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Immobilization of a Molybdenum Complex on Bipyridine-Based Periodic Mesoporous Organosilica and Its Catalytic Activity for Epoxidation of Olefins

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Abstract

The dichlorodioxomolybdenum (VI) complex (MoO_2Cl_2) is an efficient and low-cost homogeneous catalyst for a variety of organic reactions, but its activity usually decreases after immobilization on a solid support. This report describes the synthesis of heterogeneous Mo complex catalysts using a bipyridine-periodic mesoporous organosilica (BPy-PMO) as a solid chelating ligand and MoO_2Cl_2 as a precursor, and their catalysis in the epoxidation of olefins with *tert*-butyl hydroperoxide (TBHP). The $MoO_2Cl(OH)$ complex could be immobilized on trimethylsilylated BPy-PMO (BPy-PMO-TMS), which was confirmed by Fourier-transform infrared spectroscopy, Raman spectroscopy, and X-ray absorption fine-structure analysis. The Mo complex immobilized on BPy-PMO-TMS exhibited greater catalytic activity for the epoxidation of *cis*-cyclooctene compared to conventional heterogeneous Mo complex catalysts using mesoporous silica, polystyrene polymer, and naked BPy-PMO as supports. A large amount (up to 0.72 mmol g^{-1}) of the Mo complex could be loaded on BPy-PMO-TMS, which resulted in 37% of the exposed bipyridine ligands on the surface forming Mo complexes. The turnover frequency relative to Mo was nearly constant, even with a high density of Mo complex on the pore surface. The Mo-BPy-PMO-TMS catalyst exhibited a solvent effect on the catalysis and the presence of water in the reaction medium was detrimental for the catalysis. Under anhydrous conditions, Mo-BPy-PMO-TMS showed good catalytic activity for at least three reuse cycles in the epoxidation of *cis*-cyclooctene. A variety of olefins including aliphatic and aromatic olefins were successfully oxidized by Mo-BPy-PMO-TMS to give the desired epoxides in high yield.

KEYWORDS: Periodic mesoporous organosilica, bipyridine, immobilization, molybdenum, epoxidation

1. Introduction

The use of recoverable and reusable heterogeneous metal complex catalysts, instead of homogeneous catalysts, for batch and flow-through systems is of interest in the development of environmentally friendly chemical processes [1-2]. Flow-through reactions require highly active catalysts because the contact time for column reactors is generally shorter than that for batch systems [3]. Therefore, a large amount of active metal complex must be immobilized on a solid support to prevent a loss of activity. However, the intrinsic catalytic activity of metal complexes usually decreases after immobilization on conventional solid supports due to unfavorable interactions between the active sites and the heterogeneous solid surface [1,4]. In addition, high-density immobilization usually causes aggregation of the metal complex on the support, thus decreasing activity [5].

Recently, the synthesis of a new periodic mesoporous organosilica (PMO) containing 2,2’-bipyridine (BPy) ligands within the framework (BPy-PMO) has been reported[6]. The BPy-PMO had a molecularly well-defined pore surface structure in which bipyridine ligands were regularly and densely arranged in the siloxane network. The neighboring BPy-BPy distance was approximately 0.44 nm, estimated by a molecular mechanics simulation, which indicated that an extremely high density of BPy ligands existed within the pore walls (elemental analysis indicated that the total amount of BPy ligand in BPy-PMO was 3.18 mmol g^{-1}). Furthermore, BPy-PMO had a large specific surface area (> 600 m^2 g^{-1}) and large pore size (3.8 nm in diameter), which allowed the smooth diffusion of reactant and product molecules in the mesochannels. Therefore, BPy-PMO was expected to function as a unique solid support that could immobilize a large amount of metal complexes without a loss of activity. Heterogeneous catalysis has been reported for precious metal complexes formed on BPy-PMO such as Ir(OMe)(cod)(BPy-PMO) [6,7], $Ru(bpy)_2$(BPy-PMO) [6],

$RuCl_2(CO)_2$(BPy-PMO) [8], and IrClCp*(BPy-PMO) [9]. However, no report has described the formation of base metal complexes, such as a Mo complex, on BPy-PMO.

Dichlorodioxomolybdenum (VI) complexes, such as $[MoO_2Cl_2(L)_n]$ (L: neutral ligand), have attracted attention as efficient and low-cost homogeneous catalysts for a variety of organic reactions including epoxidation, acylation, hydrosilylation, reduction, and oxidation [10-17]. Due to their attractive catalytic properties and the potential for environmentally friendly ("green") chemistry, attempts have been made to heterogenize $MoO_2Cl_2(L)_n$ using solid supports such as metal-organic frameworks (MOF), mesoporous silica, and hydrotalcite [18-22]. However, in most cases, the catalytic activity of $MoO_2Cl_2(L)_n$ decreased significantly after immobilization.

The present report describes the immobilization of MoO_2Cl_2 on BPy-PMO, and its catalysis for the epoxidation of olefins using *tert*-butyl hydroperoxide (TBHP). The Mo-immobilized BPy-PMO complexes were formed successfully using BPy-PMO end-capped with trimethylsilyl (TMS) groups on the silanol groups, without changing the ordered mesoporous and pore wall structures. The obtained Mo-BPy-PMO-TMS exhibited catalytic activity for the epoxidation of *cis*-cyclooctene, which was significantly greater than the activity of heterogeneous MoO_2Cl_2(bpy) catalysts prepared by a conventional immobilization approach using bipyridine-grafted mesoporous silica, polystyrene, or non-trimethylsilylated (naked) BPy-PMO as solid supports. The relationship between the loading amount and catalytic activity, which has not been well studied for BPy-PMO [6-8], was also investigated. The Mo complexes could be formed on up to 37% of the BPy ligands exposed on the pore surface without a loss of catalytic activity. A hot-filtration experiment clearly indicated that the catalytic reaction proceeded without leaching of Mo species from BPy-PMO. Mo-BPy-PMO-TMS showed good recyclability for the epoxidation of *cis*-cyclooctene for at least three times and could be used for the epoxidation of a variety of olefins such as cyclic, terminal and internal aliphatic olefins, and aromatic olefins.

