS of the catalysts after the reaction of glycerol. The glycerol hydrogenolysis reaction was performed using the autoclave. Therefore, after the reaction, the H_2 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. Mo K-edge EXAFS spectra were measured by transmission mode at room temperature. After back ground subtraction, k^3 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 Fourier transform of Mo K-edge EXAFS oscillations of $Rh-MoO_x/SiO_2$ after H_2 reduction and after glycerol hydrogenolysis reaction. The FT of Mo foil, Na_2MoO_4 are shown as a reference for Mo-Mo bond or Mo-O bond, respectively. Theoretical functions for the Mo-Rh bond were calculated using the FEFF8.2 program.

For $Rh-MoO_x/SiO_2$, a peak between 0.13 and 0.28 nm was observed in the FT; they are assignable to the Mo–O and Mo–Rh (or Mo) bond. In the EXAFS analysis, it is impossible to distinguish between Rh and Mo as a backscattering atom theoretically. Table 1 lists their curve fitting results. From the result, it was suggested that $Rh-MoO_x/SiO_2$ after H_2 reduction and after glycerol hydrogenolysis reaction were very analogous. This means the catalyst in the glycerol hydrogenolysis reaction is reduced by H_2 gas in the autoclave. And, to be observed Mo–Rh bond in the EXAFS of $Rh–MoO_x/SiO_2$ means that there is an interaction between Mo and Rh. In addition, the two Mo–O bonds which were observed in the EXAFS of $Rh-MoO_x/SiO_2$ mean that Mo was not completely reduced in the reaction.
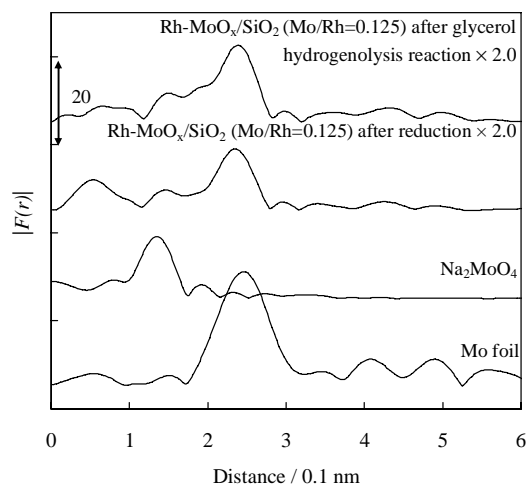

Fig. 1 Results of Fourier transform of k^3-weighted Mo K-edge EXAFS oscillation of $Rh-MoO_x/SiO_2$ after the H_2 reduction and glycerol hydrogenolysis reaction, Na_2MoO_4 and Mo foil. The results of Na_2MoO_4 and Mo foil are also shown as a reference.

Table 1 Curve fitting of Mo K-edge EXAFS of various catalysts.

Catalyst	Pretreatment	Shells	CN	$R / 10^{-1}$ nm
Rh-MoO_x/SiO_2[a]	after reduction	Mo-O	0.5±1.0	2.00±0.170
		Mo-Rh (or Mo)	3.7±1.4	2.60±0.010
Rh-MoO_x/SiO_2[a]	after glycerol reaction	Mo-O	1.1±0.7	2.08±0.050
		Mo-Rh (or Mo)	3.2±0.6	2.64±0.010
Na_2MoO_4	-	Mo-O	4.0	1.78
Mo foil	-	Mo-Mo	8.0	2.72

[a] Mo/Rh=0.125

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