

## XAFS Characterization of Molecularly Imprinted Ru-Complex Catalysts for Asymmetric Transfer Hydrogenation Acting in Water Media

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### Introduction

Molecularly imprinted Ru-complex catalysts acting in water were prepared on a SiO<sub>2</sub> surface by molecular imprinting of a SiO<sub>2</sub>-supported Ru complex using organic polymers as surface matrix overlayers. The local coordination structures of the prepared molecularly imprinted Ru-complex catalysts, which exhibited fine shape selectivity for the asymmetric transfer hydrogenation of *o*-fluoroacetophenone and its derivatives in water media, were investigated by Ru K-edge EXAFS.

### Experimental

A Ru precursor complex [(*p*-cymene)Ru{NH<sub>2</sub>CH(Ph)CH(Ph)NSO<sub>2</sub>C<sub>7</sub>H<sub>7</sub>}Cl] was attached on a SiO<sub>2</sub> surface via *p*-styryl moiety functionalized. A template alcohol molecule was coordinated to the supported Ru complex, and surface-matrix overlayers were stacked on the surface by the photopolymerization of Threebond 3026E polymer. Finally, the template was released from the supported Ru complex under appropriate reaction conditions, and a molecularly imprinted Ru complex was obtained on the SiO<sub>2</sub> surface.

Ru K-edge EXAFS was measured in a transmission mode at 20 K at the NW10A station with a Si(311) double-crystal monochromator. Ionization chambers filled with pure Ar and pure Kr were used to monitor incident and transmitted X-rays, respectively. EXAFS spectra were analyzed using Rigaku REX2000 package. Curve-fitting analysis was carried out in *k*-space and *k*<sup>3</sup>-weighted EXAFS oscillations were Fourier transformed into *R*-space. Fitting parameters were coordination number (CN), interatomic distance (*R*), Debye-Waller factor ( $\sigma^2$ ), and correction-of-edge energy ( $\Delta E_0$ ). Phase shifts and backscattering amplitudes for Ru-C, Ru-N, and Ru-Cl were calculated by the FEFF8 code.

### Results and Discussion

The local coordination structures of the supported Ru complexes were examined by Ru K-edge EXAFS analysis, whose structural parameters are listed in Table 1. The supported Ru complex before the coordination of the template had Ru-N interaction at  $2.11 \pm 0.01$  Å, whose coordination number (CN) was estimated to be  $2.0 \pm 0.4$ . After the coordination of the template, the average of bond distances of Ru-N (diamine ligand) and Ru-O

(template) was estimated to be  $2.14 \pm 0.01$  Å (CN =  $3.4 \pm 0.4$ ).

The structural parameters of the local coordination of the molecularly imprinted Ru complexes after the stacking of polymer matrices were also investigated by Ru K-edge EXAFS. The CNs and bond distances of the template-coordinated Ru complex with surface matrix overlayers were similar to those of the template-coordinated Ru complex without the matrix overlayers. Accompanied with the stoichiometric elimination of the template, the local coordination structure of the supported Ru complex recovered to the initial state as shown in Table 1.

**Table 1** Structural parameters of the supported Ru complexes and molecularly imprinted Ru complexes with organic matrix overlayers obtained by curve-fitting analyses of Ru K-edge EXAFS measured at 20 K<sup>a</sup>

Shell	CN	<i>R</i> / Å	$\Delta E_0$ / eV	$\sigma^2$ / Å
<b>Supported Ru complex</b> <i>R<sub>f</sub></i> = 1.2 %				
Ru-C	$5.5 \pm 0.9$	$2.22 \pm 0.01$	10	0.07
Ru-N	$2.0 \pm 0.4$	$2.11 \pm 0.01$	6	0.03
Ru-Cl	$1.5 \pm 0.2$	$2.44 \pm 0.01$	17	0.08
<b>Template-coordinated Ru complex</b> <i>R<sub>f</sub></i> = 0.4 %				
Ru-C	$6.4 \pm 0.7$	$2.33 \pm 0.01$	24	0.10
Ru-N(O)	$3.4 \pm 0.4$	$2.14 \pm 0.01$	7	0.08
<b>Template-coordinated Ru complex with surface matrix overlayers</b> <sup>b</sup> <i>R<sub>f</sub></i> = 1.2 %				
Ru-C	$6.0 \pm 0.7$	$2.30 \pm 0.01$	20	0.10
Ru-N(O)	$3.0 \pm 0.3$	$2.12 \pm 0.01$	9	0.07
<b>Molecularly imprinted Ru complex</b> <sup>b</sup> <i>R<sub>f</sub></i> = 0.6 %				
Ru-C	$5.6 \pm 0.7$	$2.21 \pm 0.02$	8	0.07
Ru-N	$1.8 \pm 0.5$	$2.10 \pm 0.01$	14	0.04
Ru-Cl	$1.6 \pm 0.4$	$2.42 \pm 0.02$	13	0.12

<sup>a</sup> *k* range and *R* range were 3-14 Å<sup>-1</sup> and 1.0-2.4 Å, respectively.

<sup>b</sup> The height of the polymer matrices was 2 nm.

### Reference

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

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