2. Experimental

2.1. Chemicals and characterization

All chemicals were purchased from commercial suppliers (Sigma-Aldrich, Tokyo Chemical Industry Co., Ltd., and Wako Pure Chemical Industries, Ltd.) and used without further purification. The BPy-PMO and BPy-PMO end-capped with trimethylsilyl groups (BPy-PMO-TMS) were prepared according to a previously reported procedure [4]. Gas chromatography (GC) mass analyses were performed using an Agilent 6890GC/5973MSD instrument equipped with a capillary column (HP-5MS, 0.25 mm × 30 m) and a flame ionization detector. ^{1}H NMR spectra were obtained using a Jeol ECX-400 spectrometer operating at 400 MHz. Chemical shifts are reported in δ parts per million referenced to tetramethylsilane as an internal standard. For the NMR experiments, the product yield was determined using the integral value of internal standards such as mesitylene or 1,4-dioxane. X-ray diffraction (XRD) profiles were recorded by a Rigaku RINT-TTR diffractometer using Cu-Kα radiation (50 kV, 300 mA). Nitrogen adsorption/desorption isotherms were obtained using a Quantachrome Nova3000e sorptometer at liquid nitrogen temperature (-196 °C). Brunauer-Emmett-Teller (BET) surface areas were calculated from the linear sections of BET plots (P/P_0 = 0.1–0.25). Pore-size distributions were calculated using the DFT method (DFT kernel: N_2 at -196 °C on silica, cylindrical pores, nonlinear density functional theory (NLDFT) equilibrium model). Pore volumes were estimated using the *t*-plot method. Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX) were performed using a Hitachi S-3600N instrument. Fourier-transform infrared spectroscopy (FT-IR) was performed using a Thermo Fisher Scientific Nicolet Avatar-360 FT-IR with an attenuated total reflection attachment. Raman analysis was conducted on a Jasco NRS-3300 instrument using an Ar laser (532 nm). X-ray absorption fine structure (XAFS) measurements at the Mo *K*-edge were conducted using a quick XAFS (QXAFS) method in transmission mode at BL14B2 of SPring-8. X-rays from the synchrotron were monochromatized using a Si(311) double-crystal monochromator. An ion chamber was used to detect I_0 (intensity of incident X-rays), and another placed behind the samples was used to detect I (intensity of transmitted X-rays). Background subtraction was performed with an Autobk and Spline smoothing algorithm. The extended X-ray absorption fine structure (EXAFS) was analyzed with Athena and Artemis using IFEFFIT. k^3-Weighted Mo *K*-edge EXAFS oscillations (20-130 nm^{-1}) were Fourier transformed into R-space and curve fitting was carried out in R-space. The fitting parameters were the coordination number (CN), interatomic distance (R), Debye-Waller factor (σ^2), and correction-of-edge energy (ΔE_0). The phase shift and backscattering amplitudes were calculated using the FEFF6 code.

2.2. Immobilization of dichlorodioxomolybdenum (VI) complex

For preparation of Mo-BPy-PMO-TMS, reagent-grade acetonitrile (> 99.5%, undried) was used. First, a 10 mM MoO_2Cl_2 solution was prepared using acetonitrile as the solvent (Caution! MoO_2Cl_2 is hydroscopic and highly reactive with metals to form insoluble materials. We rapidly weighed MoO_2Cl_2 by using a PTFE spatula). Next, 1, 2, 4, or 6 mL of MoO_2Cl_2 solution were added to a solution containing BPy-PMO-TMS (68.5 mg, 0.20 mmol) dispersed in 9, 8, 6, or 4 mL, respectively, of acetonitrile. The solution obtained was stirred at room temperature for 24 h. After filtration and washing with acetonitrile, the obtained powder was dried under reduced pressure to give x% Mo-BPy-PMO-TMS, where x represents the molar ratio of Mo against the bipyridine in BPy-PMO-TMS, and was determined by ICP analysis (x = 5, 10, 20, 23). The MoO_2Cl_2 was immobilized over bipyridine-grafted mesoporous silica, polystyrene, and non-trimethylsilylated BPy-PMO using the same procedures.

2.3. Catalytic reaction

Epoxidation of *cis*-cyclooctene was carried out under both undried and anhydrous conditions. The former condition was applied to a variety of Mo-immobilized heterogeneous catalysts and a homogeneous MoO_2Cl_2(bpy) complex as a benchmark reaction. These reactions used reagent-grade solvent and TBHP solution in decane (undried). The latter condition was applied to Mo-BPy-PMO-TMS for experiments concerning the solvent effect and substrate scope and limitations. These reactions were conducted using anhydrous solvent and TBHP solution in decane dried over molecular sieves 4A.

2.3.1 Epoxidation of *cis*-cyclooctene under undried conditions

A 20-mL two-necked flask, with a stir bar and septum, was charged with a reaction solution of *cis*-cyclooctene (0.65 mL, 5.0 mmol, substrate), 5-6 M TBHP solution in decane (0.96 mL, 5 mmol, oxidant), toluene (3.19 mL, 30 mmol, internal standard, > 99.5%), and decane (5.20 mL, solvent, > 99.0%). The heterogeneous catalyst (20 mg) or MoO_2Cl_2(bpy) (2.1 mg, 5.8 μmol Mo) was added to the reaction solution, and the flask was placed in an oil bath heated to 45–90 °C. The reaction time was measured from the time the flask was placed in the oil bath. Samples of the reaction solution were collected at regular intervals and centrifuged to separate the solid catalyst. After centrifugation, the reaction solution was analyzed by GC using a Shimadzu GC-8A equipped with a capillary column (HP-5, 0.53 mm × 30 m) and FID. After the reaction was completed, the catalyst was filtered and washed with hexane before drying under reduced pressure. The used catalyst was subjected to another reaction under the same reaction conditions.

2.3.2 Epoxidation of *cis*-cyclooctene under anhydrous conditions

A 20-mL test tube, with a stir bar, was equipped with a two-neck gas adaptor. The side neck was connected to a vacuum/argon manifold. The main neck was capped with a rubber septum. The test tube was charged with 10% Mo-BPy-PMO-TMS (20 mg, 5.8 μmol Mo), then evacuated and backfilled with argon three times. To the test tube were added *cis*-cyclooctene (0.65 mL, 5 mmol), dry mesitylene (1 mmol, internal standard), dry solvent (9.0 mL), and dry 5-6 M TBHP solution in decane (0.96 mL, 5 mmol). The test tube was placed in an aluminum block pre-heated to 75 °C. The reaction time was measured from the time the test tube was placed in the aluminum block. Samples of the reaction solution were collected at regular intervals and diluted with chloroform-*d*. The sample solution was passed through a membrane filter (0.20 μm) to separate the solid catalyst. The obtained sample solution was analyzed by ^{1}H NMR spectroscopy. After the reaction was completed, the catalyst was filtered and washed with diethyl ether (30 mL) before drying under reduced pressure. The used catalyst was subjected to another reaction under the same reaction conditions. For the recharging system, *cis*-cyclooctene (0.65 mL, 5 mmol) and dry 5-6 M TBHP solution in decane (0.96 mL, 5 mmol) were added to the reaction test tube and another reaction was carried out at the same reaction temperature.

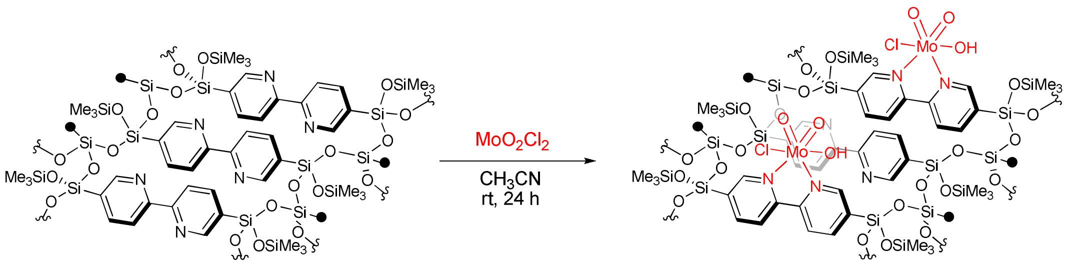
2.3.3 Epoxidation of olefins

A 20-mL test tube, with a stir bar, was equipped with a two-neck gas adaptor. The side neck was connected to a vacuum/argon manifold. The main neck was capped with a rubber septum. The test tube was charged with 10% Mo-BPy-PMO-TMS (35 mg, 10 μmol Mo), then evacuated and backfilled with argon three times. To the test tube were added olefin (2.5 mmol), dry mesitylene or dry 1,4-dioxane (1 mmol, internal standard), dry 1,2-dichloroethane (4.3 mL), and dry 5-6 M TBHP solution in decane (0.72 mL, 3.75 mmol). The test tube was placed in an aluminum block pre-heated to 75 °C. The reaction time was measured from the time the test tube was placed in the aluminum block. Samples of the reaction solution were collected at regular intervals and diluted with chloroform-*d*. The sample solution was passed through a membrane filter (0.20 µm) to separate the solid catalyst. The obtained sample solution was analyzed by ^{1}H NMR spectroscopy.

