Heterogeneous Catalysis

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Photoinduced Reversible Structural Transformation and Selective Oxidation Catalysis of Unsaturated Ruthenium Complexes Supported on SiO_2**

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Dedicated to the Catalysis Society of Japan on the occasion of its 50th Anniversary

The photoirradiation of a SiO_2-supported Ru complex was found to promote the selective formation of two different, novel unsaturated Ru structures on the surface, dependent on an O_2 or N_2 atmosphere, differing in the orientation of an Ru−H moiety. One of these structures, owing to an appropriate Ru−H conformation, catalyzed the selective photooxidation of cycloalkanes with O_2. The two surface-bound unsaturated Ru complexes undergo reversible structural interconversion by photoexcitation at different wavelengths under different atmospheres.

On heterogeneous catalyst surfaces, owing to the limited accessibility of reactants, rate-enhancement and new catalytic strategies can often be developed using novel, coordinatively unsaturated metal structures, which are hard to isolate in homogeneous solutions. Attachment of metal complexes onto a surface results in their stabilization and prevents aggregation and decomposition.[1] Recently, we produced a novel three-coordinate unsaturated ruthenium complex on a SiO_2 surface by coupling with SiO_2-bound *p*-styryltrimethoxysilane.[2] The unsaturated Ru complex was highly active for selective alkene epoxidation using a mixture of isobutyraldehyde and O_2. However, the Ru complex was inactive for selective oxidation of saturated hydrocarbons with O_2 as a sole oxidant, which may be more important from the viewpoint of practical use as a catalyst.

A SiO_2-supported Ru complex (**B**) was prepared using a *N*-sulfonyl-1,2-ethylenediamine–Ru complex (**A**)[3] and *p*-styryltrimethoxysilane-functionalized SiO_2 (Scheme 1, Supporting Information 1).[2] The local coordination structure of **B** was similar to that of **A**. Ultraviolet irradiation ($\lambda >$ 275 nm) of **B** under N_2 was found to cause the stoichiometric elimination of a coordinated *p*-cymene ligand from the supported Ru complex. 87 % of free *p*-cymene was detected in a solution after the photoirradiation of **B** under N_2 for 2 h (Table 1) affording the coordinatively unsaturated Ru complex **C2**. The elimination of *p*-cymene was also evidenced by ^{13}C solid-state magic-angle spinning (MAS) NMR spectroscopy (Figure 1).

X-ray photoelectron spectroscopy (XPS) revealed a shift in binding energy of Ru $3d_{5/2}$, on elimination of *p*-cymene, from 282.0 eV for **B**, to 282.2 eV for **C2**, (Table 1 and Supporting Information 2). The shift in the binding energy of Ru $3d_{5/2}$ indicates that the surface Ru complex is positively charged by the photoirradiation.[4] However, the similar ratio of the XPS signal intensities for Cl 2p to Ru $3p_{3/2}$ in **B** and **C2** indicates that the supported Ru complex **C2** retains a Cl ligand. A change was also evident in the Ru K-edge X-ray absorption near-edge structure (XANES) spectroscopic signal (see Supporting Information 3). Ru K-edge extended X-ray absorption fine structure (EXAFS) spectroscopic analysis revealed two coordinations, Ru−O(N) and Ru−Cl, with bond orders of 3.2 and 1.0 , and bond distances of (2.10 ± 0.01) Å and (2.38 ± 0.01) Å, respectively (see Supporting Information 4), which confirms the retention of Cl, suggested by XPS, and also indicates surface coordination to Ru by oxygen, alongside the immobilization by silane coupling. ^{13}C solid-state NMR spectroscopy indicated that the organic diamine ligand was retained during photoinduced *p*-cymene elimination (Figure 1).

