

A Novel Molecular-imprinted Rh-monomer Catalyst Attached on a SiO₂ Surface

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Introduction

The artificial design of molecular recognition catalysis with 100% selectivity for a variety of catalytic reactions is one of the most wonderful subjects for catalytic chemistry. In order to prepare enzyme-mimicking catalysts with high selectivity for desired molecules, we designed a SiO₂-attached molecular-imprinted Rh-complex catalyst by combining two methods of metal-complex attachment on an oxide surface and a molecular imprinting technique on the surface [1]. The imprinted Rh catalyst exhibited high activity, high durability, and high shape selectivity for alkene hydrogenation [2]. In this study, we demonstrated the structures of attached Rh complexes and how to prepare the active Rh species by analysis of EXAFS.

Experimental

Sample preparation: An Ox.50 support preevacuated at 673 K was impregnated with a toluene solution of RhCl(P(OCH₃)₃)₃. The solvent was removed under a vacuum, followed by evacuation at 363 K for 3 h (supported catalyst). Si(OCH₃)₄ and H₂O were deposited on the surface of the supported catalyst. Then the sample was heated at 348 K for 7 h and evacuated at 363 K for 12 h (imprinted catalyst).

EXAFS measurement and analysis: Rh K-edge EXAFS spectra for the Rh catalysts were measured at 15 K at BL-10B in a transmission mode. After background subtraction, k^3 -weighted EXAFS functions were Fourier transformed into a R space and curve-fitting analyses were carried out in the R space using the FEFFIT program [3]. The k and R ranges for the Fourier transformation and curve fitting were 30–110 nm⁻¹ and 0.12–0.21 nm, respectively. Backscattering amplitudes and phase shifts were calculated by the FEFF8 code [4].

Results and Discussion

The imprinted Rh catalyst exhibited remarkable catalytic property – high catalytic activity, durability, and sharp shape selectivity – for alkene hydrogenation. The catalytic activity increased 11 times after the imprinting, therefore the structures of attached Rh complexes on SiO₂ surfaces were characterized by means of IR, NMR, XPS, and EXAFS. Figure 1 shows Fourier-transformed EXAFS spectra for the supported and imprinted Rh catalysts, whose structural parameters are given in Table 1. The attached Rh complex had a bidentate structure on the SiO₂ surface with two P(OCH₃)₃ ligands at 2.25 Å. After the imprinting, the coordination number of Rh-P bondings reduced from 2.2 to 1.2, indicating removal of a template

P(OCH₃)₃ from the attached Rh complex. The formed surface species was a terdentate conformation with a P ligand, which was highly active species for the reaction. The imprinted Rh complex was surrounded by the wall of surface SiO₂-matrix overlayers as shown in Fig. 2, protecting decomposition of the active species. Further, sharp shape selectivity discriminating a methyl group of alkenes was observed on the imprinted catalyst. This is the first success of molecular-imprinting catalysts on surfaces with significant catalytic features.

Table 1: Structural parameters derived from EXAFS curve-fitting analyses for the Rh catalysts

Shell	CN	R / Å	$\sigma^2 / \text{Å}^2$
Supported			
Rh-O	1.8±0.7	2.04±0.02	(5±1)×10 ⁻³
Rh-P	2.2±0.7	2.25±0.02	(6±2)×10 ⁻³
Imprinted			
Rh-O	2.8±0.3	2.08±0.01	(9±2)×10 ⁻³
Rh-P	1.2±0.3	2.25±0.01	(4±1)×10 ⁻³

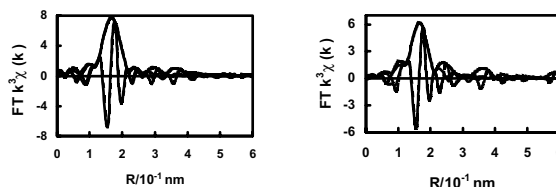


Fig. 1 Fourier-transformed EXAFS spectra for the supported (left) and imprinted (right) Rh catalysts.

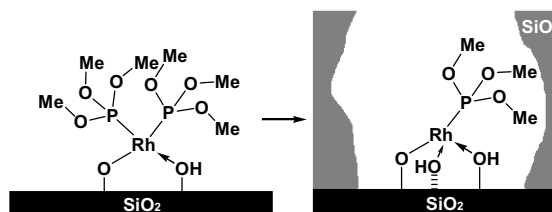


Fig. 2 Structures of the supported (left) and imprinted (right) Rh-monomer catalysts on SiO₂.

References

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