3. Results and discussion

3.1 Synthesis and characterization

To immobilize the dioxomolybdenum-bipyridine complex over the pore surface of BPy-PMO-TMS, commercially available MoO_2Cl_2 was used as a precursor. A MoO_2Cl_2 solution in acetonitrile was added to a suspension of BPy-PMO-TMS in acetonitrile and stirred at room temperature for 24 h. After filtration and washing with acetonitrile followed by drying under reduced pressure, Mo-BPy-PMO-TMS was obtained in quantitative yield as a white powder (Figure 1).



BPy-PMO-TMS

x% Mo-BPy-PMO-TMS

Figure 1. Schematic for direct Mo-complex formation on the pore surface of BPy-PMO-TMS.

The loading amount of the Mo complex on BPy-PMO-TMS could be controlled simply by varying the concentration of the MoO_2Cl_2 solution. Figure 2 shows the relationship between preparative Mo/BPy molar ratios in the reaction mixtures and the observed Mo/BPy molar ratios in BPy-PMO-TMS. The Mo/BPy molar ratios in BPy-PMO-TMS were determined from the Mo/Si ratios measured by ICP analysis, with the assumption that the ratio of Si/BPy was 10/3 because the pore walls were composed of three layers of Si-BPy-Si units, and the silanol groups (Si-OH) at the inner and outer pore surface (2/3 of the total Si) were almost completely trimethylsilylated [6]. Preparative Mo/BPy ratios less than 0.20 agreed well with observed Mo/BPy molar ratios, but Mo amounts greater than 0.20 resulted in saturation. The maximum Mo/BPy ratio of 0.246, corresponding to 0.72 mmol Mo g^{-1}, was achieved when the total amount of BPy ligand in BPy-PMO-TMS was 2.92 mmol g^{-1} by elemental analysis [6]. This indicates that 37% of the surface BPy ligands were coordinated with Mo in three layers of pore walls, and that a high density of Mo complex could be loaded on BPy-PMO-TMS. Four Mo-loaded BPy-PMO-TMS with Mo/BPy ratios of 0.05, 0.10, 0.20, and 0.23 were used to evaluate catalysis (denoted *x*% Mo-BPy-PMO-TMS, where $x = 5$, 10, 20 and 23). The Cl/Mo ratios of Mo-BPy-PMO-TMS were 1.2–1.5, which were less than that of the MoO_2Cl_2 precursor (Cl/Mo = 2), indicating that some Cl was released from MoO_2Cl_2 during the immobilization process. This is not surprising because Cl in MoO_2Cl_2 undergoes easy substitution with polar anion species such as $CH_3CH_2O^-$ [23]. The acetonitrile solvent or a small amount of water contaminating the solvent may have promoted the replacement of the chloride ligand from MoO_2Cl_2 on BPy-PMO-TMS.

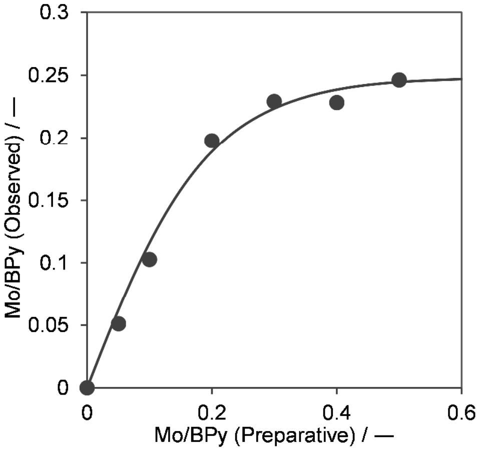


Figure 2. Relationship between preparative and observed Mo/BPy ratios determined by ICP analysis.

The mesoporous and pore wall structures of Mo-BPy-PMO-TMS were investigated by XRD and nitrogen adsorption/desorption analyses (Figures 3 and 4). The XRD diffraction patterns for Mo-BPy-PMO-TMS showed a peak at $2\theta = 1.78°$, attributed to the periodicity of the mesoporous structure. Peaks at $2\theta = 7.54°$, 15.2°, 22.9, and 30.8° were attributed to the molecular-scale periodicity of bipyridine ligands in the pore walls, similar to that of the parent BPy-PMO-TMS [6]. No additional peaks corresponding to impurities, such as inorganic salts of MoO_2Cl_2, were observed. These results indicate that the ordered structure of the parent BPy-PMO-TMS was maintained after immobilization of the Mo complex on the pore surface. The nitrogen adsorption/desorption isotherms for Mo-BPy-PMO-TMS were type-IV isotherms, similar to those for the parent BPy-PMO-TMS, which indicates preservation of uniform mesoporosity. The Brunauer-Emmett-Teller surface area (S_{BET}), mesopore volume (V_p) and density functional theory pore diameter (d_{DFT}) are listed in Table 1. The S_{BET} and V_p values decreased gradually with increasing Mo complex loading amount due to the increase in sample weight. No change in d_{DFT} was found after immobilization of the Mo complex on the pore surface.

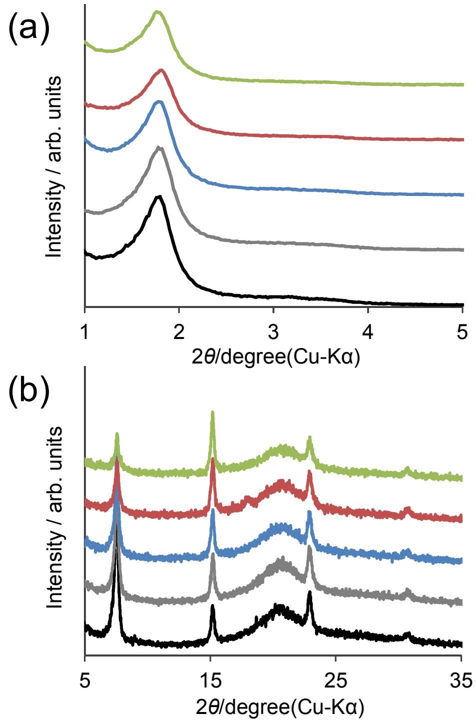


Figure 3. (a) Low-angle and (b) high-angle XRD patterns for BPy-PMO-TMS (black lines) and *x*% Mo-BPy-PMO-TMS (5%, gray lines; 10%, blue lines; 20%, red lines; 23%, green lines).

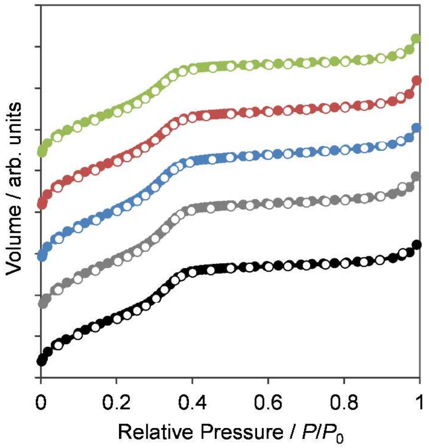


Figure 4. Nitrogen adsorption/desorption isotherms for BPy-PMO-TMS (black line) and *x*% Mo-BPy-PMO-TMS (5%, gray line; 10%, blue line; 20%, red line; 23%, green line). Closed symbols: adsorption; open symbols: desorption.