Photoirradiation ($\lambda >$ 275 nm) of **B** under an O_2 atmosphere also resulted in dissociation of a *p*-cymene ligand (Table 1, Figure 1, Scheme 1) but afforded a different structure, **C1**, as evidenced by a very different UV/Vis spectrum to that of **C2** (Figure 2). The spectrum for **C2**, produced under N_2, shows two signals in the visible-light region, at 468 nm and 696 nm (Figure 2 d), whereas that for **C1**, produced under O_2, has one signal, at around 517 nm (Figure 2 e). However, the XPS Ru $3d_{5/2}$ signal (at 282.2 eV), solid-state NMR spectrum, and Ru K-edge EXAFS spectrum of **C1** were almost the same as those of **C2**. Notably, **C1** and **C2** are interconverted reversibly: **C1** was converted into **C2** by photoirradiation ($\lambda >$ 275 nm) under N_2, and **C2** was converted into **C1** by photoirradiation ($\lambda >$ 370 nm) under O_2 (Figure 2 e–h). Neither O_2

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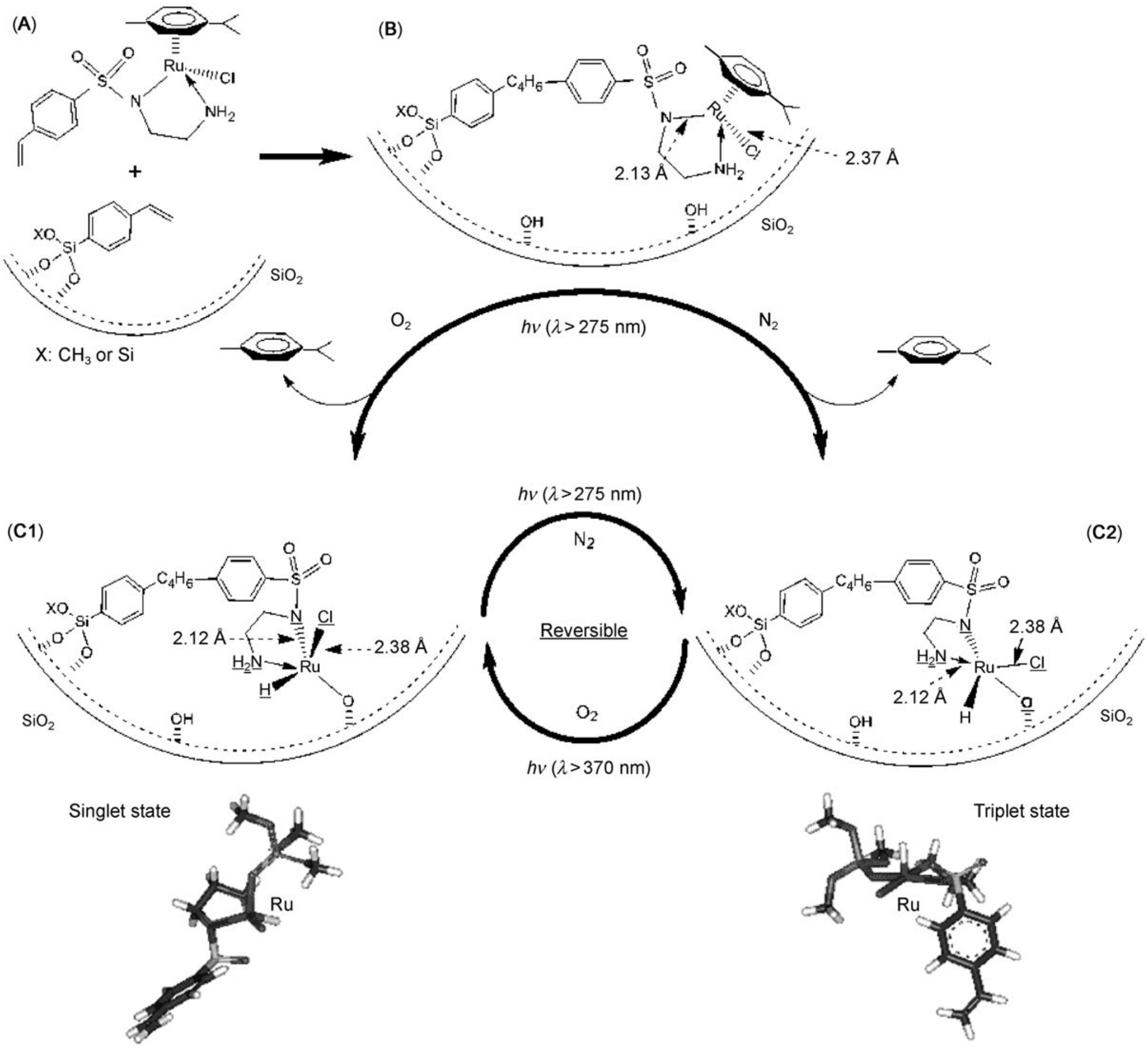


