# Selectivity control of oxygen transfer reactions catalyzed by the ruthenium complexes with monodentate oxygen or nitrogen ligand bound to FSM

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### ARTICLE INFO

### ABSTRACT

Two kinds of immobilized ruthenium complex with tetradentate BABP (6,6′-bis(benzoylamino)-2,2′-bipyridine) ligand are prepared. One is compound **1** (FSM-Ru) directly bound to silica of the FSM-surface through Ru–O–Si bond, and others are compounds **2** (FSM-Aps-Ru) and **3** (FSM-Ims-Ru) with monodentate nitrogen ligands bound to silica surface. These ruthenium complexes encapsulated into mesopore of FSM showed interesting activity for oxygen transfer reaction of cyclohexene using tert-butylhydroperoxide (TBHP) as an oxidant. The FSM-Ru catalyst (**1**) having oxygen donor gave 1,2-epoxycyclohexane (epoxide) selectively through stepwise addition of TBHP, although **2** and **3** having nitrogen donor gave 2-cyclohexen-1-yl tert-butyl peroxide (peroxide) mainly. This remarkable selectivity control in the oxygen transfer reaction is interpreted in terms of the *trans*-influence of the ruthenium complex with the axially coordinating monodentate ligand on the silica support. Moreover, the heterogeneous catalyst **1** was recycled and used three times in epoxidation of cyclohexene, since leaching of the ruthenium species from **1** was not observed under argon atmosphere.

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## 1. Introduction

Immobilized catalysts are of great interest for environmentally benign synthesis in the viewpoint of green and sustainable chemistry [1,2]. Using a complex immobilized on an organic support, such as polystyrene or polyacrylic acid, is not suitable for oxidation reactions, because aggressive oxidants can ruin the weak C–H bond of the organic polymer [1]. On the other hand, an inorganic support, such as silica, zeolite, and clay, providing thermally, chemically, and mechanically stable reaction site, has been often utilized for various catalytic reactions, because it has high surface area and appropriate pore size and is, moreover, not much affected by various oxidants [3,4]. Mesoporous silica, FSM (folded-sheet mesoporous material), has been reported to form a chlorophyll–FSM conjugate, exhibiting photoinduced ability to catalyze the reduction of methyl viologen, where mesopore of FSM acted as a site for inter-action between chlorophyll molecules and the silica support [5]. Ruthenium porphyrin complexes immobilized into mesoporous silica also showed high catalytic activity for oxidation of olefins [6]. We have previously reported the selective epoxidation of cyclohexene using the ruthenium complex immobilized into FSM [7]. When used as an inorganic support in preparation of oxidation catalyst, FSM provides a suitable reaction site in its mesoporous sphere [8].

High-valent metal-oxo species have been proposed as one of the active intermediates not only in metalloenzymes but also in the oxidation of organic compounds catalyzed by transition metal complexes [9–12]. We have also reported the catalysis of ruthenium complexes for oxygen transfer reaction, where the oxidation activity of high-valent Ru=O species was controlled by the axial ligand coordinated at the *trans*-position [13–19]. In order to characterize the oxo species generated upon the ruthenium complex, some mechanistic investigations have been carried out using tripodal polypyridylamine derivatives [17–19] or porphyrin ligands [20,21]. The Ru(IV)=O species with pyridine ligand hardly showed epoxidation activity but dominantly showed radical character for abstraction of hydrogen atom [22,23]. On the other hand, the higher valent Ru(V)=O or Ru(VI)=O species showed epoxidation activity [12,24,25]. The activity of the metal-oxo species surrounded with square planar ligand was regulated by another axial ligand at its *trans*-position (Scheme 1) [15,16,26]. The *trans*-influence of
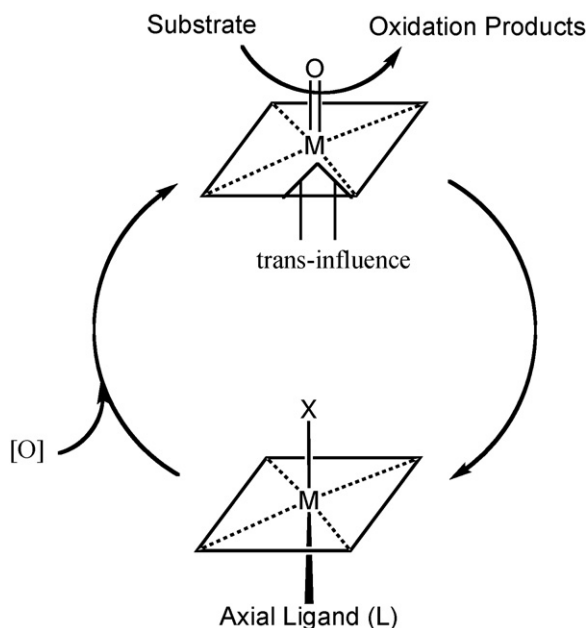
**Scheme 1.** Oxygen transfer reaction controlled by the axial ligand (L) coordinating at the *trans*-position of metal-oxo species (X = unidentified ligand).

the iron-oxo species on the catalytic activity was also observed in cytochrome P-450 reactions [26–28].

