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Sol–gel synthesis of oxodiperoxo molybdenum-modified organic–inorganic materials for the catalytic epoxidation of cyclooctene

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Abstract

Hybrid organic–inorganic materials were synthesized by sol–gel copolymerization of the N,N-chelate ligand (3-triethoxysilylpropyl) [3-(2-pyridyl)-1-pyrazolyl]acetamide (**1**) and tetraethoxysilane (TEOS). Active solid oxidation catalysts can be obtained by introducing oxodiperoxo molybdenum species $MoO(O_2)_2$ into the hybrid sol–gel materials with a ligand-exchange reaction. The molybdenum-containing catalyst, prepared from a sol–gel precursor with relatively large pore volume and high specific surface area, showed a very high stability against leaching of the active species into the liquid phase during the epoxidation of cyclooctene with *tert*-butyl hydroperoxide (^{t}BuOOH).

Keywords: Epoxidation; Hybrid materials; Molybdenum; Peroxides; Sol–gel synthesis

1. Introduction

The heterogenization of homogeneous catalysts for liquid-phase olefin epoxidation is an attractive and important research subject. Extensive effort has been focused on the incorporation of metal-based catalysts onto or into inert supports by different methods, such as substituting active metal sites into molecular sieves or amorphous silica, or encapsulating and grafting organometallic complexes into nano- and mesoporous materials [1–3]. An alternative and highly effective method for the preparation of heterogeneous catalysts is to copolymerize an organic functionalized compound, usually bearing an organoalkoxysilane group, and an alkoxysilane by a sol–gel procedure [4–7]. The relatively mild reaction condition of the sol–gel process allows incorporation of various organic moieties in different inorganic materials and tuneing the material properties in a wide range. Additionally, it is possible to produce hybrid materials with high loading of organic functional groups in combination with a uniform coverage of the resulting surfaces by this technique [5].

Recently, we reported the synthesis of a hybrid heterogeneous catalyst system by covalent grafting of oxodiperoxo molybdenum complexes of the type $[(\text{L-L})MoO(O_2)_2]$ (L-L = (3-triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl] acetamide (**1**)) into the mesoporous MCM-41 material [8,9]. The grafted materials are highly active and stable catalysts for the liquid-phase epoxidation of cyclooctene with ^{t}BuOOH as the oxygen source. The high stability against leaching of active species to liquid phase can be mainly attributed to the strong binding between the $MoO(O_2)_2$ unit and the chelate ligand [10–13], and to the formation of covalent bonds (Si–O–Si) between the organic ligand system and the inorganic mesoporous material [8]. However, a drawback of the grafting procedure is that the loading of organic functionalities is often low, mainly limited by the distribution of reactive Si–OH groups and the diffusion limitations of the mesoporous channel. Besides, it is believed that organic groups in a grafted mesoporous material are mainly located on the external surfaces and those parts of the internal surface, which are close to the pore windows, leading to a nonuniform distribution of the organic sites [14].

In this work, we present an alternative for the preparation of a hybrid material with a high loading of oxodiperoxo molybdenum complexes in the matrix of the silicate. The precursors were synthesized by copolymerizing the chelate ligand **1** with TEOS under traditional uncatalyzed and catalyzed sol–gel conditions. The desired molybdenum-based catalysts are thus obtained by introducing the oxodiperoxo molybdenum units into the sol–gel precursor by a ligand-exchange reaction. The catalytic performance of the

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molybdenum containing materials was investigated for the liquid-phase epoxidation of cyclooctene with ${}^tBuOOH$.