Scheme 1. Photoinduced synthesis of unsaturated SiO_2-supported Ru complexes **C1** and **C2**, and atmosphere/wavelength-dependent photoinduced interconversion between **C1** and **C2**. Bond distances were determined by EXAFS.

Table 1: The amounts of free *p*-cymene detected by GC and chlorine estimated by XPS, and XPS binding energies of Ru $3d_{5/2}$

Catalyst	Free *p*-cymene [mol %][a]	Cl [mol %][b]	Ru $3d_{5/2}$ binding energy [eV][c]
B	0	102	282.0
C1	60–85[d]	99	282.2
C2	87	99	282.2

[a] The solution after the photoirradiation was analyzed by GC. Percentages given with respect to Ru. [b] Estimated by the intensity ratio of Cl 2p to Ru $3p_{3/2}$. Percentages given with respect to Ru. [c] Determined by XPS. [d] Free *p*-cymene in the solution was further oxidized to many products, depending on the photoirradiation conditions.

nor N_2 adsorption were detected in the structural transformations. These results indicate that the photoinduced reversible structural transformation of the supported Ru complexes on SiO_2 is ascribed to a change in the coordination symmetry of the Ru center.

Similar photoirradiation of a solution of precursor complex **A** in cyclohexane did not bring about the elimination of *p*-cymene (< 12% dissociation after 5 h). When 1,3,5,7,9,11,14-heptacyclohexyltricyclo[7,3,3,$1^{5,11}$]heptasiloxane-3,7,14-triol (**D**), with Si−OH functional groups, was added into the homogeneous solution of **A**, the *p*-cymene ligand readily photodissociated (96% dissociation after 3 h), indicating that surface Si−OH groups positively contributed to the photodissociation of the *p*-cymene ligand (Supporting Information 5). A similar effect of Si−OH groups on SiO_2 on immobilized Ru complexes was reported previously.[5a]

In density functional theory (DFT) calculations for **C1** and **C2** (Supporting Information 6), $Si(OH)(OCH_3)_3$ was used as a model of a surface Si-OH group. Simple Ru–OH–$Si(OCH_3)_3$ coordination did not stabilize the unsaturated Ru complex. However, the cleavage of Si−OH provides several potential H−Ru−O(Si) structures with different coordination symmetries. Among these possible structures, we found two stable configurations (**C1** and **C2**) with square-pyramidal conformations (Scheme 1), in which the Ru−H bond was located either in an equatorial site (singlet state, **C1**) or an axial site (triplet state, **C2**).

UV/Vis spectra of these two structures calculated by DFT successfully reproduced the observed spectra of **C1** and **C2**. The wavelength- and atmosphere-dependent reversible transformation between **C1** and **C2** can be explained by the energy diagram of the Ru species by the DFT calculations, where the **C2**→**C1** transformation may be assisted by O_2 (Supporting Information 7). It was also reported that Si–H species contributed to formation of a Ru–H complex on a SiO_2 surface.[5b]

η^6-Arene ligands on Ru^{II} can be labilized by ultraviolet irradiation or heating.[6] The possibility that *p*-cymene is eliminated thermally in this reaction was examined by heating **B** at 373 K for 3 h under O_2 or N_2 without irradiation. Neither dissociation of *p*-cymene nor change in the UV/Vis spectrum of **B** occurred in either case (Figure 2a–c). No structural transformation between **C1** and **C2** occurred by thermal reaction at 373 K either. The photoexcitation threshold energies were 275 nm for **C1** and 370 nm for **C2**, which were attributed to Ru d + Cl p→Ru d + Ph π and Ru d→Ph π transitions, respectively, as suggested by time-dependent density functional theory (TDDFT) calculations.