Using FSM as an inorganic support, we previously developed a new catalytic method for the selective formation of cyclohexene oxide, in which the ruthenium species was directly bonded to the surface of the mesopore of FSM [7]. The Ru–O–Si species generated upon the FSM-surface is an active intermediate for epoxidation. We have found an interesting selectivity control for the oxygenation of cyclohexene through a further investigation of the binding methods of the ruthenium complex to FSM. When the monodentate coordination atom to the ruthenium center at the axial position was changed from oxygen to nitrogen, alternative selectivity on the oxygen transfer reaction was observed. Here, we describe different reactivities in epoxidation or allylic oxidation of cyclohexene catalyzed by the immobilized ruthenium complex with square planar ligands. Interestingly, the coordination atom, oxygen or nitrogen, bound to mesoporous silicate is able to control the reaction selectivity. The remarkable difference in the catalysis was demonstrated when different immobilization methods were examined in the heterogeneous system. This is the first report controlling the selectivity in the oxygen transfer reaction mediated by the ruthenium complex, consisting of square planar tetradentate ligand attached into the mesopore of inorganic support. The method of fixing the complex to inorganic support is the key factor for selectivity control, although the previous metal complexes covalently anchored to silica are unable to show the *trans*-influence [1,2,29].

## 2. Experimental section

### 2.1. Materials

Reagents used for synthesis were of the highest grade available, which were employed without further purification. tert-Butyl hydroperoxide (TBHP), of which active oxidant 97% estimated by iodometric titration, was purified by dehydration and distillation. All solvents for spectroscopic measurements were purified by distillation before use.

Ruthenium complexes with babp ligand, [Ru(babp)(dmso)(im)] (**4**) and [Ru(babp)(dmso)$_2$] (**5**), were prepared according to the

methods previously reported [14,16]. The immobilized catalysts were prepared as follows by using **5** as a starting complex. Characterization of mesoporous compounds was carried out according to the method previously reported [7,46]. Amounts of the immobilized ruthenium complex into mesopores of FSM in **1**, **2**, and **3** were determined by the measurement of the decrease in the absorption band of the starting complex in solution phase.

### 2.1.1. Preparation of 1 (FSM-Ru)

To dried FSM (100 mg) 13 mg of **5** in dichloromethane (10 mL) was added, and the mixture was stirred at room temperature under argon atmosphere. After 1 h, the white powder of FSM turned yellow, and the color of the reaction solution changed to colorless. When polar solvents, such as methanol and acetone were used, adsorption of the complex to the FSM did not proceed. The yellow powder of **1** was obtained after filtration and stocked under an anaerobic condition. The proposed structure of **1** is illustrated in Scheme 2.

### 2.1.2. Preparation of 2 (FSM-Aps-Ru) and 3 (FSM-Ims-Ru)

To dried FSM (100 mg) in toluene (5 mL) solution (3-aminopropyl)triethoxysilane (Aps-(OEt)$_3$, 111 mg) or (3-(2-imidazolin-1-yl)propyl)triethoxysilane (Ims-(OEt)$_3$ was added, 137 mg) and the mixture was refluxed under argon atmosphere for 12 h [24]. After cooling, the pretreated FSM (FSM-Aps or FSM-Ims) was washed with toluene. To this pretreated FSM (100 mg) appropriate amount of [Ru(babp)(dmso)$_2$] (**5**) complex in dichloromethane (10 mL) was added and the mixture was stirred at room temperature under argon atmosphere. After 1 h, the white powder of FSM changed to orange, and the color of the reaction solution turned colorless as in case of **1**. The orange powder of **2** or **3** was obtained after filtration and stocked under an anaerobic condition. The pore size of **1**, **2**, and **3** was measured by the Barret–Joyner–Halenda (BJH) analysis method.

### 2.2. Oxidation of cyclic olefins

Oxidation of (Z)-cyclooctene and cyclohexene was carried out under argon atmosphere at 40 °C using PhIO or TBHP as an oxidant. To a suspension of the heterogeneous catalysts (**1**–**3**, 0.005 mmol of ruthenium) or a solution of homogeneous catalysts (**4** and **5**, 0.005 mmol of ruthenium) in 1,2-dichloroethane (5 mL) olefin (55 mg cyclooctene or 40 mg cyclohexene, 0.5 mmol) and the oxidant (PhIO 110 mg or TBHP 45 mg, 0.5 mmol) were added. The color of the FSM compound changed from orange to green. In the oxidation of cyclooctene, remarkable reactivity was not observed whether TBHP was added to the reaction solution at once or stepwise. The reaction solution was monitored by GC analysis at appropriate time and the oxidation products were determined by comparison with the authentic samples.

