Selective Epoxidation of Cyclohexene by a Square-planar Ru Complex Immobilized into Mesoporous Silicate FSM-16

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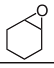
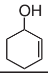
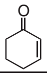
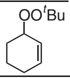
The Ru complex, [Ru^{II}(babp)$(dmso)_2$] (**1**) (H_2babp = 6,6′-bis(benzoylamino)-2,2′-bipyridine), was immobilized into mesoporous silicate FSM-16. The heterogeneous catalyst demonstrated a more selective epoxidation compared with the homogeneous **1**.

High-valent metal–oxo species have been proposed as one of the active intermediates not only in metalloenzymes but also in the oxidative transformation of organic compounds catalyzed by transition-metal complexes.[1] In metalloenzymes, the secondary coordination sphere contributes to high specificity and reactivity.[2] There are many reports of the immobilized transition-metal complex catalysts.[3] The second coordination sphere of the complex immobilized into a mesopore must contribute as a regulated reaction field to form the enzyme–substrate complex.[4] Mesoporous silica, FSM (Folded Sheet Mesoporous Material), is expected to give a suitable reaction field for the catalysis, because it has regularly arranged 2D hexagonal cylinders.[5] Easy immobilization of transition-metal complex into FSM through the coordination of the axial ligand may afford an efficient catalysts. We previously reported that Ru complexes with a square-planar ligand, [Ru^{II}(babp)(dmso)L] (babp = 6,6′-bis(benzoylamino)-2,2′-bipyridine, L = dmso (**1**)), proceed the catalytic oxidation for various olefins, in which the axial ligands L controlled the oxidation ability. Selective epoxidation of cyclohexene performed by a Ru complex with *t*-BuOOH (TBHP) is still difficult because cyclohexene has weak C–H bond at allylic position. Here, we describe preparation of the heterogeneous catalyst containing the Ru complex **1**, and its ability to catalyze selective oxidation of cyclohexene. Under the coexistence of TBHP as an oxidant, the immobilized Ru complex catalyst showed higher selectivity for epoxidation of cyclohexene in comparison with the corresponding homogeneous reaction systems.

Immobilization of **1** into FSM-16 (pore size is about 3 nm) in solution phase was carried out under an Ar atmosphere.[7] Using less polar solvent, such as dichloromethane, efficient adsorption of the Ru complex **1** into FSM was observed through disappearance of color in the solution, whereas adsorption of **1** into FSM was not detected when a polar solvent such as methanol and acetone was employed. Adsorption of **1** reached to equilibrium within 1 h in dichloromethane to give orange powder of the immobilized complex, FSM-**1**. The complex **1** once adsorbed into FSM-16 did not leach out in the less polar solvent.[8] The pore size distributions of FSM-**1**, which was estimated by BJH analysis of N_2 adsorption isotherm (Figure S1),[9] revealed that **1** was immobilized not on outer surface but into pores of FSM-16. The average pore size (26.5 Å) of FSM-**1** used for oxidation experiment was enough to accommodate cyclohexene and TBHP molecules (the sizes of both molecules are estimated to be below 10 Å). On the basis of X-ray photoelectron spectroscopic and elemental analyses, sulfur atom was not detected in FSM-**1**. This result indicates that the dmso ligand of **1** has been replaced by Si–OH groups existing on the inner surface of FSM, although Si–O–Ru bond formation could not be characterized directly.

The oxidation reaction of cyclohexene was carried out by using **1** and FSM-**1** in the presence of PhIO or TBHP as an oxidant in 1,2-dichloroethane at 40 °C under an Ar atmosphere. Generally, oxidation of cyclohexene gives two types of products through the different processes; one is epoxidation by an electrophilic attack of an active oxygen species to the double bond to give cyclohexene oxide, and another is allylic oxidation by nucleophilic or radical attack to the α-position of the double bond to give 2-cyclohexen-1-ol and 2-cyclohexen-1-one. When PhIO was employed as an oxidant (Table 1, Entries 1 and 2), heterogeneous FSM-**1** showed a reactivity similar to homogeneous **1** for the oxidation of cyclohexene, where $Ru^V{=}O$ species was spectroscopically characterized as a reaction intermediate.[6,10] In the presence of dry TBHP (content of active oxygen was 93 wt %), the epoxidation selectivity decreased compared with the cases of PhIO. When TBHP was added at once into the reaction solution of **1**, a large amount of 1-(*tert*-butylperoxy)-2-cyclohexene was obtained as a result of the allylic peroxidation (Table 1, Entry 3). There have been some reports on the formation of such a peroxy ether, which may be generated from

Table 1. Oxidation product distributions for cyclohexene[a]

Entry	Catalyst	Oxidant	Turnover number				Selectivity[g] /%
							
1	**1**	PhIO	19	trace	5	nd	79
2	FSM-**1**[b]	PhIO	20	trace	3	nd	87
3	**1**	TBHP	9	4	9	20	21
4	FSM-**1**[b]	TBHP	22	2	5	20	45
5	FSM-**1**[b]	TBHP[f]	26	3	9	1	67
6	**1**	TBHP[f]	19	5	19	7	38
7	FSM-**1**[c]	TBHP[f]	26	2	4	3	74
8	FSM-**1**[d]	TBHP[f]	23	1	3	2	79
9	FSM-**1**[e]	TBHP[f]	19	2	4	3	69

[a]Reaction conditions: Ru:TBHP (93.1 wt %):Cyclohexene = 1:100:100 mM. All reactions were performed in CH_2ClCH_2Cl under Ar atmosphere at 40 °C. The amount of **1** immobilized into FSM is 36.3 µmol/100 mg of FSM. The yields of reaction products were determined by GC at 4 h for PhIO and 8 h for TBHP. [b]1st use (Fresh). [c]2nd use. [d]3rd use. [e]4th use. [f]Successive addition of 12.5 equiv. at every 1 h. [g]Selectivity of epoxidation, which is based on the sum of oxidation products.