The unsaturated Ru complex **C1** was found to be catalytically active and reusable for the selective photooxidation of cycloalkanes to the corresponding alcohols and ketones using O_2. SiO_2, Ru metal, RuO_2, $RuCl_3$, $[Ru_2(p\text{-cymene})_2Cl_4]$,and the homogeneous Ru precursor complex **A** were all essentially inactive for this process (Table 2). The complex **C1** (prepared under O_2) produced cyclohexanol (turnover frequency (TOF) = 3.1 h^{-1}) and cyclohexanone (TOF = 2.8 h^{-1}) from cyclohexane without any induction period at room temperature (Supporting Information 8). Cyclohexane oxidation proceeded linearly for at least 6 h and turnover number (TON) of the photooxidation reached 35 after 6 h with 96% selectivity. Cyclohexane oxidation on **C1** did not proceed thermally at 353 K after 24 h.

Initially, neither **B** (with coordinated *p*-cymene) nor **C2** (prepared under N_2) catalyzed photooxidation. However, after an induction period of 2 h, similar catalytic activities to that for **C1** were obtained (Supporting Information 8). Elimination of *p*-cymene from **B** under O_2 was completed in 2 h, indicating that the induction period, in the **B**-catalyzed reaction, corresponded to a structural change from **B** to **C1** releasing *p*-cymene ligand. The induction period (2 h) for the **C2**-catalyzed photooxidation is explained as the time taken for phototransformation from **C2** to **C1** under an O_2 atmosphere. After the induction periods, UV/Vis spectra of the Ru species were similar to that of **C1**, in both cases. These results suggest that **C1** was the active species for selective photooxidation using O_2.

Formation of peroxide intermediate Ru–OOH on the supported Ru complex, and in the solution phase, was investigated by iodometry. After the photooxidation of cyclohexane on the supported Ru catalyst, 20 mol% peroxide (with respect to Ru) was detected, whereas no free organic peroxide was detected in the reaction solution. The peroxide Ru–OOH may be formed by the insertion of O_2 into Ru–H in species **C1** at an excited state (Scheme 2). The **C2** structure is

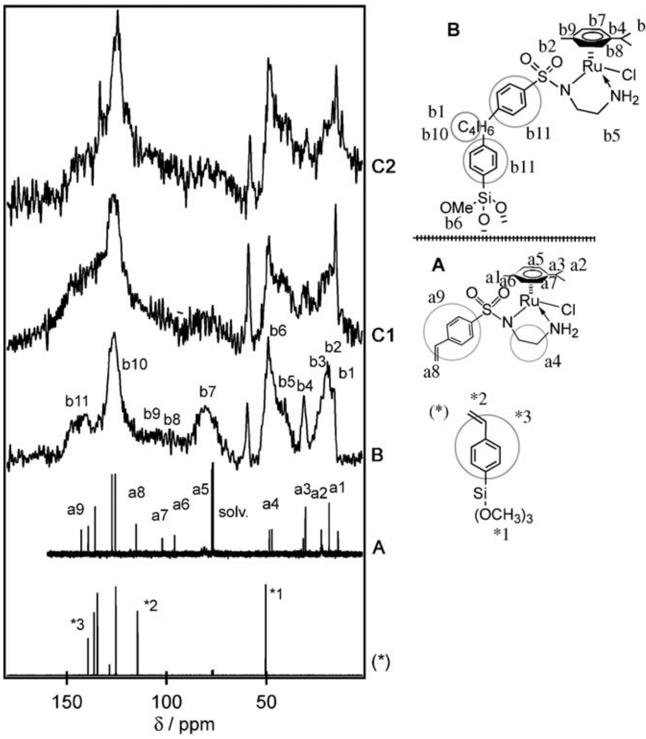


Figure 1. ^{13}C liquid/solid-state NMR spectra for *p*-styryltrimethoxysilane (*), *N*-sulfonyl-1,2-ethylenediamine–Ru complex **A**, the SiO_2-supported Ru complex **B**, and the unsaturated Ru complexes **C1** and **C2**.

