

The Structures of SiO₂-Supported, Unsaturated Ru-Complex Catalysts for Aldehyde Oxidation and Alkene Epoxidation

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Introduction

Supporting transition metal complexes on surfaces is one of the promising ways to produce molecularly-regulated structures of active metal sites at surfaces and various surface metal structures can be arranged by stepwise structural transformations in a controllable manner. We have succeeded in preparing novel unsaturated Ru-diamine monomer complexes on a SiO₂ surface, which was highly active for selective aldehyde oxidation and alkene epoxidation using O₂¹, and have clarified the complete switchover of two reaction pathways. The local coordination structures of these Ru-complexes were determined by Ru K-edge EXAFS.

Experimental

An unsaturated Ru-complex for selective oxidation (C) was prepared by a reaction with isobutyraldehyde (IBA) and O₂ on a SiO₂-supported Ru-(*p*-cymene)-diamine complex (B). Ru K-edge EXAFS were 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 UWXAFS package and curve-fitting analyses were carried out using the FEFFIT program in *R*-space.

Results and Discussion

The local coordination structures of the Ru complexes were determined by Ru K-edge EXAFS curve-fitting analysis. The prepared SiO₂-supported Ru-complex before the reaction with IBA/O₂, (B) was a coordinately saturated structure with one *p*-cymene ligand, one diamine ligand, and one coordinated chloride ligand, which maintains the structure of the precursor Ru-complex (A) as shown in Table 1.

After the release of the coordinating *p*-cymene ligand by IBA and O₂, Ru K-edge EXAFS for the supported Ru complex (C) showed that three chemical bonds (two Ru-N bonds and one Ru-Cl bond) still remained coordinating to Ru as shown in Table 1. After the catalytic epoxidation on the supported Ru catalyst (C), the structure of the unsaturated Ru complex remained unchanged (Table 1) with the two kinds of chemical bonds (Ru-Cl and Ru-N), and these structural parameters were almost similar to those for the 3-coordinated unsaturated structure of (C) before the epoxidation reaction.

We have found that the supported Ru complex (C) is highly active for both of the IBA oxidation with O₂ and the *trans*-stilbene epoxidation with IBA/O₂. Ru K-edge EXAFS analysis revealed that the structures of catalytically active Ru complexes for the IBA oxidation and the epoxidation were similar to each other. The reaction rate of the IBA oxidation to isobutyric acid is much faster than that of *trans*-stilbene epoxidation under the identical IBA/O₂ concentration for both reactions; however the complete switchover of the reaction pathways from the IBA oxidation to the *trans*-stilbene epoxidation was observed when *trans*-stilbene was present with IBA/O₂.²

Table 1: Curve fitting results of Ru K-edge EXAFS measured at 15 K of a Ru complex (precursor) ((A)), and supported Ru complexes on SiO₂ ((B) and (C))

Shell	CN	Distance /nm	$\sigma^2 / \times 10^{-5} \text{nm}^2$
Ru precursor (A) ^a			
Ru-Cl	1.0	0.236±0.003	2±3
Ru-N	2.0	0.213±0.002	-1±2
Ru-C	6.0	0.227±0.021	2±24
Supported complex (B) ^b Ru 2.7 wt%			
Ru-Cl	1.0	0.236±0.006	3±6
Ru-N	2.0	0.214±0.002	0±2
Ru-C	6.0	0.226±0.023	13±23
Supported complex (C) ^c Ru 2.7 wt%			
Ru-Cl	1.3±1.5	0.234±0.004	5±8
Ru-N	2.2±1.5	0.207±0.003	1±2
(C) after epoxidation ^d Ru 2.7 wt%			
Ru-Cl	1.5±2.3	0.232±0.006	4±12
Ru-N	2.2±1.8	0.206±0.003	8±2

^a $k = 30\text{-}140 \text{ nm}^{-1}$, $R = 0.10\text{-}0.22 \text{ nm}$, $\Delta E_0 = 10 \pm 8$, $R_f = 1.74\%$. CNs were fixed.

^b $k = 30\text{-}140 \text{ nm}^{-1}$, $R = 0.10\text{-}0.22 \text{ nm}$, $\Delta E_0 = 10 \pm 9$, $R_f = 2.31\%$. CNs were fixed.

^c $k = 30\text{-}140 \text{ nm}^{-1}$, $R = 0.13\text{-}0.24 \text{ nm}$, $\Delta E_0 = 10 \pm 3$, $R_f = 1.29\%$.

^d $k = 30\text{-}140 \text{ nm}^{-1}$, $R = 0.13\text{-}0.24 \text{ nm}$, $\Delta E_0 = 9 \pm 5$, $R_f = 1.01\%$.

References

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