Table 1. Physicochemical properties of *x*% Mo-BPy-PMO-TMS

Sample	Mo amount /mmol g^{-1}		S_{BET} /m^2 g^{-1a}	V_p /cc g$^{-1\ a}$	d_{DFT} /nm^a
	Preparative	ICP			
BPy-PMO-TMS	—	—	654	0.41	3.8
5% Mo	0.14	0.15	657	0.41	3.8
10% Mo	0.29	0.30	647	0.39	3.8
20% Mo	0.58	0.58	608	0.37	3.8
23% Mo	0.87	0.67	585	0.36	3.8

[a] Determined from nitrogen adsorption-desorption isotherms at liquid-nitrogen temperature and calculated using the BET method (S_{BET}), *t*-plot method (V_p) or density functional theory (d_{DFT}).

The molecular structures of the Mo complexes formed on BPy-PMO-TMS were characterized by FT-IR spectroscopy (Figure 5a), Raman spectroscopy (Figure 5b), and XAFS analysis. The *x*% Mo-BPy-PMO-TMS showed an additional three bands at 945 cm^{-1} and 917 cm^{-1} in the IR spectrum and at 953 cm^{-1} in the Raman spectrum, compared to the parent BPy-PMO-TMS. Band intensities increased with the loading amount of Mo. MoO_2Cl_2(bpy), which was prepared as a model complex, showed Mo=O symmetric stretching at 932 cm^{-1} in the IR spectrum and 935 cm^{-1} in the Raman spectrum, and a Mo=O asymmetric stretching band at 902 cm^{-1} in the IR [14,24]. Thus, the additional bands observed in *x*% Mo-BPy-PMO-TMS were assigned to symmetric and asymmetric Mo=O stretching in the MoO_2Cl_2(bpy) complex. However, the wavenumbers of these bands were blue-shifted compared with those of the model complex MoO_2Cl_2(bpy). Kühn *et al.* reported that an electron-deficient Mo center due to coordination of the electron-withdrawing bipyridine ligand increased the Mo=O bond strength [14, 24]. Therefore, the silicon attached to the bipyridine ligand (Si-bpy-Si) could promote greater electron withdrawal than the bpy ligand alone. The FT-IR spectra of *x*% Mo-BPy-PMO-TMS also showed absorption bands derived from TMS groups and no absorption bands related to silanol groups, indicating that TMS was strongly attached during the MoO_2Cl_2 immobilization process (Figure S1). The XAFS measurements revealed the electronic state and local structure of the Mo center in *x*% Mo-BPy-PMO-TMS. The X-ray absorption near edge structure (XANES) spectra of 10% Mo-BPy-PMO-TMS showed a characteristic shoulder at 20004 eV, which is typically observed for hexavalent Mo compounds such as MoO_2Cl_2(bpy), MoO_2Cl_2, and MoO_3 (Figure S2). The spectral shape for 10% Mo-BPy-PMO-TMS was slightly different to that for model complex MoO_2Cl_2(bpy). In order to elucidate the local structure of the Mo complex in 10% Mo-BPy-PMO-TMS, an EXAFS analysis was carried out. Figures S3a and S3b show Mo *K*-edge EXAFS oscillations and their Fourier transforms with MoO_2Cl_2 and MoO_3 as references. The radial structure functions for 10% Mo-BPy-PMO-TMS were different from those for MoO_2Cl_2(bpy). This presumably stems from elimination of the chloride ligand from the Mo complex in 10% Mo-BPy-PMO-TMS as observed by EDX analysis. Thus, the EXAFS curve fitting of 10% Mo-BPy-PMO-TMS was carried out using MoO_2Cl(OEt)(bpy) as a model complex where one chloride ligand in MoO_2Cl_2(bpy) was replaced with ethoxide (Figures S4 and S5). The fitted curve was consistent with Mo coordinated to two oxygen centers at 1.68 Å (Mo=O), an oxygen center at 1.83 Å (Mo-O), a bipyridine unit by two nitrogen centers at 2.23 Å (Mo-N), and a chloride center at 2.43 Å (Mo-Cl) (Tables S1 and S2). These results strongly suggest the formation of a MoO_2Cl(OR)(bpy) complex. Since the preparation solvent contained a small amount of water, the MoO_2Cl(OH)(bpy) complex would be formed on the surface of the BPy-PMO-TMS. XAFS measurements were also carried out for other compositions of *x*% Mo-BPy-PMO-TMS (x = 5, 20, and 23). The Mo *K*-edge XANES, EXAFS oscillations, and

EXAFS Fourier transforms for *x*% Mo-BPy-PMO-TMS (x = 5, 20, and 23) were similar to those for 10% Mo-BPy-PMO-TMS (Figures S6 and S7), suggesting the same electronic state and local structure for the Mo complexes even at low and high packing densities.

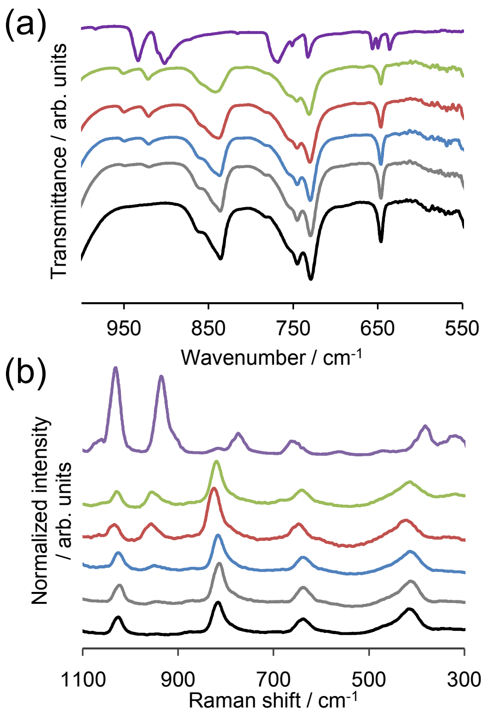


Figure 5. (a) FT-IR and (b) Raman spectra of BPy-PMO-TMS (black lines), *x*% Mo-BPy-PMO-TMS (5%, gray lines; 10%, blue lines; 20%, red lines; 23%, green lines), and MoO_2Cl_2(bpy) (purple lines).

3.2 Catalytic activity in epoxidation of *cis*-cyclooctene under undried conditions

Epoxidation reactions of *cis*-cyclooctene (5 mmol) were conducted using TBHP (5 mmol) in a solvent of undried decane. Figure 6 shows the yield of 1,2-epoxycyclooctane (Ecyo) as a function of reaction time over 10% Mo-BPy-PMO-TMS, homogeneous MoO_2Cl_2(bpy), and Mo-bipyridine complexes supported on various supports at 75 °C. The TON values were calculated as moles of product (Ecyo)/moles of Mo in the catalysts. Initial turnover frequencies (TOF, h^{-1})

based on the amounts of Ecyo per unit of Mo for the first 30 min were calculated and are listed in Table 2 along with Ecyo yields after 7–8 h.

