

XAFS Characterization of SiO₂-Supported Ru Complex for Sulfoxidation

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Introduction

Advantage of a supported metal-complex catalyst is not only simpler separation between catalyst and reaction medium but also their unique activity and higher stability of the catalyst. In particular, the site-isolation of a supported metal complex often provides unique catalytic performance on a surface. We have succeeded in preparing site-isolated Ru complex supported on a SiO₂ surface and found that the supported Ru complex was active for sulfoxidation using O₂/aldehyde system.¹ The local coordination structures of the SiO₂-supported Ru complexes were investigated by Ru K-edge EXAFS.

Experimental

A SiO₂-supported Ru complex (**B**) was prepared by reacting a Ru precursor complex [(*p*-cymene)Ru{H₂NCH₂CH₂NSO₂C₈H₇}Cl] (**A**) with a *p*-styryl moiety on SiO₂. The supported Ru complex was converted to an active structure (**C**) with unsaturated coordination by a reaction with isobutyraldehyde (IBA) and O₂ on **B**. Ru K-edge EXAFS spectra were measured in transmitted mode at 20 K at the NW10A station of the KEK PF-AR ring with Si(311) channel-cut crystals. Ionization chambers filled with pure Ar and Kr gases were used to monitor the incident and transmitted X-rays, respectively. Ru K-edge EXAFS spectra were analyzed with IFEFFIT (Athena and Artemis) and *k*³-weighted EXAFS oscillations (30-170 nm⁻¹) were Fourier transformed into *R*-space and curve-fitting analysis was carried out in *R*-space.

Results and Discussion

Structural parameters (CNs (coordination numbers) and bond distances) of the local coordination of **A**, **B**, and **C** were estimated by the curve-fitting analysis of Ru K-edge EXAFS Fourier transforms. The CNs and bond distances of Ru-N, Ru-C, and Ru-Cl in **B** were found to maintain those of **A** as shown in Table 1, indicating the supported Ru complex **B** had a similar local coordination structure to precursor complex **A**, whose coordination structure was determined by X-ray diffraction.

The reaction with **B** and IBA/O₂ released the coordinating *p*-cymene ligand from Ru in **B**, which was detected by GC, and local coordination structure of **C** was determined by Ru K-edge EXAFS (Ru-N at 0.206 ±

0.002 nm; CN = 3.0 ± 1.1; Ru-Cl at 0.236 ± 0.005 nm; CN = 1.3 ± 1.2). No Ru-Ru interaction was found, suggesting that the elimination of the *p*-cymene ligand did not produce the aggregation of Ru particles and **C** had a Ru monomer structure on the SiO₂ surface. There were no significant differences between the local coordination structures of **B** and **C** with Ru loadings of 0.4 and 1.6 wt%.

We found that the supported Ru complexes (**B** and **C**) were active for the sulfoxidation of sulfides using IBA/O₂ systems, in which sulfoxide was selectively formed at the beginning of reaction and the formation of sulfone proceeded by the further oxidation of produced sulfoxide, not directly from sulphide. After the sulfoxidation, the monomer structure of **C** was found to be maintained on the SiO₂ surface (Table 1) and there was no Ru-Ru bond observed by Ru K-edge EXAFS.

Table 1: Curve-fitting results of Ru K-edge EXAFS Fourier transforms of **A**, **B**, and **C** (before and after the sulfoxidation)

Shell	CN	Distance /nm	σ^2 /nm ²
Ru precursor (A) ^a			
Ru-N	2.0	0.208±0.002	(0.7±2.3)×10 ⁻⁶
Ru-C	6.0	0.219±0.002	(1±1)×10 ⁻⁵
Ru-Cl	1.0	0.242 ± 0.003	(2±1)×10 ⁻⁵
Supported complex (B) ^b Ru 0.4 wt%			
Ru-N	1.9±0.7	0.210±0.002	0.7×10 ⁻⁶
Ru-C	4.8±1.7	0.221±0.002	1×10 ⁻⁵
Ru-Cl	1.1±0.2	0.244±0.002	2×10 ⁻⁵
Supported complex (C) ^c Ru 0.4 wt%			
Ru-N	3.0±1.1	0.206±0.002	(2±2)×10 ⁻⁵
Ru-Cl	1.3±1.2	0.236±0.005	(7±8)×10 ⁻⁵
(C) after sulfide oxidation ^d Ru 0.4 wt%			
Ru-N	3.7±0.7	0.208±0.001	(3±1)×10 ⁻⁵
Ru-Cl	1.4±1.2	0.238±0.007	(13±8)×10 ⁻⁵

^a *k* = 30-170 nm⁻¹, *R* = 0.115-0.25 nm, *R_f* = 1.0%. CNs were fixed.

^b *k* = 30-140 nm⁻¹, *R* = 0.115-0.25 nm, *R_f* = 0.6%.

^c *k* = 30-140 nm⁻¹, *R* = 0.13-0.24 nm, *R_f* = 1.2%.

^d *k* = 30-140 nm⁻¹, *R* = 0.13-0.24 nm, *R_f* = 0.3%.

References

[1] N. Maity, C. Wattanakit, S. Muratsugu, N. Ishiguro, Y. Yang, S. -I. Ohkoshi, M. Tada, *Dalton Trans.* **2012**, 132, 713.

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