## 3. Results and discussion

### 3.1. Preparation of catalysts

For preparation of a high-performance oxidation catalyst, it is important to avoid collapsing of the complex. The tolerant ruthenium complex with tetradentate BABP (6,6′-bis(benzoylamino)-2,2′-bipyridine) ligand previously reported is expected to resist the oxidative self-degradation [14]. Using this complex, two kinds of immobilized catalysts were prepared. One was compound **1** (FSM-Ru) bound to silica support through Ru–O–Si bond, the activity of which was partially reported [7]. In **1**, the coordination atom of the fifth ligand (L in Scheme 1) at the axial position was oxygen (O). Preparation of **1** was very easy. The reaction of the starting
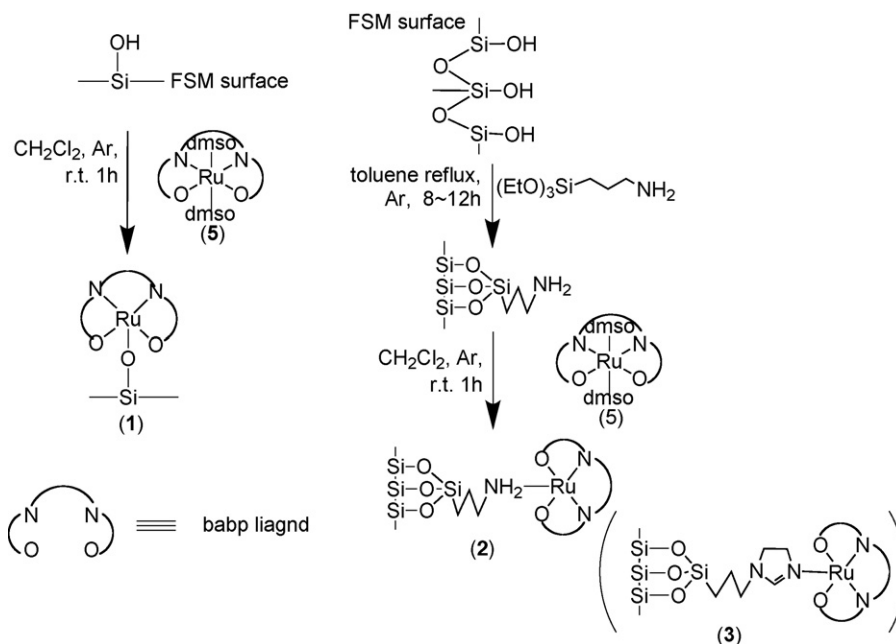
**Scheme 2.** Preparation of immobilized catalysts (**1**–**3**). The structure of the ruthenium complexes with babp ligand (**4** and **5**) was referred to the references [14,16].

complex and mesoporous silica in less polar solvent under anaerobic condition gave **1**. This ligand exchange reaction from dimethyl sulfoxide (dmso) to silicate provides a useful method for preparation of **1**, which has advantage of preparation in comparison with other methods using multidentate ligand covalently anchored to organic or inorganic support. The others were compound **2** (FSM-Aps-Ru) and **3** (FSM-Ims-Ru). In **2** and **3**, the coordination atom of the fifth ligand (L in Scheme 1) was nitrogen (N). The pretreated FSM (FSM-Asp and FSM-Ims) was prepared from the reaction of FSM and a silane-coupling reagent with amine or imidazolynyl function [30]. The reaction of FSM and 3-(aminopropyl)triethoxysilane or 3-((2-imidazolin-1-yl)propyl)triethoxysilane in toluene solution gave FSM-Asp or FSM-Ims, respectively. In this pretreated FSM, the 3-aminopropyl or 3-(2-imidazolin-1-yl)propyl group acts as a monodentate ligand for the ruthenium center and as a linker that joins the complex to the silica surface of FSM. In the preparation of **2** and **3**, ligand exchange reaction from monodentate dmso attached on the starting complex [Ru(babp)(dmso)$_2$] (**5**) to the nitrogen atom smoothly proceeded in dichloromethane solution. These preparation methods for **1**, **2**, and **3** are illustrated in Scheme 2. The complex [Ru(babp)(dmso)(im)] (**4**) as a homogeneous catalyst for a reference to the immobilized complex, **2** or **3**, was also prepared according to the previous method [14,16]. In the case of acetonitrile solution, however, immobilization of **5** into FSM derivatives hardly progressed.

In the reaction of **5** and FSM in dichloromethane solution under argon atmosphere, the color of FSM powder changed from white to orange and that of the reaction solution turned colorless. This finding indicated that the starting complex in solution phase was immobilized into FSM. FT-Raman and XPS spectra of **1** revealed the dissociation of the dmso ligand. Moreover, the silent ESR spectrum of **1** indicated that the oxidation state of ruthenium in immobilized complex was +2. The ligand exchange reaction at the axial position of the starting [Ru(babp)(dmso)$_2$] complex (**5**) might take place and the silane-oxide species was formed in **1**, although the characteristic stretching band derived from Ru–O–Si was not identified in FT-Raman or IR spectra [31]. We were unable to spectroscopically characterize what was the six ligand (X in Scheme 1) attached to the immobilized complex **1**. The above spectroscopic analysis might indicate that the sixth ligand was absent, because the coordinatively

unsaturated ruthenium species without the sixth ligand was stable in the mesopore of FSM [32]. Ruthenium complexes with a monodentate oxygen ligand were scarcely formed, because the HSAB rule suggests the difficulty of the coordination of an oxygen atom to the low-valent ruthenium center [33,34]. Notably, the monodentate coordination of the oxygen atom to the ruthenium center was achieved only in this FSM system.

