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Behavior of Active Rh species in/on Ordered Mesopores during Liquid Phase Heterogeneous Catalysis

Seiki Wada, Yasuo Izumi*
Department of Chemistry, Graduate School of Science, Chiba University, Inage-ku, Chiba 263-8522

Introduction

Diffusion control mechanism of reaction intermediate species was proposed to selectively synthesize butanol (100 – 60%) in gas-phase propene hydroformylation reaction inside mesopores of Rh/FSM-16 [1]. In this study, more practical liquid-phase hydroformylation was tested over solid catalyst Rh/FSM-16. High selectivity toward C_9 aldehydes has been already achieved in our laboratory in 1-octene hydroformylation reaction. To give fundamental insight into the active Rh species and the transformation during catalysis, Rh K-edge XAFS spectra before and after catalysis were measured and analyzed.

Methods

0.10 M of $Rh(NO_3)_3$ aqueous solution and ordered mesoporous SiO_2 FSM-16 slurry were mixed. 25% of NH_3 was added to set the pH of suspension to 9.5. This mixture was stirred for 1 h at 290 K. Then, the suspension was filtered and washed. Obtained powder was heated at 673 K in 25 kPa of H_2. Hydroformylation reaction of 1-octene (50 mL) was carried out in autoclave with 0.25 g of Rh/FSM-16 powder. 2.0 MPa of CO and H_2 was introduced with the molar ratio 1:1. The temperature of reactor was raised to 353 K and maintained at the temperature for 4 h. After reaction, the catalyst was filtered in argon and introduced again into autoclave to repeat the catalytic reaction tests.

The Rh K-edge XAFS spectra were measured at beamline NW10A. Fresh Rh/FSM-16 catalysts and ones after hydroformylation were introduced to 10 mm-thick Pyrex glass cell equipped with Kapton film on both sides. The cell was purged with argon and sealed by fire to transport to Tsukuba. Besides structural study for powder catalysts, reaction solution was also introduced in N_2 atmosphere to 20 mm-thick Pyrex cell equipped with Kapton windows and stopcocks.

Results and discussion

Based on the Rh K-edge jump values before and after 1-octene hydroformylation (reaction batch repeated: once – three times), Rh content in sample was given (Table 1). 1 – 28% of Rh leaching was suggested when reaction batch was repeated under the reaction conditions.

Corresponding best-fit results of Rh K-edge EXAFS were listed in Table 1. The first shell bond distance was given invariably at 2.67 Å, indicating metallic Rh species formed. The coordination number of Rh-Rh bond was limited smaller than 7.4, suggesting the metallic Rh species were inside mesopores of 27 Å aperture.

The coordination number increased when the hydroformylation reaction was repeated (Table 1). This trend contradicts with Rh leaching evaluated above because Rh nanoparticle size should become smaller and the Rh–Rh coordination number decreases as the Rh leaches. Tentative interpretation is that smaller cationic Rh species preferably leached during liquid-phase hydroformylation and that relatively stable Rh nanoparticles of 10 – 20 Å remained inside the mesopores of FSM-16.

Based on Rh K-edge XAFS spectra for reaction solutions after batch repetition once – three times, leached Rh species was suggested to be mononuclear Rh complex. However, the Rh species leached was found to be not selective to aldehyde/alcohol in catalysis in the absence of solid catalyst.

Reference

[1] Y. Izumi, K. Konishi, M. Tsukahara, D. M. Obaid, K. Aika, *J. Phys. Chem. C* **111**(27), 10073 – 10081 (2007).

*yizumi@faculty.chiba-u.jp

Table 1. Evaluation of Rh content in sample based on edge jump value and best fit results to Rhodium K-edge EXAFS for Rh/FSM-16

Catalyst	Repetition of reaction batch	Rh content (wt%) evaluated from edge jump	Rh-Rh R (Å)	 N	 ΔE (eV)	 $\Delta(\sigma^2)$ ($Å^2$)	goodness of fit
Rh/FSM-16	0	1	2.67	6.7	–0.57	0.0011	4.5×10^5
	1	0.99	2.67	6.8	1.0	0.0012	7.6×10^5
	3	0.72	2.67	7.4	2.5	0.0012	9.1×10^5