

Site structure determination of rhodium-molybdenum catalysts supported in ordered mesoporous silica for selective butanol synthesis

Yasuo Izumi*, Kazushi Konishi, and Masayasu Tsukahara

¹Tokyo Institute of Technology, Nagatsuta 4259-G1-16, Midori-ku, Yokohama 226-8502

Introduction

Hydroformylation reaction has been developed for better chemo-selectivity to oxygenates and better regio-selectivity to *n*-*i*-form. Recently, selective *n*-butanol synthesis was discovered in hydroformylation of propene over Rh-Mo/FSM-16 catalysts [1]. The selectivity of butanol was exceptionally high (> 98 mol%) compared to Rh-Mo/silica gel catalysts before. Therefore, the site structure of Rh-Mo/FSM-16 was determined using EXAFS in this study.

Experimental section

$[\text{NH}_4]_3[\text{RhMo}_6\text{O}_{18}(\text{OH})_6]^{3-}$ was dissolved in minimal amount of deionized water and reacted with FSM-16 (Fuji Sylysia) for 12h. Then, the solvent was evaporated. Similarly, $[\text{NH}_4]_3[\text{AlMo}_6\text{O}_{18}(\text{OH})_6]^{3-}$ was impregnated on FSM-16. $[\text{Rh}(\text{COD})_2]^+[\text{BF}_4]^-$ in ethanol was reacted with $[\text{AlMo}_6\text{O}_{18}(\text{OH})_6]^{3-}$ /FSM-16 for 12h. Obtained powder was washed well until the filtrate became colorless.

XAFS spectra were measured at beamlines 10B and NW10A in transmission mode at 30 – 290 K. The data was analyzed using a package XDAP version 2.2.7.

Results and discussion

Based on the Rh and Mo K-edge EXAFS (Tables 1 and 2), metallic nanoparticles $\approx 20\text{\AA}$ in the mesopores were formed under hydroformylation conditions. Mo atomically mixed in/on Rh nanoparticles to segregate surface Rh ensemble to be selective CO insertion. Distorted heteropolyacid species coexisted in the catalysts under hydroformylation conditions. Detailed discussion can be found in Ref. 1.

References

[1] Y. Izumi, K. Konishi, M. Tsukahara, D. M. Obaid, K. Aika, *J. Phys. Chem. C* **111**, in press (2007).

* izumi.y.ac@m.titech.ac.jp

Table 1. Best Fit Results to Rhodium K-edge EXAFS for Various Rhodium-Molybdenum Catalysts Supported in/on FSM-16 and Reference Rh Catalysts

Rh wt%	Rh-O		Rh-C		Rh(-C)-C		Rh-Rh or Rh-Mo		Rh(-O-)Mo	
	N	R(\AA)	N	R(\AA)	N	R(\AA)	N	R(\AA)	N	R(\AA)
(A) Before Hydroformylation										
$[\text{RhMo}_6\text{O}_{18}(\text{OH})_6]^{3-}$ /FSM-16										
0.22	6.6	1.88								
3.0	6.2	2.014						4.2	3.34	
5.2	7.0	2.030						5.3	3.35	
$[\text{Rh}(\text{COD})_2]^+[\text{AlMo}_6\text{O}_{18}(\text{OH})_6]^{3-}$ /FSM-16										
1.6	1.8 ^a	2.05	8.0 ^a	2.092	8.0 ^a	2.962				
(B) After Hydroformylation (433 K, 5h)										
$[\text{RhMo}_6\text{O}_{18}(\text{OH})_6]^{3-}$ /FSM-16										
0.22							8.4	2.679		
3.0	5.2	2.028					1.6	2.709	0.8	3.37
5.2	4.0	2.041					1.3	2.676	1.0	3.364
$[\text{Rh}(\text{COD})_2]^+[\text{AlMo}_6\text{O}_{18}(\text{OH})_6]^{3-}$ /FSM-16										
1.6							8.2	2.688		

^a Equalized to the values for $[\text{Rh}(\text{COD})_2]^+[\text{BF}_4]^-$.

Table 2. Best Fit Results to Molybdenum K-edge EXAFS for Various Rhodium-Molybdenum Catalysts Supported in/on FSM-16 and Reference Rh Catalysts

Rh wt%	Mo-O		Mo-O		Mo-Rh		Mo(-O-)Mo or Mo(-O-)Rh			
	N	R(\AA)	N	R(\AA)	N	R(\AA)	N	R(\AA)	N	R(\AA)
(A) Before Hydroformylation										
$[\text{RhMo}_6\text{O}_{18}(\text{OH})_6]^{3-}$ /FSM-16										
0.22	6.1	1.60	1.3	2.07			4.0	3.41		
3.0	0.6	1.67	1.1	2.00			2.5	3.356		
$[\text{Rh}(\text{COD})_2]^+[\text{AlMo}_6\text{O}_{18}(\text{OH})_6]^{3-}$ /FSM-16										
1.6	1.6	1.664	1.9	1.99			2.2	3.324		
(B) After Hydroformylation (433 K, 5h)										
$[\text{RhMo}_6\text{O}_{18}(\text{OH})_6]^{3-}$ /FSM-16										
0.22	1.0	1.664	5.3	1.98	0.9	2.74	1.4	3.185		
3.0	1.8	1.66	2.4	1.99	1.5	2.59				
5.2	0.7	1.67	4.7	1.94	1.4	2.56	0.8	3.35		
$[\text{Rh}(\text{COD})_2]^+[\text{AlMo}_6\text{O}_{18}(\text{OH})_6]^{3-}$ /FSM-16										
1.6	1.7	1.66	2.8	1.89	0.2	2.563	1.3	3.286		