The immobilized complexes, **2** and **3**, were prepared in the reaction of the pretreated FSM and [Ru(babp)(dmso)$_2$] complex (**5**) in dichloromethane solution under argon atmosphere. The similar color change as mentioned above indicated the formation of **2** and **3**. This immobilization procedure was the same irrespective of the pore size of FSM, where the average diameters employed were here about 2.8 nm (FSM(a)) and 4.0 nm (FSM(b)), respectively. In the cases of compound **2** (FSM-Aps-Ru) and **3** (FSM-Ims-Ru), two kinds of FSM as mentioned above were used. The information on the textural properties of the catalysts can be gathered by the nitrogen adsorption–desorption isotherms at −196 °C in Fig. 1. The specific surface area and pore volumes are given in Table 1, indicating that
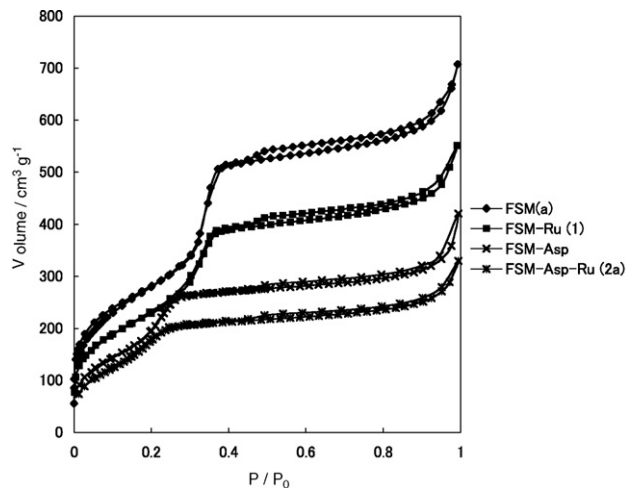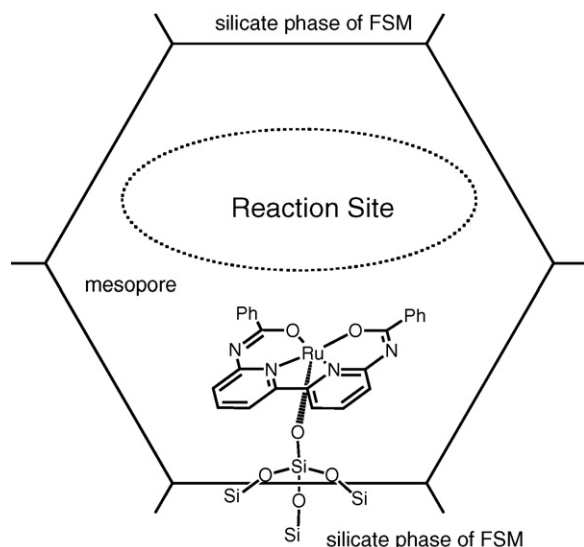


**Fig. 1.** Nitrogen adsorption–desorption isotherms of mesoporous compounds.

**Table 1**
Character of mesoporous compounds.

| | FSM(a) | FSM-Ru (1) | FSM-Aps | FSM-Aps-Ru (2a) |
|---|---|---|---|---|
| Pore volume ($cm^3/g$) | 0.79 | 0.45 | 0.40 | 0.31 |
| Averaged pore diameter (nm) | 2.8 | 2.65 | 2.2 | 2.0 |



**Scheme 3.** Immobilization of ruthenium complex with square planar ligand and reaction site generated in the mesopore of FSM.

FSM and the derivatives have the mesoporous structure. The pore size of **1** decreased as compared with that of the starting FSM: in **1**, the pore volume ($V_p$) was 0.45 $cm^3\,g^{-1}$ and its average diameter was 2.6 nm, whereas the $V_p$ of the original FSM(a) was 0.79 $cm^3\,g^{-1}$ and its average diameter was 2.8 nm. In **2** prepared from FSM(a), the $V_p$ was 0.31 $cm^3\,g^{-1}$ and its average diameter was 2.0 nm, whereas the $V_p$ of the original pretreated FSM(a) was 0.40 $cm^3\,g^{-1}$ and its average diameter was 2.2 nm. The decrease in the pore volume indicated that the ruthenium complex was immobilized into the mesopore of FSM. The plausible structure of **1** is illustrated in Scheme 3.