The 10% Mo-BPy-PMO-TMS showed high catalytic activity with an Ecyo yield of 67% and TON of 609 at 75 °C, while homogeneous MoO_2Cl_2(bpy) showed greater activity with an Ecyo yield of 90% and TON of 819 under identical conditions (Table 2, entries 1 and 2). BPy-PMO-TMS without a Mo complex was used as a blank reaction. The experiment showed negligible conversion of *cis*-cyclooctene (< 1%) after 24 h at 75 °C. In order to confirm whether leaching of Mo species from 10% Mo-BPy-PMO-TMS occurred during the reaction, a hot filtration experiment was conducted. The PMO catalyst was removed by filtration after 30 min of reaction, and the resulting clear solution was allowed to react under identical conditions for another 7.5 h (Figure S8). No significant change in product yield was observed, which clearly indicated that the reaction was catalyzed by the Mo complex fixed on BPy-PMO, and not leached Mo. An increase in reaction temperature to 90 °C improved the Ecyo yield to 84% and the TON to 797 for 10% Mo-BPy-PMO-TMS (Table 2, entry 3), values comparable to those for homogeneous MoO_2Cl_2(bpy) at 75 °C. However, a decrease in reaction temperature to 60 °C reduced the Ecyo yield to 51% and the TON to 485 (Table 2, entry 4). For comparison, conventional catalyst supports, a mesoporous silica (FSM) grafted with bipyridine ligands using a molecular linker followed by trimethylsilylation (denoted as BPy-FSM-TMS) and polystyrene grafted with bipyridine ligands (denoted as BPy-Polymer), were used for immobilization of the Mo complex (Figures 7, S9 and S10). Mo-BPy-FSM-TMS produced a lower product yield of 48% and a TON of 409 compared to 10% Mo-BPy-PMO-TMS at 75 °C even with the same Mo amount (Table 2, entry 5), perhaps due to undesirable interactions between the Mo active center and the pore surface of FSM in the presence of a flexible linker. The Mo-BPy-Polymer produced a much lower product yield of 22% and a TON of 275 (Table 2, entry 6), due to the flexible nature of the polymer matrix. Interestingly, 11%

Mo-BPy-PMO without trimethylsilylation possessed very low catalytic activity (TOF of 43 h^{-1} at ~75 °C, Table 2, entry 7). Silanol groups inside the mesopores interact with oxygenated compounds, such as TBHP and epoxide, due to their hydrophilic nature, and prevent smooth diffusion of these compounds inside the mesopores [25,26]. Therefore, the treatment of silanol groups with hydrophobic TMS groups is sometimes effective for catalysis, and has been reported for mesoporous silica-based oxidation catalysis [25-28]. Thus, BPy-PMO-TMS is a very good support for immobilization of Mo complexes, and minimizes the loss of the original activity of the homogeneous MoO_2Cl_2(bpy) catalyst.

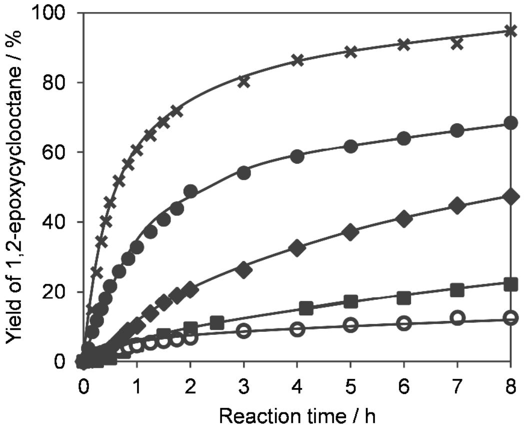
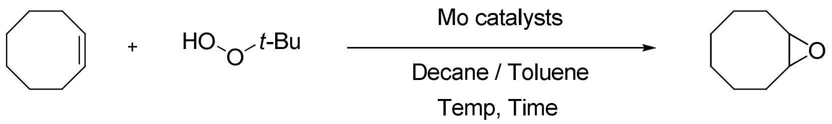


Figure 6. Epoxidation of *cis*-cyclooctene with TBHP under undried conditions catalyzed by various Mo-bipyridine complex catalysts at 75 °C. ×, MoO_2Cl_2(bpy); ●, 10% Mo-BPy-PMO-TMS; ◆, Mo-BPy-FSM-TMS; ■, Mo-BPy-Polymer; ○, 11% Mo-BPy-PMO.

Table 2. Catalytic activity of heterogeneous and homogeneous Mo-bipyridine catalysts for epoxidation of *cis*-cyclooctene with TBHP.[a]



Entry	Mo catalyst	Mo loading (mmol Mo/g)	T (°C)	Time (h)	Yield (%)[b]	TON[c]	TOF[d]
1	MoO_2Cl_2(bpy)	—	75	8	90	819	881
2	10% Mo-BPy-PMO-TMS	0.30	75	8	67	609	382
3	10% Mo-BPy-PMO-TMS	0.30	90	7	84	797	1155
4	10% Mo-BPy-PMO-TMS	0.30	60	8	51	485	175
5	Mo-BPy-FSM-TMS[e]	0.30	75	8	48	409	141
6	Mo-BPy-Polymer[f]	0.13	75	8	22	275	96
7	11% Mo-BPy-PMO	0.35	75	8	12	75	43

[a]Reactions were conducted with *cis*-cyclooctene (5 mmol), TBHP (5 mmol), and toluene (30 mmol, internal standard) in the presence of heterogeneous (2.6-5.8 μmol Mo) or homogeneous Mo-bipyridine catalysts (5.8 μmol Mo) in decane (total volume: 10 mL) [b]GC yields based on internal standard. [c]TON was calculated as moles of product/moles of Mo in the Mo-bipyridine catalyst. [d]TOF (h^{-1}) was calculated as moles of product within the first 30 min/moles of Mo in Mo-bipyridine catalysts. [e]Mo/BPy ratio was 0.08. [f]Mo/BPy ratio was 0.64.

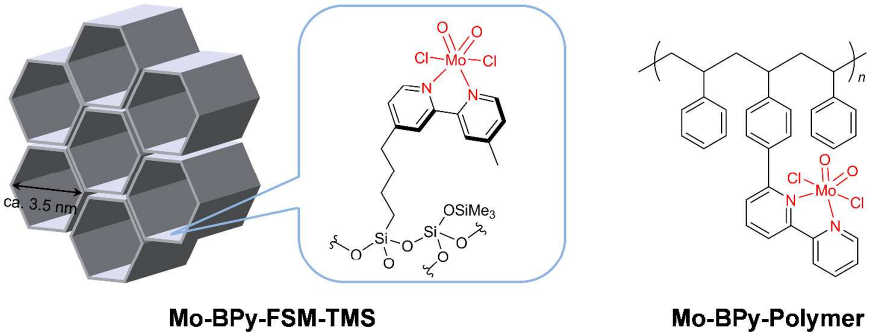


Figure 7. Schematic representations of Mo-BPy-FSM-TMS and Mo-BPy-Polymer.