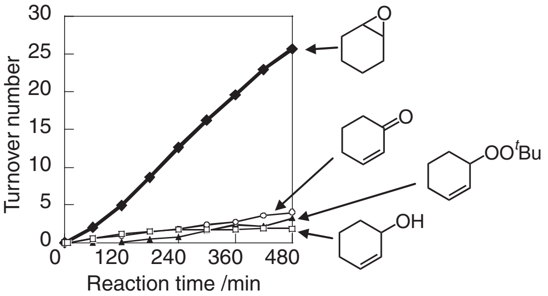


Figure 1. Time course for the product distributions of cyclohexene oxidation, catalyzed by FSM-**1** (2nd use) and successive addition of TBHP (12.5 equiv. per hour).

a coupling reaction of *t*-BuOO$^\bullet$ and cyclohexenyl radicals.[11] In the heterogeneous system catalyzed by FSM-**1**, however, the ratio of epoxide to allylic oxidation products increased (Table 1, Entry 4). In general, the oxidation reaction catalyzed by $Ru^{IV}{=}O$ species causes C–H bond activation[12] and that by $Ru^{V}{=}O$ species promotes epoxidation of cyclohexene.[1b,13] Therefore, the increase of epoxidation selectivity in FSM-**1** indicates that the generation of $Ru^{V}{=}O$ species was promoted. This may be explained as follows; first, coordination of Si–O(H) groups to the Ru complex at the axial position accelerates the reactivity of $Ru^{V}{=}O$ species, as reported in metallo–porphyrin complexes that the heterolytic O–O bond cleavage of coordinated peroxide is promoted by the "push effect" of donor ligands.[14] Second, a hydrophilic reaction pocket in mesopores of FSM[15] provides a polar environment to promote the ionic pathway leading to the heterolytic O–O bond cleavage of TBHP.

In Entries 3 and 4 (Table 1), the active intermediate species might react with not only cyclohexene but also excess TBHP, generating 1-(*tert*-butylperoxy)-2-cyclohexene via formation of *t*-BuOO$^\bullet$ by H atom abstraction reaction. So, successive addition of TBHP was examined in order to clarify the genuine reactivity of Ru=O species for oxidation of cyclohexene. In Entry 5 (Table 1), the selectivity of epoxidation increased and that of allylic peroxidation decreased clearly. While, in homogeneous **1** (Table 1, Entry 6), the amount of 2-cyclohexen-1-one increased as much as epoxide. As described above, the successive addition of TBHP to the immobilized Ru complex catalysts is a good method for epoxidation of olefins.

During the reaction under an Ar atmosphere, Ru species was not eluted from FSM-**1** and the catalyst could be recovered after the reaction.[8] Notably, increase in the selectivity for epoxidation was observed in the recycle use of the catalyst in comparison with the case of the fresh use (Table 1, Entries 5 and 7). In the second use of FSM-**1**, as shown in Figure 1, the yield of cyclohexene oxide increased drastically and linearly with the successive addition of TBHP every 1 h, although that of the allylic oxidation products did not increase so much. This finding may indicate that oxidation of Ru^{II} to Ru^{III} through the reaction promotes the generation of $Ru^{V}{=}O$ species by two-electron oxidant, TBHP. After oxidation reaction, trivalent Ru ion was confirmed by detection of LMCT band from $babp^{2-}$ to Ru^{III} in the region >500 nm and of characteristic ESR signals to Ru^{III} species. Similar improvement of epoxidation was also observed in preoxidized FSM-**1** by treatment with oxygen.[16] In the fourth run (Table 1, Entry 9), the turnover number (TON) of epoxidation was maintained at ca. 20.

In summary, we have prepared the immobilized epoxidation catalyst, FSM-**1**, by adsorption of a square-planar Ru complex **1** into FSM-16 through the liquid phase adsorption method. This easy preparation of immobilized complex gave the reusable oxidation catalyst. Moreover, FSM-**1** showed higher selective epoxidation of cyclohexene using TBHP as an oxidant in comparison with the case of **1** in the homogenous system. Especially, successive addition of TBHP to immobilized FSM-**1** catalyst was quite effective for selective epoxidation of olefins.

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7 In typical procedure, FSM-16 (100 mg) was added to a CH_2Cl_2 solution of **1** (26.0 mg, 40 μmol) under an Ar atmosphere, and stirred for 1 h. The adsorbed amount of **1** was determined by measuring UV–vis spectrum of supernatant solution. The resultant orange powder was filtrated and dried in vacuo.

8 The amount of leached catalyst was monitored by measuring the absorption intensity of the supernatant solution at 400 nm, which was estimated to be below 1% based on the immobilized Ru complex.

9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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16 The solid FSM-**1** was exposed to air for one week. The oxidation of Ru ion was confirmed by detecting the LMCT band of $babp^{2-}$ to Ru^{III} that appeared in the longer wavelength region more than 500 nm in UV–vis reflectance spectrum.

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