### 3.2. Activities of the ruthenium catalysts for (Z)-cyclooctene oxidation

Oxidation of (Z)-cyclooctene was carried out under argon atmosphere at 40 °C using iodosobenzene (PhIO) or $^t$BuOOH (TBHP) as an oxidant. The results are summarized in Table 2. Generally, epoxidation of (Z)-cyclooctene catalyzed by ruthenium complexes does not proceed quantitatively. For example, 1,2-epoxycyclooctane was

obtained in a 19% yield when the mononuclear ruthenium(III) complex with Schiff base ligand was used as a catalyst [35], and Ru(III) salen complexes gave epoxide in poor yield in comparison with the corresponding Mn(III) complexes [36]. The slight difference in the activity between **4** and **5** in the homogeneous system was caused by the *trans*-influence of the axial ligand [16]. In case of PhIO, which was known to be an efficient 2-electron oxidant for generation of Ru=O species [25], epoxidation activity of **1** or **2a** in the heterogeneous system was similar to that in the homogeneous system using **4** or **5**, even though slightly long reaction time was needed. The relatively lower epoxidation activity compared with periodate oxidant ($IO_4{}^-$) is explained by the oxidation ability of PhIO [37]. When TBHP was used as an oxidant, the yield of 1,2-epoxycyclooctane at 4 h reaction was 26% in the homogeneous system catalyzed by **5**, and the same yield was obtained at 24 h reaction in the heterogeneous system catalyzed by **1**. The slightly lower activity of **2a** in comparison with **1** in Table 2 was interpreted in terms of the loading amount of the ruthenium complex into FSM. The loading amount of the ruthenium complex to FSM in **1** was 13 mg/100 mg (Ru/FSM) and that in **2** was 9 mg/100 mg. When cyclooctene was used as a substrate, the coordinating atom at the *trans*-position in **1** or **2a** (oxygen or nitrogen) might not affect the oxidation activity, which resembles the activity of an immobilized Mn(III) complex [38]. In addition, leaching of the complex was not detected in the dichloromethane solution under anaerobic conditions.

### 3.3. Oxidation of cyclohexene catalyzed by the heterogeneous ruthenium catalysts with PhIO oxidant

Cyclohexene is known to be a versatile substrate for investigation of the active intermediate in oxidation. Epoxidation of double bonds is accelerated by the electrophilic character of the high-valent metal-oxo species and allylic oxidation is accelerated by the radical character [16,39]. When PhIO and ruthenium catalysts, **1**, **2**, and **3**, are used in the heterogeneous system, oxidation of cyclohexene mainly gave 1,2-epoxycyclohexane as well as the cases of **4** and **5** in the homogeneous system, even though slightly long reaction time was needed. In all cases in Table 3, the epoxidation selectivity in the all oxidation products (1,2-epoxycyclohexane, 2-cyclohexen-1-ol, and 2-cyclohexen-1-one) was about 80% both in the heterogeneous and homogeneous systems, indicating that the difference in the oxidation activity due to the coordinating atom axially attached to the ruthenium center was not observed. This high selectivity is explained by the contribution of the Ru(V)=O species, generated from PhIO and the starting ruthenium complex [12,16,24,25]. The relatively high yield of the epoxide in entry 1 compared with entry 2 is interpreted in terms of the loading amount of ruthenium complex in the FSM compounds as mentioned above.

**Table 2**
Oxidation of (Z)-cyclooctene catalyzed by the ruthenium compounds.[a]

| Catalyst | System | PhIO oxidant | | TBHP oxidant | |
|---|---|---|---|---|---|
| | | Reaction time (h) | Epoxide[d] yield (%) | Reaction time (h) | Epoxide[d] yield (%) |
| FSM-Ru(**1**)[b] | Heterogeneous | 4 | 20 | 4 | 18 |
| | | 24 | 45 | 24 | 26 |
| FSM-Aps-Ru(**2a**)[c] | Heterogeneous | 4 | 17 | 4 | 8.2 |
| | | 10 | 24 | 24 | 16 |
| [Ru(babp)(dmso)(im)](**4**) | Homogeneous | 4 | 30 | 4 | 3.6 |
| | | | | 24 | 28 |
| [Ru(babp)(dmso)$_2$](**5**) | Homogeneous | 4 | 24 | 4 | 26 |

[a] Reaction conditions: catalyst:oxidant:cyclooctene = 1:100:100, 40 °C, 1,2-dichloroethane, under Ar.
[b] **5** (13 mg)/FSM(a) (100 mg).
[c] **5** (9 mg)/FSM(a)-Asp (100 mg).
[d] 1,2-Epoxycyclooctane.

**Table 3**
Oxidation of cyclohexene catalyzed by ruthenium compounds with PhIO oxidant.[a].

| Entry | Catalyst | System | Products yield (%) | | | | |
|---|---|---|---|---|---|---|---|
| | | | Reaction time (h) | Epoxide[g] | Enone[h] | Enol[i] | Selectivity for epoxide |
| 1 | FSM-Ru(**1**)[b] | Heterogeneous | 4 | 19 | 3.2 | trace | 87 |
| 2 | FSM-Aps-Ru(**2a**)[c] | | 5 | 14 | 2.4 | 0.7 | 82 |
| 3 | FSM-Aps-Ru(**2b**)[d] | | 5 | 15 | 4.0 | trace | 79 |
| 4 | FSM-Ims-Ru(**3a**)[e] | | 5 | 6.1 | 1.4 | 0.4 | 77 |
| 5 | | | 24 | 12 | 2.5 | 0.5 | 80 |
| 6 | FSM-Ims-Ru(**3b**)[f] | | 5 | 12 | 1.7 | 0.5 | 85 |
| 7 | [Ru(babp)(dmso)(im)](**4**) | Homogeneous | 4 | 22 | 5.3 | 0.8 | 78 |
| 8 | [Ru(babp)(dmso)₂](**5**) | | 4 | 19 | 5.2 | 0.4 | 79 |