In order to compare the catalytic activity to previously reported Mo-bipyridine-based heterogeneous catalysts, the catalytic reactions were conducted under the same conditions as the reported ones. First, the activity was compared to Mo-immobilized bipyridine MOF (Mo-BPy-MOF), where the reaction was conducted at 50 ºC with a molar ratio of *cis*-cyclooctene/TBHP/Mo = 140: 280:1 [18]. 10% Mo-BPy-PMO-TMS showed an initial TOF of 170 h^{-1} and a TON of 90 after 45 min, while the MOF catalyst showed an initial TOF of 12 h^{-1} and a TON of 82 after 24 h. The higher catalytic activity of 10% Mo-BPy-PMO-TMS compared to Mo-BPy-MOF can be ascribed to the smooth diffusion of substrate/product molecules owing to the larger pore diameter (ca. 3.8 nm for BPy-PMO and > 1 nm for BPy-MOF). Second, we adopted reaction conditions of the Mo-immobilized bipyridine-grafted mesoporous silica (Mo-BPy-MCM-41) catalyst [20]. Mo-BPy-MCM-41 shows an initial TOF of 16 h^{-1} and a TON of 36 at 55 °C under neat conditions after 24 h at a molar ratio of *cis*-cyclooctene/TBHP/Mo = 48:72:1. In contrast, 10% Mo-BPy-PMO-TMS showed a higher TOF of 5200 h^{-1} and a TON of 1850 after 3 h, although the amount of PMO catalyst was reduced to 40 times that for Mo-BPy-MCM-41 due to difficulty in stirring the reaction mixture. These results indicate that the catalytic activity of 10% Mo-BPy-PMO-TMS is greater than those of previously reported Mo-bipyridine-based heterogeneous catalysts.

Next, the effect of Mo loading amount (5, 10, 20, or 23%) for Mo-BPy-PMO-TMS on catalysis was examined. As the loading amount increased, the reaction rate within the first 30 min also increased (Figure S11). Figure 8a shows TOF values in *x*% Mo-BPy-PMO-TMS as a function of Mo loading. The TOF value relative to Mo loading in Mo-BPy-PMO-TMS remained nearly constant between 300 and 400 h^{-1}. Catalytic activity was almost completely preserved, indicating that the Mo complex acts as a single-site catalyst for the epoxidation even with a high density of Mo complex on BPy-PMO-TMS. For comparison, the effect of Mo loading amount of Mo-BPy-Polymer was examined since it had the greatest bipyridine loading amount (up to 2.0 mmol BPy/g) among commercially available solid supports. The results showed that immobilization of MoO_2Cl_2 over BPy-Polymer was difficult when the loading amount of Mo exceeded 0.2 mmol Mo/g, indicating low coordination ability. The four Mo-BPy-Polymer catalysts obtained were then evaluated in the epoxidation of *cis*-cyclooctene. The TOF values for Mo-BPy-Polymer decreased as the Mo amount increased perhaps due to an increase of undesirable interactions among Mo complex centers in the polymer matrix upon an increase in loading amount of MoO_2Cl_2. These results indicate that BPy-PMO-TMS is a unique chelating support that can accept a high density of Mo-bipyridine complex (up to 0.67 mmol g^{-1}) on the pore surface without a loss of activity for the epoxidation of *cis*-cyclooctene (Figure 8b). From a practical viewpoint, this is an attractive feature for flow-through systems because the same catalysis can be achieved using a much lower amount of catalyst, meaning that the column reactor size can be minimized.

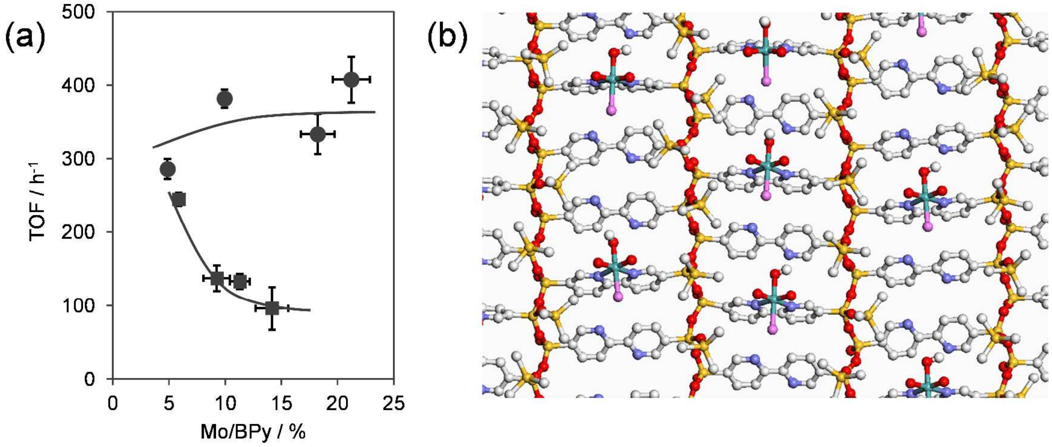


Figure 8. (a) TOF value per Mo in Mo-BPy-PMO-TMS (●) and Mo-BPy-Polymer (■). Immobilized Mo amounts were determined by ICP analysis. (b) CG image of pore surface of Mo-BPy-PMO-TMS with Mo/BPy molar ratio of approximately 23% (Mo/BPy$^{\mathrm{surface}}$ = approximately 35%). Mo: sky blue; Cl: pink; O: red; Si: orange; C: light gray; N: purple; H: omitted except for hydrogen atoms of OH ligands in Mo complexes.

3.3 Catalytic activity in epoxidation of *cis*-cyclooctene under anhydrous conditions

We investigated the catalytic reactions in different solvents under anhydrous conditions (Figure 9). Gonçalves *et al.* previously reported enhanced catalysis by a solvent effect on the epoxidation of *cis*-cyclooctene catalyzed by Mo(CO)$_3$-immobilized phenylene-bridged PMO [29]. The report also demonstrated that the presence of water was detrimental to the reaction rate, possibly due to undesired coordination to the active Mo complex center. When the epoxidation of *cis*-cyclooctene was carried out using anhydrous TBHP dried over molecular sieves 4A in dry decane, the initial TOF for 10% Mo-BPy-PMO-TMS was dramatically improved to 2030 h^{-1} at 75 °C, and the Ecyo yield was 89% after 3 h. This indicates that a small amount of water in the reaction solvent and/or reagent is very detrimental to the catalysis with the Mo complex. In fact, addition of a small amount of water (5 mmol) to the reaction media severely suppressed the catalysis.

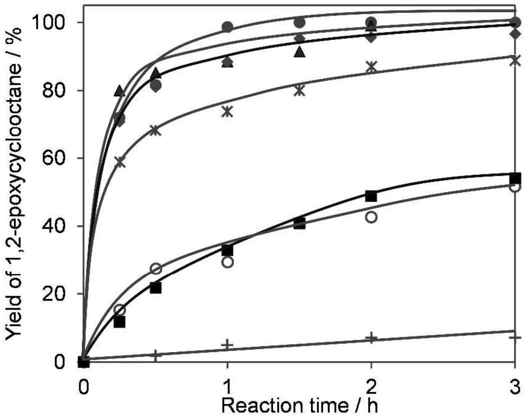


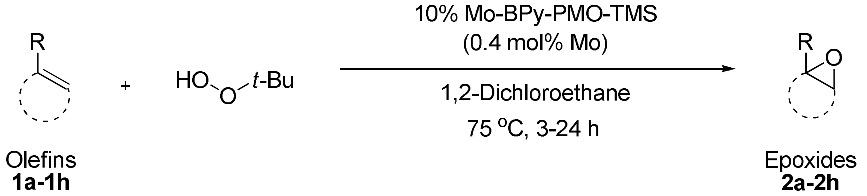
Figure 9. Solvent effect on epoxidation of *cis*-cyclooctene with TBHP at 75 °C in dry 1,2-dichloroethane (●), dry acetonitrile (▲), dry toluene (◆), dry decane (*), dry ethanol (■), undried decane (○), and decane containing water (5 mmol) (+).

