

## Structural requisites for selective butanol synthesis over Rh-Mo/FSM-16 studied by EXAFS

Yasuo Izumi\* and Kazushi Konishi

Department of Chemistry, Graduate School of Science, Chiba University, Inage-ku, Chiba 263-8522

### Introduction

Butanol selectivity of 100 – 30% was reported over Rh-Mo/FSM-16 catalysts in propene hydroformylation [1]. The Rh and Mo K-edge EXAFS analyses for Rh-Mo/FSM-16 catalysts were reported [2]. Rh/FSM-16 still exhibited specific butanol synthesis of 73 – 46% in propene hydroformylation [1] and thus the Rh K-edge EXAFS spectra were analyzed in this report to specify the structural requisites for selective butanol synthesis.

### Methods

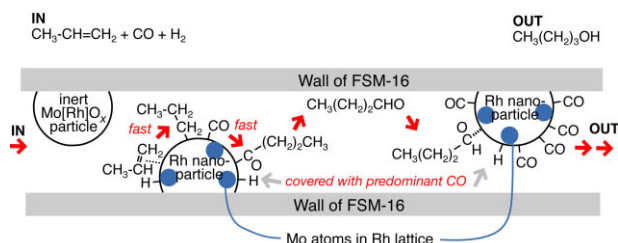
The  $[\text{Rh}^{\text{I}}(\text{COD})_2]^+[\text{BF}_4]^-$  (COD = cyclooctadiene) was synthesized from  $[\text{RhCl}(\text{COD})_2]$ , 1,5-COD, and  $\text{AgBF}_4$ . Obtained dark red crystal powder was dissolved in ethanol in an argon atmosphere and mixed with FSM-16. Separately,  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  was impregnated in/on FSM-16 from the aqueous solution.

Hydroformylation reactions of propene were carried out in closed system of  $132 \text{ cm}^3$  at total pressure of 60 kPa of propene, CO, and  $\text{H}_2$  with molar ratio 1:1:1. Catalysts prepared from metal complexes were evacuated at 290 K for 2 h before catalytic tests.  $\text{RhCl}_3/\text{FSM-16}$  catalysts were heated in hydrogen (27 kPa) at 673 K for 1 h and evacuated at 673 K for 30 min before tests.

### Results and discussion

The Rh K-edge EXAFS analysis result for  $[\text{Rh}^{\text{I}}(\text{COD})_2]^+/\text{FSM-16}$  was listed in Table 1A. The coordination of the Rh complex to internal surface of FSM-16 was suggested via two Rh–O bonds. The catalyst was selective to propane and unimportant.

The Rh K-edge EXAFS was analyzed for  $\text{RhCl}_3/\text{FSM-16}$  after hydroformylation at 433 K for 5 h (Table 1B). The Rh–Rh coordination number of 7.3 and 7.7 was



**Figure 1.** Proposed mechanism of selective butanol synthesis over Rh[-Mo]/FSM-16 catalysts.

consistent with nanoparticle mean size of 2.2 and 2.8 nm for the samples of 0.5 and 33 wt% of Rh, respectively, based on transmission electron microscope images.

Combined with Rh and Mo K-edge EXAFS analyses [2], structural requisites for the selective butanol synthesis were found to

- (1) the presence of Rh nanoparticles of  $\approx 2 \text{ nm}$
- (2) additional effects of atomic Mo dissolved in Rh nanoparticles to segregate Rh atoms ensemble and favor the CO insertion step
- (3) slow diffusion of oxygenates intermediates in FSM-16 mesopores leading to multiple-step hydrogenations to convert finally to butanol.

### References

- [1] Y. Izumi, K. Konishi, M. Tsukahara, D. M. Obaid, K. Aika, *J. Phys. Chem. C* **111**(27), 10073 – 10081 (2007).
- [2] Y. Izumi, K. Konishi, M. Tsukahara, *Photon Factory Act. Rep. 2006* **24B**, 15 (2007).

\* yizumi@faculty.chiba-u.jp

**Table 1.** Best Fit Results to Rhodium K-edge EXAFS for Some Rhodium Catalysts Supported in/on FSM-16

Rh wt%	Rh–O		Rh–C		Rh(–C–)C		Rh–Rh	
	N	R(Å)	N	R(Å)	N	R(Å)	N	R(Å)
<b>(A) Before Hydroformylation</b>								
$[\text{Rh}(\text{COD})_2]^+/\text{FSM-16}$								
1.1	2.0	2.04	8.0 <sup>a</sup>	2.09	8.0 <sup>a</sup>	2.99		
<b>(B) After Hydroformylation (433 K, 5h)</b>								
$\text{RhCl}_3/\text{FSM-16}$								
0.5							7.3	2.686
33							7.7	2.685

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