[a] Reaction conditions: catalyst:PhIO:cyclohexene = 1:100:100, 40 °C, 1,2-dichloroethane, under Ar.
[b] **5** (13 mg)/FSM(a) (100 mg).
[c] **5** (9 mg)/FSM(a)-Asp (100 mg).
[d] **5** (6 mg)/FSM(b)-Aps (100 mg).
[e] **5** (8 mg)/FSM(a)-Ims (100 mg).
[f] **5** (8 mg)/FSM(b)-Ims (100 mg).
[g] 1,2-Epoxycyclohexane.
[h] 2-Cyclohexen-1-one.
[i] 2-Cyclohexen-1-ol.

Although the high selectivity for the oxidation products was not demonstrated on the catalyst system employed here, relatively high activity was demonstrated in FSM-Aps-Ru catalyst (**2a**), in comparison with FSM-Ims-Ru one (**3a**) (entries 2 and 4). The axially coordinating nitrogen atom derived from alkylamine of Asp more strongly affects the character of Ru=O species at the *trans*-position than that derived from heterocycle of Ims [16]. In entries 4–6, the catalytic activity of the FSM-Ims catalyst (**3b**) with the larger pore size (about 4.0 nm in the original FSM(b)) was higher than that of **3a** with the smaller pore (about 2.8 nm in the original FSM(a)). Diffusion of the substrate and product in the pore of the catalyst affected this activity. These findings indicate that the catalytic reaction occurred inside the mesopore of FSM.

### 3.4. Oxidation of cyclohexene catalyzed by the heterogeneous ruthenium catalysts with ᵗBuOOH oxidant

As shown in Table 4, the homogeneous system comprising **5** showed the moderate activity for epoxidation of cyclohex-

ene accompanied with the formation of a large amount of peroxide (2-cyclohexen-1-yl tert-butyl peroxide), when tert-butylhydroperoxide was added at once into the reaction solution (entry 10) [7]. Selectivity for the peroxide formation was also observed in all heterogeneous system except entry 3. In entry 3, however, the FSM-Ru catalyst (**1**) having oxygen donor at the *trans*-position gave 1,2-epoxycyclohexane selectively through stepwise addition of TBHP to the reaction solution. The formation ratio of the epoxide to the peroxide was over 22. To achieve the high selectivity for epoxidation, it is important to control the intermediate species. Notably, iodimetric titration of the reaction solution revealed that TBHP was not detected when the product yields had not increased yet in entry 2. Since this titration is sensitive for hydroperoxide, such as TBHP, even in the presence of the peroxide, such as 2-cyclohexen-1-yl tert-butyl peroxide, we consider that the excess hydroperoxide in the reaction media decomposed due to the Haber–Weiss mechanism to give tert-butylperoxo species (ᵗBuOO•) [40]. Stepwise addition in **1** can avoid the decomposition of TBHP to achieve selective formation of epoxide (entries 2 and 3)

**Table 4**
Oxidation of cyclohexene catalyzed by the ruthenium compounds with TBHP oxidant.[a].

| Entry | Catalyst | System | Reaction time (h) | Products yield (%) | | | | Selectivity for epoxide | Selectivity for perxoxide | Ratio for epoxide/peroxide |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Epoxide[g] | Enone[h] | Enol[i] | Peroxide[j] | | | |
| 1 | FSM-Ru(**1**)[b] | Heterogeneous | 5 | 18 | 3.1 | 1.6 | 19 | 43 | 46 | 0.94 |
| 2 | | | 8 | 22 | 4.8 | 2.0 | 20 | 45 | 40 | 1.12 |
| 3 | | S-add[k] | 8 | 26 | 8.5 | 3.3 | 1.2 | 67 | 3.0 | 22.5 |
| 4 | FSM-Aps-Ru(**2a**)[c] | | 5 | 1.8 | 2.8 | 2.5 | 22 | 6.2 | 76 | 0.08 |
| 5 | FSM-Aps-Ru(**2b**)[d] | | 5 | 1.5 | 3.2 | 2.1 | 22 | 5.2 | 76 | 0.07 |
| 6 | FSM-Ims-Ru(**3a**)[e] | | 5 | 1.6 | 0.9 | trace | 6.0 | 19 | 71 | 0.27 |
| 7 | | | 24 | 3.9 | 2.8 | 1.8 | 21 | 13 | 71 | 0.19 |
| 8 | FSM-Ims-Ru(**3b**)[f] | | 5 | 1.7 | 3.4 | 2.5 | 24 | 5.4 | 76 | 0.70 |
| 9 | [Ru(babp)(dmso)(im)](**4**) | | 5 | 1.8 | 2.2 | 2.2 | 26 | 5.6 | 81 | 0.69 |
| 10 | [Ru(babp)(dmso)₂](**5**) | Homogeneous | 8 | 9.0 | 9.3 | 4.2 | 20 | 21 | 48 | 0.44 |
| 11 | | S-add[k] | 8 | 19 | 19 | 4.8 | 7.2 | 38 | 14 | 2.67 |

