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XAFS Study on SiO_2-Supported Ru-Complex Catalysts Highly Active for Selective Oxidation Using O_2

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Introduction

The immobilization of metal complexes on support surfaces in a controlled manner is still the state of the art in the assimilative field between homogeneous and heterogeneous catalyses. The potential of immobilized metal-complex catalysts remarkably interplays with the nature of support surface, resulting in significant rate enhancements and novel catalytic performances that homogeneous analogue complexes do not exhibit. We have succeeded in preparing a novel coordinatively unsaturated Ru-diamine complex on a SiO_2 surface, which was characterized by Ru K-edge EXAFS, highly active for the selective oxidation of aldehyde and alkene epoxidation using O_2.

Experimental

An unsaturated Ru-complex was prepared by the reaction with isobutyraldehyde (IBA) and O_2 on a SiO_2-supported Ru-(*p*-cymene) complex [1]. The exothermic reaction of the IBA oxidation to isobutyric acid extracted the coordinating *p*-cymene ligand from the supported Ru complex and produced the unsaturated Ru-monomer complex on the SiO_2 surface. Ru K-edge EXAFS were recorded at 15 K at the NW10A station of KEK PF-AR ring with Si(311) double monochrometor crystals. Ionization chambers filled with pure Ar and Kr gases were used to monitor the incident and transmitted X-rays, respectively. Observed EXAFS data were analyzed with the UWXAFS package and the curve-fitting analyses of EXAFS Fourier transforms were carried out using the FEFFIT program in *R*-space.

Results and Discussion

Table 1 shows the curve-fitting results of Ru K-edge EXAFS measured at 15 K for the SiO_2-supported Ru complexes. Before the catalyst activation using IBA/O_2, we found that the local coordination of the supported Ru complex was a saturated structure coordinating a *p*-cymene ligand. After the removal of *p*-cymene (catalyst activation using IBA), two chemical bonds Ru-Cl at 0.234 nm (CN = 1.3) and Ru-N at 0.207 nm (CN = 2.2) were observed and a 3-coordinated unsaturated Ru site was formed on the surface. There were no significant differences in the local coordination of the supported Ru complexes with the different Ru loading of 2.7 wt% and 0.4 wt% as shown in Table 1.

We found that the unsaturated Ru complex supported on SiO_2 was highly durable for the alkene epoxidation and selective aldehyde oxidation using O_2. The activated Ru catalysts (0.4 wt% and 2.7 wt%) exhibited high TON (38,800,000 for IBA oxidation and 2,100,000 for *trans*-stilbene epoxidation) and could be reusable for the both selective oxidation reactions. After the epoxidation, the structure of the 3-coordinated unsaturated Ru complex maintained at the surface and two chemical bonds of Ru-Cl at 0.232 nm (CN = 1.5) and Ru-N at 0.206 nm (CN = 2.2) were observed as shown in Table 1. We found the similar local coordination structure after the IBA oxidation, indicating the high durability of the unsaturated Ru catalysts for the selective oxidation.

Table 1 Curve fitting results of Ru K-edge EXAFS of supported Ru complexes on SiO_2 measured at 15 K

Catalyst (Ru wt%)	Shell	CN	Distance /nm	σ^2 /nm^2
Supported catalyst [a]	Ru-Cl	1.0	0.236	3 x 10^{-5}
(2.7 wt)	Ru-N	2.0	0.214	0 x 10^{-5}
	Ru-C	6.0	0.226	13 x 10^{-5}
Activated catalyst [b]	Ru-Cl	1.3	0.234	5 x 10^{-5}
(2.7 wt%)	Ru-N	2.2	0.207	1 x 10^{-5}
After epoxidation [c]	Ru-Cl	1.5	0.232	4 x 10^{-5}
(2.7 wt%)	Ru-N	2.2	0.206	8 x 10^{-5}
Supported catalyst [d]	Ru-Cl	1.0	0.238	1 x 10^{-5}
(0.4 wt%)	Ru-N	2.0	0.214	1 x 10^{-5}
	Ru-C	6.0	0.230	1 x 10^{-5}
Activated catalyst [e]	Ru-Cl	1.0	0.236	2 x 10^{-5}
(0.4 wt%)	Ru-N	2.0	0.209	0 x 10^{-5}
After IBA oxidation [f]	Ru-Cl	1.0	0.236	1 x 10^{-5}
(0.4 wt%)	Ru-N	2.0	0.209	0 x 10^{-5}

[a] k=3-14, R=1.0-2.2, ⊿E_0=10, R_f=2.31%. CNs were fixed.
[b] k=3-14, R=1.3-2.4, ⊿E_0=10, R_f=1.29%.
[c] k=3-14, R=1.3-2.4, ⊿E_0=9, R_f=1.01%.
[d] k=3-14, R=1.0-2.2, ⊿E_0=9, R_f=2.42%. CNs were fixed.
[e] k=3-14, R=1.3-2.4, ⊿E_0=11, R_f=1.14%.
[f] k=3-14, R=1.3-2.4, ⊿E_0=11, R_f=1.75%.

Reference

[1] M. Tada, R. Coquet, J. Yoshida, M. Kinoshita, and Y. Iwasawa, *Angew. Chem. Int. Ed.* **2007**, 46, 7220

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