2. Experimental

2.1. Catalyst preparation

*2.1.1. Synthesis of chelate ligand (3-Triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acetic amide (**1**).* The chelate ligand **1** bearing a $Si(OEt)_3$ group was synthesized as described previously [8,9]. Typically, 2-(3-pyrazolyl)pyridine [15] (10 mmol, 1.45 g) was added to a suspension of NaH (10 mmol, 0.24 g) in THF (50 mL), the mixture was stirred until the evolution of hydrogen stopped, then ethyl bromoacetate (10 mmol, 1.67 g) was added, and the resulting solution was refluxed for 4 h. After removing the solvent in vacuum, the product was extracted from the oily residue with diethyl ether and recrystallized to obtain [3-(2-pyridyl)-1-pyrazolyl]acetic acid ethyl ester. A mixture of the ester (4.02 mmol, 0.93 g) and 3-triethoxysilylpropylamine (4.02 mmol, 0.89 g) was heated to 150 °C for 2 h under an atmosphere of argon. After this, all volatiles were removed in vacuum resulting in **1** as an oily residue in almost quantitative yield.

2.1.2. Sol–gel process to synthesize hybrid precursors

*Preparation of gel **SG-1** from **1** and tetraethoxysilane (TEOS) without catalyst.* Sol–gel polymerization was carried out by hydrolysis/condensation of ligand **1** (11.7 mmol, 4.75 g) and TEOS (23.4 mmol, 4.97 g) in the presence of 10 mL of water with 60 mL of ethanol as the solvent. The resulting solution was stirred at room temperature, and gelation occurred within 24 h. After standing for 14 days, the gel was washed thoroughly with ethanol, chloroform, and diethyl ether. The white powder **SG-1** was heated to 150 °C in the air for 3 h. Yield: 1.35 g, 28% (based on complete condensation of **1** and TEOS). Anal. Found: C, 25.62; H, 3.12; N, 8.90; Calcd. for $(C_{13}H_{15}N_4O_{2,5}Si)_4 \cdot (EtOH) \cdot (H_2O)_5 \cdot (SiO_2)_{20} = C_{54}H_{76}N_{16}O_{56}Si_{24}$: C, 25.75; H, 3.04; N, 8.90; ligand/$SiO_2 = 1/5$.

*Preparation of gel **SG-2** with ethylamine as catalyst.* The amounts of 4.75 g (11.7 mmol) of ligand **1**, 4.97 g of TEOS (23.4 mmol), 10 mL of water, and 60 mL of ethanol were mixed in a flask, and then 2.2 g of a $EtNH_2$ solution (7.0% in water) was added under stirring. Gelation occurred within 5 min. After standing for 7 days, the gel was crushed and washed thoroughly with ethanol, chloroform, and diethyl ether. The white powder **SG-2** was heated to 150 °C in the air for 3 h. Yield: 3.92 g (81%). Anal. Found: C, 31.56; H, 3.61; N, 11.26; Calcd. for $(C_{13}H_{15}N_4O_{2,5}Si)_2 \cdot (H_2O)_3 \cdot (SiO_2)_6 = C_{26}H_{36}N_8O_{20}Si_8$: C, 31.06; H, 3.60; N, 11.15; ligand/$SiO_2 = 1/3$.

*Preparation of the precipitate **SG-3** with HCl/$EtNH_2$ as catalyst.* The amounts of 4.75 g (11.7 mmol) of ligand **1**, 4.97 g of TEOS (23.4 mmol), 10 mL of water, and 60 mL of ethanol were mixed, and then 1.2 g of 3.7% aqueous HCl solution was added as catalyst under stirring. No gelation occurred in 2 days, then 2.2 g of 7.0% $EtNH_2$ was added, and precipitation not gelation occurred immediately. After standing for 7 days, the precipitate was filtered and washed thoroughly with ethanol, chloroform, and diethyl ether. The white powder **SG-3** was heated to 150 °C in the air for 3 h. Yield: 2.95 g (61%). Anal. Found: C, 26.81; H, 3.08; N, 9.42. Calcd. for $(C_{13}H_{15}N_4O_{2,5}Si)_8 \cdot (EtOH) \cdot (H_2O)_{10} \cdot (SiO_2)_{36} = C_{106}H_{146}N_{32}O_{104}Si_{44}$: C, 26.70; H, 3.09; N, 9.40; ligand/$SiO_2 = 1/4.5$.