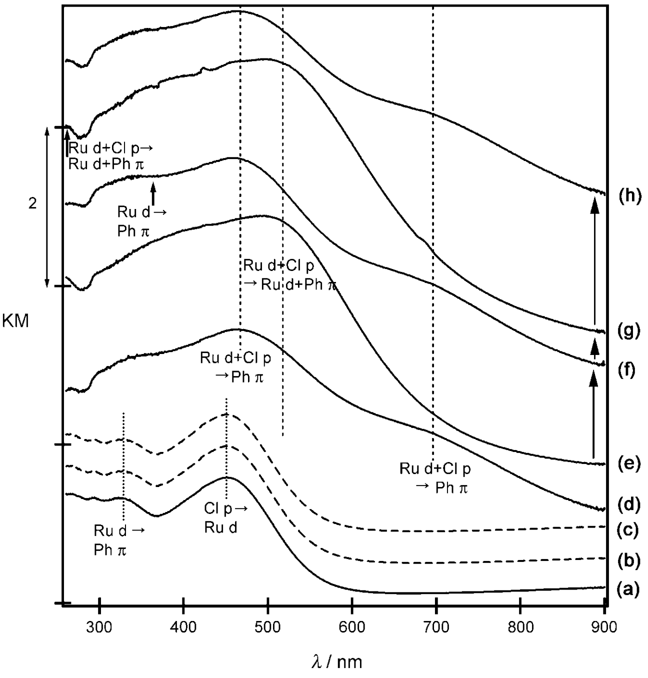
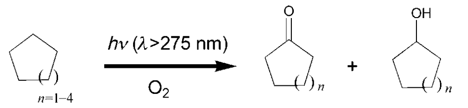


Figure 2. Diffuse-reflectance UV/Vis spectra of the SiO_2-supported Ru complexes and assignments of the peaks. a) Complex **B**; b) **B** heated at 373 K for 2 h under N_2; c) **B** heated at 373 K for 2 h under O_2; d) **C2** (formed by photoirradiation of **B** at $\lambda > 275$ nm for 1 h under N_2; e) **C1** (formed by photoirradiation of **B** at $\lambda > 275$ nm for 1 h under O_2; f) (after e) photoirradiation of **C1** at $\lambda > 275$ nm for 2 h under N_2 (**C1**→**C2**); g) (after f) photoirradiation of **C2**(λ>370 nm) for 1 h under O_2 (**C1**→**C2**→**C1**); h) (after g), photoirradiation of **C1** at $\lambda > 275$ nm for 2 h under N_2 (**C1**→**C2**→**C1**→**C2**).

Table 2: Catalytic performance for photooxidation of cycloalkanes using O_2.[a]

