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Photo-Induced Reversible Structural Transformation of a SiO_2-Supported Ru-Complex Catalyst for Selective Cycloalkane Oxidation

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Introduction

On heterogeneous catalyst surfaces with the limited accessibility of reactants, rate enhancement and new catalysis can be often be obtained on novel unsaturated metal structures, which are hard to be isolated in homogeneous solutions. Metal complex attaching on a surface stabilizes and prevents such active isolated single-site metal complexes aggregating and decomposing on the surface. We have found that the photo-irradiation of a SiO_2-supported Ru-diamine complex promoted the selective formation of two different, novel unsaturated Ru structures on the surface. Depending on O_2 or N_2 atmosphere, one of the structures with an appropriate Ru-H conformation catalyzed selective photo-oxidation of cycloalkanes using O_2. The local coordinations of the two Ru complexes produced by photo-excitation were investigated by Ru K-edge EXAFS.

Experimental

A SiO_2-supported Ru complex (B) was prepared using a *N*-surfonyl-1,2-ethylenediamine-Ru complex (A) and *p*-styryl moiety-functionalized SiO_2 [1, 2]. UV-light irradiation ($\lambda > 275$ nm) promoted the elimination of its *p*-cymene ligand from the supported Ru complex (B) as shown in Scheme 1. Two different structures were prepared by photo-irradiation: (C1) was obtained under O_2 atmosphere and (C2) was obtained under N_2 atmosphere.

Ru K-edge EXAFS were recorded at 15 K at the NW10A station of KEK PF-AR ring with Si(311) double monochrometer. 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 packages and the curve-fitting analyses of EXAFS Fourier transforms were carried out using the FEFFIT program in *R*-space.

Results and Discussion

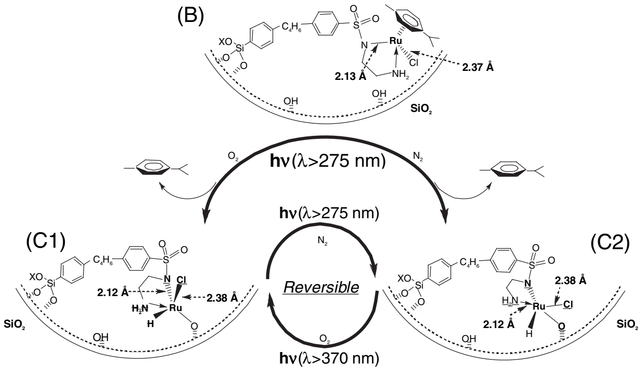
Ru K-edge EXAFS curve-fitting analysis revealed that (C1) and (C2) with different UV/Vis transition had similar local coordination structures on SiO_2. (C1) had a Ru-Cl bond at 0.238 nm and three Ru-N bonds at 0.212 nm, indicating (C1) was saturated coordination on its Ru center. (C2) had a Ru-Cl bond at 0.238 nm and three Ru-N bonds at 0.212 nm and there were no significant differences between (C1) and (C2).

UV/Vis spectra and solid-state NMR indicated that the structural differences between these two structures were derived from the direction of their Ru-H coordination as shown in Scheme 1. (C2) with similar coordination to (C1) was inactive for cycloalkane oxidation, while (C1) catalyzed cycloalkane oxidation to corresponding cycloalcohol and cycloketone. We proposed the detail of the structural transformation at the surface by photo-irradiation.

Table 1 Ru K-edge EXAFS curve fitting results of (C1) and (C2) measured at 15 K

Catalyst	Shell	CN	Distance /nm	σ^2 /nm^2
(C1) [a]	Ru-Cl	1.0	0.238±0.01	$(3\pm1)\times10^{-5}$
	Ru-N	3.5±0.5	0.212±0.01	$(5\pm2)\times10^{-5}$
(C2) [b]	Ru-Cl	1.0	0.238±0.01	$(3\pm1)\times10^{-5}$
	Ru-N	3.4±0.5	0.212±0.01	$(5\pm1)\times10^{-5}$

[a] k=3-14, R=1.2-2.3, ΔE_0=12, R_f=1.01%. CN of Ru-Cl was fixed.
[b] k=3-14, R=1.3-2.3, ΔE_0=12, R_f=0.85%. CN of Ru-Cl was fixed.



Scheme 1 The structures of SiO_2-supported Ru complexes prepared by photo-irradiation.

Reference

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