2.1.3. Preparation of Mo-containing sol–gel catalysts

Catalysts containing oxodiperoxo molybdenum species were obtained by stirring 0.40 g of **SG-1**, **SG-2**, or **SG-3** with 0.103 g (0.32 mmol) of $[MoO(O_2)_2 \cdot (DMF)_2]$ [16] in 40 mL of chloroform at room temperature for 24 h. The resulting catalysts **Mo-SG-1**, **Mo-SG-2**, or **Mo-SG-3** were filtered, washed, Soxhlet-extracted with $CHCl_3$, and dried in vacuum. Mo loading was 6.7 wt% in **Mo-SG-1** and **Mo-SG-3**; 0.7 wt% in **Mo-SG-2**, which was calculated according to the amount of remaining $[MoO(O_2)_2 \cdot (DMF)_2]$ in the chloroform solution after filtration of the solid catalyst.

2.2. Characterization of materials

Nitrogen adsorption/desorption isotherms were measured at the liquid nitrogen temperature, using a SORPTOMATIC 1990 analyzer. Samples were degassed at 140 °C overnight before measurements. Specific surface areas were calculated using the BET model. Pore volumes were estimated at a relative pressure of 0.94 (P/P_0), assuming full surface saturation with nitrogen. Pore-size distributions were evaluated from desorption branches of nitrogen isotherms using the BJH model.

Solid-state ^{13}C and ^{29}Si CP-MAS NMR spectra were recorded at 100.61 and 79.49 MHz, respectively, using a Bruker AVANCE 400 spectrometer.

2.3. Catalytic reactions

The catalytic epoxidation of cyclooctene was carried out in a two-neck 100-ml flask equipped with a reflux condenser and a Quickfit septum adapter. In the standard procedure, 0.50 g of cyclooctene (4.54 mmol), 50 mg of the solid catalyst, and 12 mL of $CHCl_3$ were added to the flask. The suspension was stirred and heated to reflux temperature (61 °C), and then 0.85 mL of a 5.5 M solution of ${}^tBuOOH$ in decane was added to start the reaction. The course of the reaction was monitored by quantitative GC analysis. The catalytic activity for the epoxidation of cyclooctene was evaluated by the conversion of cyclooctene to epoxycyclooctane.

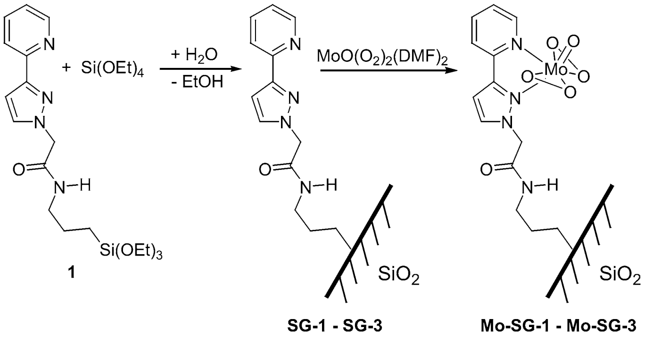
3. Results and discussion

3.1. Synthesis and characterization

As outlined in Scheme 1, three precursors **SG-1**, **SG-2**, and **SG-3** were obtained by copolymerizing the chelate ligand **1** with TEOS using traditional sol–gel processes.

Usually an acidic or basic catalyst is required in a sol–gel polymerization process with $RSi(OR')_3$ precursors. In our case, copolymerization of ligand **1** and TEOS can occur even without adding any catalyst, obviously due to the presence of a basic pyridine and/or pyrazole group in the ligand. These can catalyze the hydrolysis and cocondensation process by themselves, which leads to the precursor **SG-1**. However, a quite low yield (28%) was obtained for this synthetic route. In order to increase the yield of the sol–gel polymerization reaction, two other attempts were carried out using acid and/or base catalysts for the sol–gel process. With $EtNH_2$, a quite basic amine as the catalyst, the transition from liquid (sol) to gel occurred within several minutes. Yield of the resulting hybrid sol–gel material **SG-2** was 81%. With HCl as the catalyst no gelation occurred in between 2 days. After the addition of $EtNH_2$ to the solution, a white precipitate appeared immediately. The formation of a precipitate instead of gelation might be caused by the formation of the salt $EtNH_3Cl$. The yield of **SG-3** was 61%.