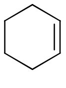
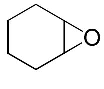
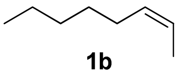
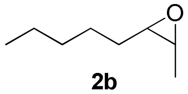
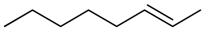
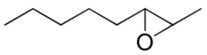
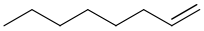
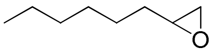
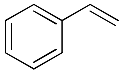
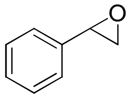
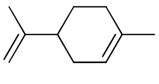
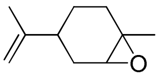
Under anhydrous conditions, we examined the influence of solvent polarity on the epoxidation of *cis*-cyclooctene with anhydrous TBHP at 75 °C. The reactions were performed in 1,2-dichloroethane, acetonitrile, toluene, and ethanol. The initial TOF values (h^{-1}) followed the order of acetonitrile (2760) > 1,2-dichloroethane (2480) ≈ toluene (2440) > decane (2030) >> ethanol (520), indicating no clear relationship between the dielectric properties and initial TOF values. The use of 1,2-dichloroethane completed the reaction within 1.5 h to afford Ecyo quantitatively. Although the use of acetonitrile and toluene also achieved high TOF, slightly prolonged reaction times were required for completing the reaction. These solvents showing high TOF likely stabilized the Mo-active intermediate and also promoted diffusion of the substrate/product molecules in the mesopores. The lowered reaction rate observed for ethanol may be due to the coordination of ethanol to the Mo-active intermediate. A similar detrimental effect of ethanol was observed for the catalytic system using $Mo(CO)_3$-immobilized phenylene-bridged PMO [29].

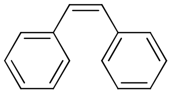
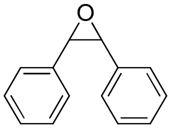
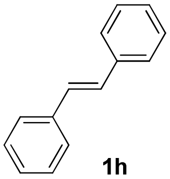
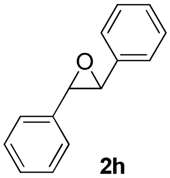
3.4 Scope and limitations of Mo-BPy-PMO-TMS for epoxidation of olefins

The scope and limitations of 10% Mo-BPy-PMO-TMS were evaluated in the epoxidation of a variety of olefins **1a-1h**. The reactions were carried out in the presence of olefin (2.5 mmol), anhydrous TBHP solution in decane (3.75 mmol), and 10% Mo-BPy-PMO-TMS (0.4 mol% Mo relative to olefin) in dry 1,2-dichloroethane at 75 °C, and the results are summarized in Table 3.

Table 3. Epoxidation of olefins with TBHP catalyzed by Mo-BPy-PMO-TMS [a]



Entry	Olefins	Epoxides (%)[b]	Yield (%)[c]
1	 **1a**	 **2a**	100 (100)
2	 **1b**	 **2b**	100 (100)
3	 **1c**	 **2c**	99 (99)
4	 **1d**	 **2d**	61 (71)
5	 **1e**	 **2e**	78 (48)
6[b]	 **1f**	 **2f**	87 (69)

7	 **1g**	 **2g**	96 (98)
8	 **1h**	 **2h**	82 (84)

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[a] All reactions were conducted with olefin (2.5 mmol), TBHP (3.75 mmol), and dry mesitylene or dry 1,4-dioxane (1.0 mmol, internal standard) in the presence of 10% Mo-BPy-PMO-TMS (35 mg, 10 μmol Mo) or $MoO_2Cl_2(bpy)$ (3.6 mg, 10 μmol Mo) in dry 1,2-dichloroethane (4.3 mL) at 75 °C. [b] The reaction was carried out at 50 °C. [c] ^{1}H NMR yields based on internal standard. ^{1}H NMR yields for homogeneous catalytic system using $MoO_2Cl_2(bpy)$ are given in parentheses.

The epoxidation of cyclohexene (**1a**) proceeded efficiently and gave 1,2-epoxycyclohexane (**2a**) quantitatively after 3 h (Table 3, entry 1). The epoxidation of internal aliphatic olefins such as *cis*-2-octene (**1b**) and *trans*-2-octene (**1c**) occurred stereoselectively to afford desired epoxides **2b** and **2c** quantitatively, respectively (Table 3, entries 2 and 3). In contrast, the reaction of terminal aliphatic olefin 1-octene (**1d**) showed moderate conversion to give 1,2-epoxyoctane (**2d**) in 61% yield (Table 3, entry 4). Mo-BPy-PMO-TMS also catalyzed the epoxidation of styrene (**1e**), giving styrene oxide (**2e**) as the main product in 78% yield along with unidentified side products (Table 3, entry 5). When limonene (**1f**) was used as a substrate, regioselective oxidation was observed at the endocyclic double bond to give 1,2-epoxy-*p*-menth-8-ene (limonene oxide, **2f**) in 87% yield after full conversion of **1f** (Table 3, entry 6). Small amounts of side products such as diepoxide and carveol were detected by GC-MS analysis, suggesting that the epoxidation of the terminal double bond and over-oxidation occurred.

We also examined the epoxidation of the double bonds of *cis*-stilbene (**1g**) and *trans*-stilbene (**1h**). The *cis*-isomer was perfectly consumed after 24 h and transformed into *cis*-stilbene oxide (**2g**) in 96% yield (Table 3, entry 7). On the other hand, the *trans*-isomer showed a lower conversion after 24 h to give *trans*-stilbene oxide (**2h**) in 82% yield (Table 3, entry 8). This may be due to the steric hindrance of the diphenyl groups of the *trans*-isomer against the immobilized Mo complex on the pore surface. In order to compare the catalytic activity of Mo-BPy-PMO-TMS and homogeneous MoO_2Cl_2(bpy), epoxidation of olefins **1a**-**1h** was performed using the homogeneous catalyst under the same conditions, and these results are also summarized in Table 3. The product yields for the 10% Mo-BPy-PMO-TMS system were comparable with those for homogeneous systems. These results indicated that 10% Mo-BPy-PMO-TMS is a good heterogeneous catalyst for the epoxidation of olefins.

3.5 Reusability of Mo-BPy-PMO-TMS

To investigate the reusability of 10% Mo-BPy-PMO-TMS for the epoxidation of *cis*-cyclooctene, the recovered catalyst was reused in a recycling experiment (Figure 10). Under undried conditions, the catalytic activity gradually decreased after repeated reactions. The TOF of 382 h^{-1} for fresh catalyst decreased to 73 and 26 h^{-1} for the first and second reuse cycles. The yields of Ecyo for the first and second reuse cycles after 8 h were 35% and 18%, respectively. However, under anhydrous conditions, the recovered 10% Mo-BPy-PMO-TMS still maintained good catalytic activity at least three more times in the epoxidation of *cis*-cyclooctene, although the reaction rate and product yield were gradually decreased (1st recycle: 90% after 1.5 h; 2nd recycle: 84% after 3 h; 3rd recycle: 94% after 8 h). The decrease in activity was attributed to a change in the coordination structure of the Mo complex fixed on BPy-PMO. The change in the Cl/Mo ratio of Mo-BPy-PMO-TMS was measured by EDX after the first reaction. Under undried conditions, the

Cl/Mo ratio decreased from 1.5 to 0.33 after 2 h, suggesting a change in the coordination structure of Mo. However, the Cl/Mo ratio was only slightly reduced from 1.5 to 1.1 under anhydrous conditions, indicating that chloride elimination was effectively suppressed. These results suggest that elimination of the chloride ligand may occur as a side reaction with residual water in solvent and/or *t*-BuOH formed in situ. The decomposition of the Mo-Cl complex would be accelerated by the filtration process since it removed liberated chloride ion from the reaction media. Thus, in order to prevent loss of chloride ion from the reaction media, *cis*-cyclooctene and TBHP were recharged in the reaction test tube after the reaction. In this system, > 95% yield of Ecyo was obtained within 4 h for at least three reuse cycles. This result confirms that preservation of the Mo-Cl complex is essential to maintaining the catalytic activity.

