

## Characterization of rhodium-molybdenum catalysts supported on mesoporous silica for highly selective hydroformylation of propene

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### Introduction

Mesoporous silica crystalline, *e.g.* MCM and FSM families, bears the possibility of various kinds of shape and chemo-selective catalysis inside the space of 2 – 50 nm. The low population of silanol groups in the mesopore hampered to accommodate enough metal active site in the mesopore. The anchoring using alkyl alkoxy silane with phosphine, amine, halogens, or thiol group requires complicating synthetic procedure to fix greater amount of metal active site.

In this work, simplified procedure to use heteropoly acid as a binder of rhodium metal complex site and FSM-16 was investigated. The series of model Rh-Mo catalysts were characterized using Rh and Mo K-edge synchrotron XAFS.

### Experimental section

#### Preparation of $[Rh(COD)_2]^- [AlMo_6]^- / FSM-16$

$[NH_4]_3^+ [AlMo_6O_{18}(OH)_6]^{3-}$  was dissolved in water and mixed with FSM-16 (specific surface area  $1294 \text{ m}^2 \text{ g}^{-1}$ , Fuji Sylysia). After evaporation,  $[Rh(COD)_2]^+ [BF_4]^-$  (COD = cyclooctadiene) in ethanol was added and reacted for 12h. Obtained cake was washed well with ethanol. As a control,  $[Rh(COD)_2]^+ [BF_4]^-$  solution was directly mixed with FSM-16 and obtained powder was washed well with ethanol.

#### Preparation of $[RhMo_6]^- / FSM-16$

$[NH_4]_3^+ [RhMo_6O_{18}(OH)_6]^{3-}$  was dissolved in water and mixed with FSM-16 for 12h. After evaporation, obtained cake was washed well with ethylene glycol (EG). The Rh amount introduced was fixed to 3.0 wt% but a part of Rh, Al, and Mo introduced may be lost during washing with ethanol/EG for  $[AlMo_6O_{18}(OH)_6]^- / FSM-16$ ,  $[Rh(COD)_2]^+ [AlMo_6O_{18}(OH)_6]^- / FSM-16$ , and  $[RhMo_6O_{18}(OH)_6]^- / FSM-16$ .

#### Rh and Mo K-edge XAFS measurements

XAFS spectra were measured at beamline 10B in transmission mode at 30 – 290 K. The data was analyzed using a package XDAP version 2.1.2 from XAFS Software International.

### Results and discussion

The EXAFS analysis results were summarized in Table 1.  $[Rh(COD)_2]^+$  was bound on the surface in FSM-16 mesopore with two surface oxygen atoms ( $N_{Rh-O} = 2.0$ ) in the absence of binder. The loading amount was 0.3 wt% Rh. When  $[AlMo_6O_{18}(OH)_6]^{3-}$  was used as binder,  $[Rh(COD)_2]^+$  was bound on the surface with three oxygen atoms ( $N_{Rh-O} = 3.0$ ), possibly bridging oxygen atoms on the dish-shaped Anderson-type  $[AlMo_6O_{18}(OH)_6]^{3-}$  molecule. The loading amount was 1.2 wt% Rh. Two COD ligands seems to be maintained upon supporting ( $N_{Rh-C}, N_{Rh\cdots C}$ ).

The curve fit analyses of EXAFS measured for  $[RhMo_6]^- / FSM-16$  are in progress. The  $\chi$  function and its associated Fourier transform of the Rh K-edge spectra were perturbed compared to the data for  $[NH_4]_3^+ [RhMo_6O_{18}(OH)_6]^{3-}$  crystal, suggesting the induced distortion due to the interaction between  $[RhMo_6O_{18}(OH)_6]^{3-}$  and mesopore surface.

This catalyst exhibited specific catalysis: exclusive formation of *n*-butanol and *i*-butanol starting from propene, carbon monoxide, and hydrogen at 433 K. The Rh K-edge EXAFS after the catalysis indicated the formation of rhodium nanoparticles, presumably inside nanopores based on HR-TEM measurements. Systematic Rh and Mo K-edge XAFS study on these series of Rh-Mo catalysts supported on FSM-16 before and after hydroformylation is in progress.

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**Table 1:** Best fit results of Rh K-edge EXAFS for various rhodium-molybdenum catalysts supported on FSM-16 and for reference sample

Sample	Rh-C		Rh-O		Rh $\cdots$ C	
	<i>N</i>	<i>R</i> (Å)	<i>N</i>	<i>R</i> (Å)	<i>N</i>	<i>R</i> (Å)
$[Rh(COD)_2]^- [AlMo_6]^- / FSM-16$	8.0	2.088	3.0	2.063	8.0	2.955
$[Rh(COD)_2]^- / FSM-16$	8.0	2.125	2.0	1.940	8.0	3.047
$[Rh(COD)_2]^+ [BF_4]^-$	8	2.228			8	3.043