[a] Reaction conditions: catalyst:TBHP:cyclohexene = 1:100:100, 40 °C, 1,2-dichloroethane, under Ar.
[b] **5** (13 mg)/FSM(a) (100 mg).
[c] **5** (9 mg)/FSM(a)-Asp (100 mg).
[d] **5** (6 mg)/FSM(b)-Aps (100 mg).
[e] **5** (8 mg)/FSM(a)-Ims (100 mg).
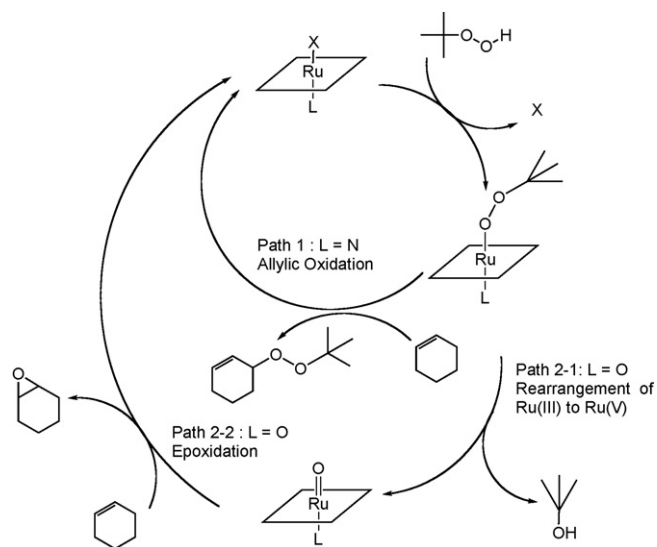[f] **5** (8 mg)/FSM(b)-Ims (100 mg).
[g] 1,2-Epoxycyclohexane.
[h] 2-Cyclohexen-1-one.
[i] 2-Cyclohexen-1-ol.
[j] 2-Cyclohexen-1-yl tert-butyl peroxide.
[k] Stepwise addition of TBHP (12.5 mmol) at every 1 h.

**Scheme 4.** Possible reaction pathways for allylic oxidation and epoxidation.

through the generation for Ru=O intermediate. The catalyst **2** and **3** having nitrogen donor in heterogeneous system, which showed similar activity to the homogeneous catalyst **4** having imidazole ligand, promoted both the decomposition of TBHP and generation of the peroxide. The highest selectivity for the peroxide formation in Table 4 was observed in the homogeneous system **4** having nitrogen donor at the axial position (entry 9).

In case of the FSM-Aps-Ru catalyst, the oxidation activity was not influenced by the pore size of FSM (entries 4 and 5). On the other hand, it was influenced by the pore size of FSM-Ims-Ru (entries 6–8). The oxidation activity of **3a** immobilized into FSM(a) with pore size of 2.8 nm was low and the long reaction time was needed for gaining the same amount of the product in comparison with the case of **3b** immobilized into FSM(b) with pore size of 4.0 nm [41]. Since the remaining pore volume in **3a** containing heterocycle was smaller than that in **2a** containing amino group, the substrates and products hardly diffused into the narrow space of the pore in **3a**. The size effect on the catalytic activity of cyclohexene epoxidation was also reported in another mesoporous compound on which Mn-salen complexes are immobilized [42].

On the selectivity control of the oxygen transfer reaction, such as epoxidation or peroxidation, we previously pointed out the *trans*-influence of the ruthenium complex caused by the axial ligand [15,16]. Sheldon and co-workers also reported the mechanism of the ruthenium-catalyzed epoxidation using TBHP, in which epoxide was generated through both homolytic and heterolytic pathways [43]. In addition, no formation of diol (cyclohexan-1,2-diol) in our experiments denied the possibility of dioxo-ruthenium as an intermediate. Accordingly, we postulate the mechanism of the selectivity control as shown in Scheme 4. Notably, the $Ru^{III}$–$OO^tBu$ species having radical character promotes peroxidation at the allylic position and $Ru^V$=O having electrophilic character promotes epoxidation [15]. Two transient species might compete with each other for the oxygen transfer reactions. In the first step of the reaction, the metal–alkylperoxide ($Ru^{III}$–$OO^tBu$) species was generated from the ligand exchange reaction between the low-valent ruthenium complex immobilized into FSM and TBHP. This Ru–$OO^tBu$ species, mainly formed in the presence of large amounts of TBHP in the reaction system, reacted with cyclohexene to give the 2-cyclohexen-1-yl tert-butyl peroxide through the $^tBuOO^•$ intermediate when the fifth ligand (L in Schemes 1 and 4) was nitrogen atom (path 1). The Ru–$OO^tBu$ species once generated might decompose to give the radical $^tBuOO^•$ intermediate through the Haber–Weiss mechanism

and finally gave the peroxide. The abstraction of allylic hydrogen of cyclohexene by this radical species accelerated this reaction. In path 2, the $Ru^{III}$–$OO^tBu$ also afforded $Ru^V$=O species through the rearrangement of Ru(III) to Ru(V) when the fifth ligand (L) was oxygen atom in the immobilized complex. The stepwise addition of TBHP to the ruthenium center effected the formation of the active intermediate, $Ru^V$=O, for the epoxidation selectivity. The quantity of TBHP in the reaction system clearly regulates the formation pathway of the transient species.

