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Structure determination of stable and selective rhodium species on TiO_2, CeO_2, activated carbon, and functionalized SiO_2 for liquid-phase catalysis

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Introduction

Heterogeneous catalysts have an advantage to easily separate them from products for practical use. On the other hand, heterogeneous catalysts tend to be complex and in general it is difficult to identify the active sites.

We have been utilized synchrotron XAFS to identify the active sites of supported Rh catalysts for gas-phase hydroformylation. In this work, the active site determination was performed for supported Rh catalysts operated in liquid phase. To satisfy the requisites of higher selectivity and catalyst stability in liquid-phase substrate and/or solvent, various Rh catalysts were analyzed by XAFS.

Methods

0.10 M of $Rh(NO_3)_3$ aqueous solution and support powder, TiO_2 (P25, anatase/rutile = 7/3), CeO_2, activated carbon, were mixed and adjusted to pH of 9.5. After stirred for 1 h, the slurry was filtered and washed with water. Typically, obtained precipitate was dried at 353 K and heated at 523 – 773 K in H_2. As liquid phase catalysis, the reaction of 1-octene (50 mL) was carried out in 2.0 MPa of CO and H_2 with 0.25 g of supported Rh catalyst. Also, synthesis of dimethyl carbonate starting from carbon dioxide and methanol was performed using supported Rh catalyst.

The Rh K-edge XAFS spectra were measured at beamline NW10A. Fresh supported Rh catalysts and the mixture of Rh/P25 and diphenylphosphinoethyl-functionalized SiO_2 ($P–SiO_2$) after liquid-phase catalysis were introduced to a Pyrex glass cell equipped with Kapton film on both sides. The inside of cell was purged with argon and was sealed with fire to transport to beamline.

Results and discussion

The best-fit results of Rh K-edge EXAFS curve fit analyses were summarized in Table 1. For fresh catalysts, the Rh–Rh bond distances were 2.621 – 2.689 Å. Corresponding coordination number (N) was 6.7 – 7.4, indicating the formation of metallic Rh nanoparticles of size populated at 15 – 20 Å. In the Fourier transform of EXAFS for Rh/P25, a shoulder peak that can be assigned to Rh–O bonds appeared. The fit results were bond distance of 2.207 Å with the N value of 1.0 (Table 1A). Thus, the interaction between the Rh nanoparticles and surface oxygen atoms (or hydroxyl groups) of TiO_2 was strongly implied.

In correlation to better stability (negligible leaching, reusable) and selectivity of Rh nanoparticles on P25 mixed with $P-SiO_2$ powder, the mixed catalysts were analyzed with the P/Rh molar ratio between 3 and 11.2. The trend to decrease the N(Rh–Rh) and the increase of N(Rh–P) was apparent. True active sites of Rh complexes anchored to P-functional group were demonstrated.

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Table 1. Best-fit Results of Rh K-edge EXAFS for Supported Rhodium Catalysts

catalyst condition	molar ratio of P/Rh	Rh–Rh		Rh–O		Rh–P	
		N	R(Å)	N	R(Å)	N	R(Å)
(A) Fresh catalysts							
Rh/P25		7.4	2.621	1	2.207		
Rh/CeO$_2$	0	6.7	2.689				
Rh/activated C		6.8	2.668				
Rh/FSM-16		6.7	2.664				
(B) Catalysts after liquid-phase catalysis							
Rh/FSM-16	0	6.8	2.67				
Rh/P25 + P–SiO$_2$	3	1.4	2.63	4.5	2.079		
	11.2	0.71	2.672	2.2	2.052	1.6	2.469
	18.7	0.35	2.649	2.4	2.11	1.3	2.498

1wt% Rh before mixing with $P–SiO_2$.