Table 1 shows the experimental conditions to yield the materials **SG-1**, **SG-2**, and **SG-3**, as well as the textural parameters of these compounds as obtained by N_2 adsorption. Fig. 1 presents the N_2 isotherms of **SG-1** and **SG-3**, recorded at 77 K.



Scheme 1.

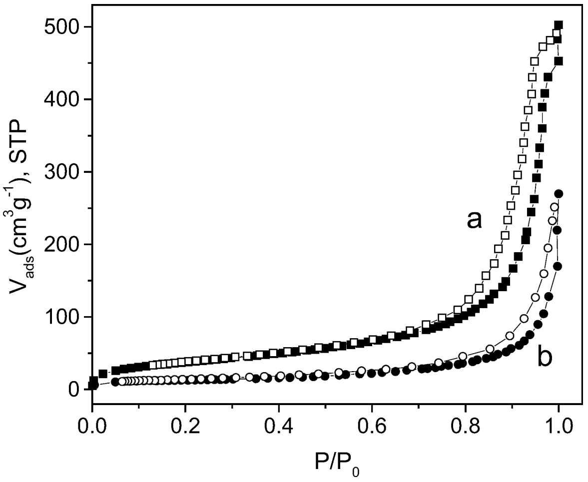


Fig. 1. N_2 adsorption–desorption isotherms at 77 K of the sol–gel materials (a) **SG-1** and (b) **SG-3**.

The isotherm of **SG-2** was not obtained, since its N_2 uptake is undetectable under the experimental conditions, indicating a very low BET surface area. **SG-1** displays isotherms characteristic for mesoporous materials with pore diameters between 2 and 50 nm and minor contributions from macropores [17]. The isotherm of **SG-3**, which shows a much lower uptake of N_2 than the **SG-1** sample, corresponds to a combination of meso- and macropores. Compared to **SG-3**, **SG-1** has a higher BET surface area ($138\ m^2\,g^{-1}$), a larger pore volume ($0.67\ cm^3\,g^{-1}$), and a narrower pore-size distribution (mean diameter: 10–30 nm, Table 1).

Solid-state ^{13}C CP-MAS NMR spectra of the three hybrid sol–gel precursors (**SG-1**, **SG-2**, and **SG-3**) are presented in Fig. 2. All spectra are similar to the ^{13}C NMR spectrum of the free ligand **1** in solution (the dashed lines are giving the relative intensities) [9].

These results indicate that the molecular structure of the chelate ligand **1** survives during the preparation procedure. Besides, the absence of the two resonances at around 58 and 18 ppm, which correspond to $SiOCH_2CH_3$ (ethoxysilyl) groups, suggests that the hydrolysis of ligand **1** is nearly complete during the sol–gel process, which corroborates with the elemental analyses (EtOH content). The solid-state ^{29}Si CP-MAS NMR spectra provide a direct evidence for the linkage between the organic and the inorganic components of the materials (Fig. 3).

Table 1
Preparation conditions and structure parameters of the sol–gel materials

Sol–gel samples	Catalysts[a]	Yield[b] (%)	Content of **1**[c] ($mmol\,g^{-1}$)	Surface area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Pore diameter (nm)
SG-1	No catalyst	28	1.59	138	0.67	10–30
SG-2	$EtNH_2$	81	2.01	< 5	–	–
SG-3	$HCl + EtNH_2$	61	1.68	43	0.34	10–150

[a] Used during the sol–gel process for getting the corresponding precursors.
[b] Based on complete condensation of ligand **1** and TEOS.
[c] Calculated according to the content of nitrogen (CHN elemental analysis).