In the case of iron catalysts immobilized on silica, 2-cyclohexen-1-one was mainly formed when TBHP was used as an oxidant [44]. Recent report on the catalytic oxidation of cyclohexene using manganese porphyrin supported on FSM also discussed the steric effect induced by the nanospace constraints, in which Mn-porphyrin located at the external surface of FSM predominantly gave epoxide using PhIO and that in the channel of mesoporous FSM acted as a catalyst for allylic oxidation [45]. In contrast to these previous heterogeneous catalysts, in which the metal complexes covalently anchored to silica did not show the *trans*-influence [1,3,29], our system immobilizing the ruthenium complex into the mesopore of FSM is able to control the selectivity by the monodentate linker ligand.

### 3.5. Recycle use of the immobilized catalyst

Recycle use of the catalyst is one of the important aims of the immobilization of the homogeneous complex [1,2]. Leaching of ruthenium species from FSM in **1** was not observed under argon atmosphere in less polar solvents. Under aerobic conditions, however, leaching of ruthenium species gave complicated oxidation products. The catalyst **1** was easily recovered from the reaction mixture and reused after rinse with 1,2-dichloroethane. The color of the catalyst **1** freshly prepared was yellow, and turned to green when the oxidant was added. This green species estimated to be Ru(V)=O showed higher selectivity for epoxidation [16], and was preferentially formed during the catalytic cycle in the presence of the oxidant. Interestingly, the increasing activity and selectivity for
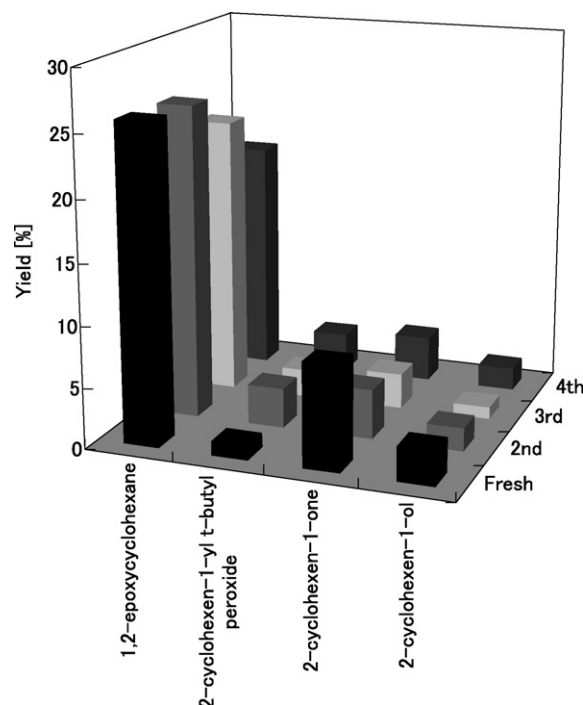


**Fig. 2.** Recycle use of the immobilized ruthenium catalyst (**1**).

the epoxidation was observed in the recycle use of **1** in comparison with the case of the fresh use. As shown in Fig. 2, selectivity for epoxide formation among the oxidation products was 67% at the fresh use of **1**, and that reached to about 80% at the first time recycle use of **1** (2nd). After isolation of the catalyst **1** which was reused three times reuse run (4th), the pore size (1 nm or less) was obviously decreased. In the recycle use of the catalyst, undesirable product might be generated to inhibit the diffusion of the substrate and oxidant in the mesopore of FSM. This is the reason why the epoxide yield gradually decreased up to the 4th run. From the above findings, the more efficient system for recycle use of the epoxidation catalyst is now in progress.

## 4. Conclusion

There have been lots of reports on immobilized complexes for oxidation catalysts, in which most of manganese or ruthenium complexes with multidentate ligands are covalently anchored to inorganic supports. However, there have been few reports on the immobilization of the complexes using linker with the monodentate coordination. Compared with the previous methods, notably, the catalysts immobilized into FSM, **1** (FSM-Ru), **2** (FSM-Aps-Ru) and **3** (FSM-Ims-Ru), have two advantages in catalyst preparation and reaction control. Preparation of these catalysts through mixing of the ruthenium complex and FSM is very easy. Ligand exchange reaction between dmso of the starting complex and silicate or monodentate nitrogen bound to silicate gives these immobilized catalysts. Selectivity in the oxygen transfer reactions for epoxidation or allylic peroxidation is controlled by the immobilization method. For epoxidation, **1** (FSM-Ru) directly bound to silica support is recommended as the catalyst when TBHP added stepwise. For allylic peroxidation, **2** (FSM-Aps-Ru) or **3** (FSM-Ims-Ru) with nitrogen linker is recommended when TBHP is added at once. Moreover, heterogeneous catalyst **1** was recycled and used three times in epoxidation of cyclohexene, since leaching of the ruthenium species from **1** was not observed under argon atmosphere.

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