

The Structure of a Molecularly Imprinted Ru-Complex Catalyst with a Molecular Binding Site on a SiO₂ Surface

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Introduction

We have designed an enzyme-inspired molecularly imprinted Ru catalyst on a SiO₂ surface with a molecular binding site toward the shape-selective transfer hydrogenation of *o*-fluorobenzophenone. The catalyst consists of a Ru complex, a shape-selective reaction space, and a molecular binding site (a NH₂ group) for *o*-fluorobenzophenone spatially arranged on the wall of a molecularly imprinted cavity. The local coordination structures of the new imprinted Ru-complexes were determined by Ru K-edge EXAFS.

Experimental

A molecularly imprinted Ru-complex catalyst with a molecular binding site was prepared from a SiO₂-supported Ru-diamine complex after the exchange reaction of its chloride ligand to a template molecule. Ru K-edge EXAFS was measured at 15 K at the NW10A station of the KEK PF-AR ring with Si(311) double monochromator crystals. Ionization chambers filled with pure Ar and Kr gases were used to monitor the incident and transmitted X-rays, respectively. Observed EXAFS spectra were analyzed with the Rigaku REX2000 package.

Results and Discussion

The coordination of an alcohol template with a NH₂ binding site to supported Ru complex on SiO₂ (A),¹ which has a *p*-cymene ligand, a chiral diamine ligand, and a chloride ligand, was conducted by an exchange reaction of the chloride ligand to the alcohol template. The analysis of Ru K-edge EXAFS of the template-coordinated, SiO₂-supported Ru complex (B) revealed that a Ru-O bond appeared in accordance with the disappearance of the Ru-Cl bond. The coordination number (CN) of Ru-N/O was determined to be 3.2 ± 1.1 at 0.213 ± 0.002 nm and that of Ru-C (*p*-cymene) was estimated to be 6.1 ± 1.4 at 0.221 ± 0.001 nm as shown in Table 1.

SiO₂-matrix overlayers were stacked on the surface of SiO₂ coordinating the Ru complex with template (C) for molecular imprinting. The local coordination structure of (C) was similar to that of (B); the CN of Ru-C (*p*-cymene) at 0.221 ± 0.001 nm was 5.9 ± 1.3 and that of Ru-N/O at 0.212 ± 0.002 nm was 3.0 ± 1.1.

The coordinating template was extracted from the Ru complex after the stacking of the SiO₂-matrix overlayers. The desired molecularly imprinted Ru complex (D) was prepared by the removal of the template from (C) by

exchange reaction with the Cl ligand, leaving the NH₂ binding site on the wall of SiO₂ matrix overlayers. The Ru K-edge EXAFS oscillation of (D) was fitted with Ru-C (*p*-cymene) (CN = 6.0 ± 3.5 at 0.219 ± 0.005 nm), Ru-N (CN = 2.1 ± 3.6 at 0.214 ± 0.005 nm), and Ru-Cl (CN = 1.0 ± 4.4 at 0.239 ± 0.025 nm), indicating the exchange of the alcohol template to the Cl ligand which is re-coordinated to the Ru site.

It was found that the molecularly imprinted Ru catalyst (D) exhibited fine shape selectivity for the transfer hydrogenation of benzophenone derivatives. The adsorption of *o*-fluorobenzophenone was promoted on the molecularly imprinted site with the NH₂ binding site spatially arranged for *o*-fluorobenzophenone and significant differences in transfer hydrogenation activities were observed between *o*-fluorobenzophenone, which can interact with the NH₂ binding site, and *o*-methylbenzophenone, which cannot interact with the NH₂ binding site by hydrogen bonding.

Table 1: Curve fitting results of Ru K-edge EXAFS of prepared Ru complexes on a SiO₂ surface

Shell	CN	Distance /nm	ΔE_0 /eV	$\sigma^2 / \times 10^{-5} \text{ nm}^2$
Supported complex (A) ^a R _i = 1.2%				
Ru-Cl	1.3±1.1	0.244±0.004	10±5	6±14
Ru-N	1.8±2.9	0.214±0.005	11±6	2±12
Ru-C	6.1±1.9	0.217±0.003	-12±3	5±10
Coordination of template (B) ^b R _i = 1.9%				
Ru-N(O)	3.2±1.1	0.213±0.002	3±3	1±5
Ru-C	6.1±1.4	0.221±0.001	-17±2	3±6
After stacking of SiO₂-matrix overlayers (C) ^b R _i = 1.9%				
Ru-N(O)	3.0±1.1	0.212±0.002	6±3	1±5
Ru-C	5.9±1.3	0.221±0.001	-13±2	3±6
After the removal of template (D) ^c R _i = 1.1%				
Ru-Cl	1.0±4.4	0.239±0.025	11±10	1±9
Ru-N	2.1±3.6	0.214±0.005	7±7	3±10
Ru-C	6.0±3.5	0.219±0.005	-14±4	6±13

^a $k = 30\text{-}140 \text{ nm}^{-1}$, $R = 0.12\text{-}0.24 \text{ nm}$, MF = 9 (fixed).

^b $k = 30\text{-}140 \text{ nm}^{-1}$, $R = 0.10\text{-}0.21 \text{ nm}$, MF = 9 (fixed).

^c $k = 30\text{-}140 \text{ nm}^{-1}$, $R = 0.10\text{-}0.24 \text{ nm}$, MF = 9 (fixed).

Reference

[1] M. Tada, S. Muratsugu, M. Kinoshita, T. Sasaki, Y. Iwasawa, *J. Am. Chem. Soc.* **2010**, *132*, 713.

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