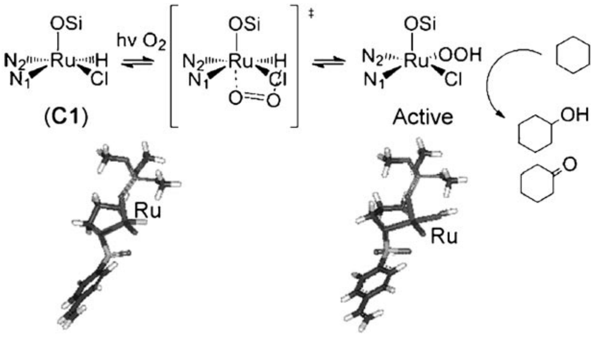


Catalyst	n	TOF(R=O) $[h^{-1}]$	TOF (R-OH) $[h^{-1}]$
none	2	0.1	0
SiO_2[b]	2	0.1	0
Ru[c]	2	trace	0
RuO_2[c]	2	0.17	0
$RuCl_3$[c]	2	0.16	0
$[Ru_2(p\text{-cymene})_2C_{l4}]$[c, d]	2	0.18	0
homogeneous **A**[c,d]	2	0.10	0
B with *p*-cymene[e, f]	2	1.1	0.9
[g]		3.3	3.3
B at 353 K[e,h]	2	0	0
C1[e, i]	2	0	0
C1 at 353 K[e, h]	2	0	0
C1[e, f]	2	3.1	3.2
[g]		2.8	3.1
C2[e, f]	2	1.2	0.9
[g]		2.9	2.8
C1 on Al_2O_3[e]	2	1.7	1.8
C1[e]	1	0.14	trace
C1[e]	3	6.1	3.1
C1[e]	4	1.4	1
C1[e]	8	0.12	trace

[a] Alkane (10.0 mL), O_2 (101.3 kPa). 400 W Hg–Xe lamp ($\lambda > 275$ nm). TOFs were estimated between 0–5 h. [b] 25 mg. [c] Ru (5.8 μmol). [d] Decomposed. [e] Catalyst (25 mg) (5.8 μmol Ru). [f] TOF for initial 1 h. [g] TOF for 3–5 h. [h] Heated at 373 K without photoirradiation. [i] Without photoirradiation.

geometrically inactive for Ru-OOH formation. The catalytic reaction was first-order with respect to photon intensity for both cyclohexanol and cyclohexanone (Supporting Information 9). Hence, initial oxygen insertion is likely to be rate-determining for the photooxidation.

In summary, we have succeeded in preparing novel unsaturated Ru complexes (**C1**, **C2**) immobilized at double sites on a SiO_2 surface by the photoinduced selective elimination of a *p*-cymene ligand in **B**, accompanied by dissociative coordination of a surface OH group to the unsaturated Ru center at the surface as a result of UV/Vis light irradiation. We also detected reversible structural transformation between the photoexcited supported Ru complexes, depending on the light wavelength and atmosphere. The structure **C1**, produced by photoirradiation under O_2, was the active species for the photooxidation of cycloalkanes using O_2.



Scheme 2. Formation of catalytically active Ru–peroxide intermediate.

Experimental Section

For full details see the Supporting Information. In brief, complex **A**[3] was treated with a SiO_2-supported *p*-styryl moiety[2] in anhydrous $CHCl_3$ in the presence of azobisisobutyronitrile (AIBN). The reaction mixture was heated at reflux for 24 h under N_2. Soxhlet extraction and subsequent drying under reduced pressure afforded the SiO_2-supported *p*-cymene–Ru complex **B** (Supporting Information 1). Selective elimination of the coordinated *p*-cymene ligand was carried out by photoirradiation using a high-pressure 400 W Hg–Xe lamp with an optical short-wavelength cut-off filter. In a quartz reactor, **B** was dipped in water at 293 K and an absolute solvent (dichloromethane or cyclohexane), and O_2, N_2, or Ar at atmospheric pressure were admitted to the reactor. The stoichiometric elimination of *p*-cymene was detected by flame ionization detector gas chromatography (FID–GC) and GC–MS. The structures were characterized by solid-state NMR, FTIR, XPS, diffuse reflectance UV/Vis, and EXAFS spectroscopy.

Catalytic photooxidation of alkanes was carried out in a neat solution of each reactant under O_2 atmosphere at 293 K. The quartz reactor with a stirrer was irradiated by the 400 W Hg–Xe lamp through a cut-off filter absorbing light with a wavelength less than 275 nm and a water layer absorbing in the infrared region. The products (alkane, alcohol, and ketone) were analyzed at appropriate intervals by FID-GC, GC–MS, and thermal conductivity detector (TCD)-GC (O_2 and CO_2).

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