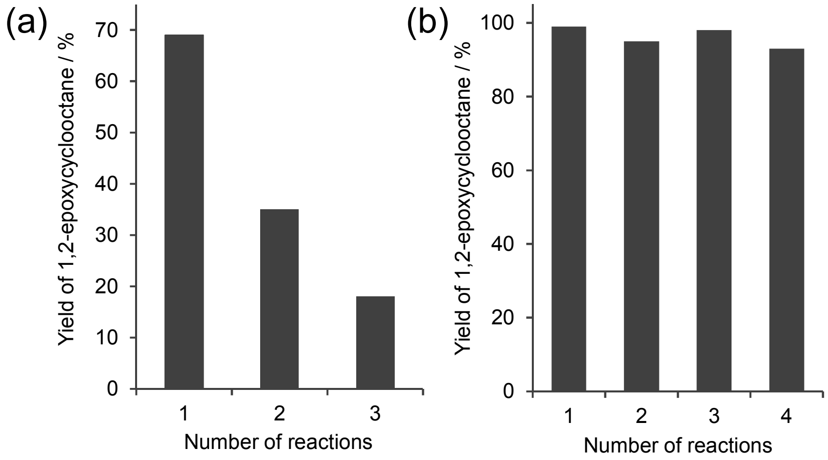

Figure 10. Reusability of 10% Mo-BPy-PMO-TMS for epoxidation of *cis*-cyclooctene (a) under undried conditions and (b) under anhydrous conditions. For (a), the recovered catalyst was reused for the recycle reaction under the same conditions. For (b), after the reaction, *cis*-cyclooctene and TBHP were recharged.

In order to evaluate the mesoporous structure, the recovered Mo-BPy-PMO-TMS under undried conditions was analyzed by XRD and nitrogen adsorption/desorption isotherm measurements. The XRD pattern for Mo-BPy-PMO-TMS changed little after the reaction, suggesting the preservation of periodic mesoporous and pore wall structures due to the strong covalent siloxane networks (Figure S12). The BET surface area and pore volume remained nearly unchanged after the 4th reaction, clearly indicating robust mesoporous structures (Figure S13). Preservation of TMS groups on the pore surface was also confirmed by IR analysis, which showed that the TMS groups on BPy-PMO were not eliminated (Figure S14).

4. Conclusions

Heterogeneous Mo complex catalysts were prepared using BPy-PMO as a solid support and MoO_2Cl_2 as a precursor, and were evaluated for their ability to catalyze the epoxidation of a variety of olefins by TBHP. The formation of $MoO_2Cl(OH)$ complexes on BPy-PMO was confirmed by FT-IR spectra, Raman spectra, and XAFS analysis. A high density of Mo complex could be loaded on BPy-PMO, in which 37% of the surface BPy ligands formed Mo complexes. The Mo-BPy-PMO-TMS exhibited greater catalytic activity for epoxidation compared to the activity of heterogeneous Mo complex catalysts supported on mesoporous silica or BPy-Polymer. The trimethylsilylation of the surface silanol groups of BPy-PMO was very effective at improving the catalytic activity, perhaps due to the smooth diffusion of oxygenated compounds, such as TBHP and epoxide products, in the mesochannels. The TOF for Mo-BPy-PMO-TMS was nearly constant up to high loading amounts of Mo complex, while the TOF decreased for Mo-BPy-Polymer. A significant solvent effect was observed for the Mo-BPy-PMO-TMS-catalyzed epoxidation of *cis*-cyclooctene. The presence of water in the reaction medium was found to strongly influence the catalysis. Mo-BPy-PMO-TMS was found to catalyze a variety of aliphatic and aromatic olefins and showed good recyclability for at least three reuse cycles in the epoxidation of *cis*-cyclooctene.–The high loading and good recyclability indicate that this supported catalyst has the potential for application to a flow-through reactor that requires a solid catalyst containing a large number of active centers and a small loss of activity.

ASSOCIATED CONTENT

Supporting Information

FT-IR spectra of BPy-PMO, BPy-PMO-TMS and *x*% Mo-BPy-PMO-TMS (*x* = 5%, 10%, 20%, and 23%); Mo *K*-edge XANES spectra of 10% Mo-BPy-PMO-TMS, $MoO_2Cl_2(bpy)$, MoO_2Cl_2, and MoO_3; Mo *K*-edge EXAFS oscillations and EXAFS Fourier transforms (κ = 20-130 nm^{-1}) of 10% Mo-BPy-PMO-TMS, $MoO_2Cl_2(bpy)$, MoO_2Cl_2, and MoO_3; Curve fitting of Mo *K*-edge EXAFS Fourier transform for $MoO_2Cl_2(bpy)$ using the crystal data of $MoO_2Cl_2(bpy)$; Curve-fitting parameters for Mo *K*-edge EXAFS Fourier transform of $MoO_2Cl_2(bpy)$; Curve fitting of Mo *K*-edge EXAFS Fourier transform for 10% Mo-BPy-PMO-TMS using the crystal data of $MoO_2Cl(OEt)(bpy)$; Curve-fitting parameters of Mo *K*-edge EXAFS Fourier transform of 10% Mo-BPy-PMO-TMS; Mo *K*-edge XANES spectra of *x*% Mo-BPy-PMO-TMS (*x* = 5%, 10%, 20%, and 23%); Mo *K*-edge EXAFS oscillations and EXAFS Fourier transforms (κ = 20-130 nm^{-1}) of *x*% Mo-BPy-PMO-TMS (*x* = 5%, 10%, 20%, and 23%); Hot filtration experiment for epoxidation catalyzed by 10% Mo-BPy-PMO-TMS; Mo *K*-edge XANES spectra of 10% Mo-BPy-PMO-TMS, Mo-BPy-FSM-TMS, Mo-BPy-Polymer, and $MoO_2Cl_2(bpy)$; Mo *K*-edge EXAFS oscillations and EXAFS Fourier transforms (κ = 20-130 nm^{-1}) of 10% Mo-BPy-PMO-TMS, Mo-BPy-FSM-TMS, Mo-BPy-Polymer, and $MoO_2Cl_2(bpy)$; Yield of 1,2-epoxycyclooctane as a function of reaction time and yield changes of 1,2-epoxycyclooctane up to 30 min from the start of the reaction using *x*% Mo-BPy-PMO-TMS (*x* = 5%, 10%, 20%, and 23%); XRD patterns of 10% Mo-BPy-PMO-TMS before and after the 1st reaction run and after the 2nd reaction run; Nitrogen adsorption/desorption isotherms of 10% Mo-BPy-PMO-TMS before and after the 1st reaction run and after the 4th reaction run; IR spectra at 2500 – 3500 cm^{-1} and 1200 – 1400 cm^{-1} of BPy-PMO-TMS, 10% Mo-BPy-PMO-TMS before and after the 1st reaction run and after the 2nd reaction run.

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