

# A Novel Molecular-Imprinted Rh-Amine Catalyst on a SiO<sub>2</sub> Surface for Shape-Selective $\alpha$ -Methylstyrene Hydrogenation

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## Introduction

The artificial design of enzymatic catalysts with molecular recognition capability is one of the important subjects in chemistry. We have proposed a strategy to design novel oxide-surface attached metal-complex catalysts with high shape-selectivity for desired molecules by combining two different techniques of metal-complex attaching and molecular imprinting [1]. A ligand of attached metal complex is used as a template molecular for imprinting, and a template cavity with a similar shape to the template is created on an unsaturated active metal site. In this study, a surface cavity with a similar shape to  $\alpha$ -methylstyrene hydrogenation intermediate was designed on a supported Rh complex on SiO<sub>2</sub> by using of an amine template [2]. The step-by-step structural change in the active Rh complexes on the surface during the molecular imprinting was characterized by EXAFS.

## Experimental

**Preparation:** Rh(C<sub>3</sub>H<sub>5</sub>)<sub>3</sub> was reacted with SiO<sub>2</sub> (Aerosil 200) in toluene under N<sub>2</sub> atmosphere. After the removal of the solvent,  $\alpha$ -methylbenzylamine template was added to the attached Rh-allyl species in an ethanol solution. The supported catalyst was treated with Si(OCH<sub>3</sub>)<sub>4</sub> by chemical vapor deposition, followed by evacuation at 373 K to eliminate the amine template.

**EXAFS measurement and analysis:** Rh K-edge EXAFS spectra for the Rh catalysts were measured at 15 K in a transmission mode at BL -10B station. After the subtraction of background by AUTOBK,  $k^3$ -weighted EXAFS functions were Fourier transformed into R-space. The obtained FT spectra were fitted using FEFFIT program. The  $k$  and  $R$  ranges were 3-11 Å, and 1.1-2.0 Å<sup>-1</sup>, respectively. Backscattering amplitudes and phase shifts were calculated by the FEFF8 code.

## Results and discussion

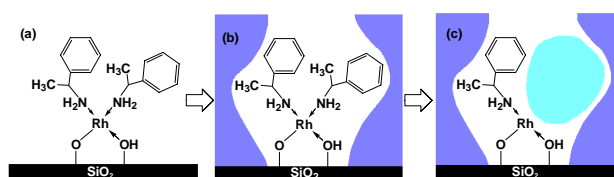
The reaction of Rh(C<sub>3</sub>H<sub>5</sub>)<sub>3</sub> precursor with surface Si-OH groups forming C<sub>3</sub>H<sub>6</sub> was characterized by gas analysis, FT-IR, XPS, and EXAFS. The supported Rh(C<sub>3</sub>H<sub>5</sub>)/SiO<sub>2</sub> was converted to Rh-amine complex with two template amines (a) on the surface. Table 1 shows the curve-fitting results of EXAFS functions at Rh K-edge for the Rh catalysts. The coordination number of the supported catalyst (a) is 4, indicating that the Rh complex possesses two Rh-N coordination and two Rh-O interactions, as shown in Scheme 1. After the chemical

vapor deposition of Si(OCH<sub>3</sub>)<sub>4</sub>, the CN of (b) (3.8) shows that the template ligands remain on the Rh site. The final evacuation at 373 K promoted the elimination of a template, and the CN of (c) reduced from 3.8 to 3.2, as shown in Table 1. The imprinted Rh complex has an unsaturated structure, which is active for hydrogenation.

Indeed, the amine-imprinted Rh catalyst after the removal of the template exhibited a high catalytic activity for  $\alpha$ -methylstyrene hydrogenation though the Rh-allyl precursor and supported catalyst were completely inactive. Furthermore, the active Rh complex is durable under the reaction conditions despite the unsaturated conformation that usually tends to gather each other. The inhibition of the hydrogenation by the use of seven amines with different shapes demonstrates the shape-selective behavior of the imprinted Rh complex discriminating one methyl group and the position of the phenyl ring. We are assured that the strategy will be a promising way to produce novel materials with a higher degree of shape selectivity.

Table 1 Curve-fitting results of the Fourier-transformed EXAFS spectra for the supported and imprinted Rh catalysts measured at 15 K

Sample	Shell	CN	R / Å	$\sigma^2 / \text{Å}^2$
(a)	Rh-N	4.2±0.5	2.12±0.01	(3±1)×10 <sup>-3</sup>
(b)	Rh-N	3.8±0.3	2.09±0.01	(3±1)×10 <sup>-3</sup>
(c)	Rh-N	3.2±0.3	2.05±0.01	(1±1)×10 <sup>-3</sup>



Scheme 1. Molecular imprinting of supported Rh-amine complex on SiO<sub>2</sub>. (a) supported catalyst, (b) Rh species in silica-matrix overlayers, and (c) imprinted catalyst after the evacuation at 373 K.

## Reference

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 [2] M. Tada, T. Sasaki, and Y. Iwasawa, *J. Phys. Chem. B* **2004**, 108, 2918-2930.

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