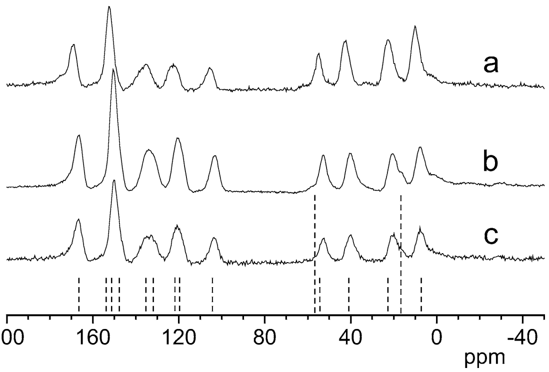


Fig. 2. Solid-state ^{13}C CP-MAS NMR spectra of the sol–gel precursors (a) **SG-1**, (b) **SG-2**, and (c) **SG-3** compared with the resonances of the free ligand **1** in solution (dashed lines giving relative intensities).

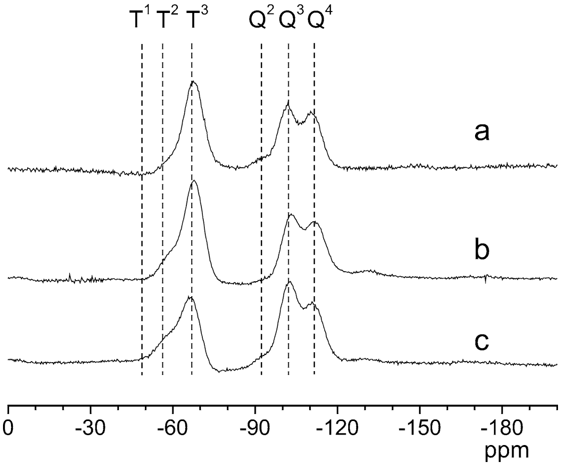


Fig. 3. Solid-state ^{29}Si CP-MAS NMR spectra of the sol–gel precursors (a) **SG-1**, (b) **SG-2**, and (c) **SG-3**.

All three sol–gel precursors show a major resonance centered at −67 ppm, which can be assigned to organosilica T^3 species [C-*Si*$(OSi)_3$] [9]. Only very small amount of T^2 species [C-*Si*$(OSi)_2(OR)$] (R = H, or Et) exists in the materials as evidenced by a weak resonance at around −57 ppm (overlapped partly with the T^3 signal). This gives further evidence for the nearly complete condensation reaction during the sol–gel process. Two signals at −112 and −103 ppm correspond to Q^4 and Q^3 species of the inorganic silica framework [18,19]. While the Q^3 sites are associated with the isolated hydroxyl group [$(SiO)_3$*Si*(OH)], and the Q^4 sites correspond to silicon atoms without hydroxyl groups [$(SiO)_4$*Si*]. By comparing these NMR spectra with that of grafted mesoporous MCM-41 materials [8,9], it can be concluded that there is a considerably higher amount of organosilica species in all three sol–gel precursors. Besides, the very high loading with the organic ligand **1** can also be confirmed according to the results of elemental analyses (see Section 2).

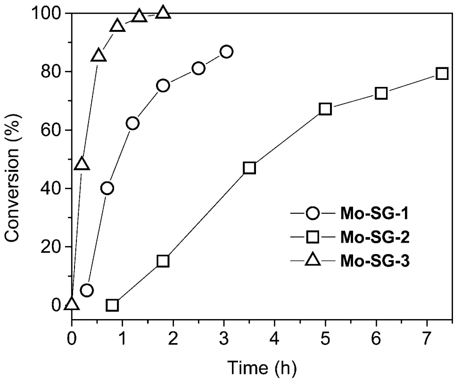


Fig. 4. Kinetic profiles of the epoxidation of cyclooctene to epoxycyclooctane with ^tBuOOH over various catalysts. Reaction conditions: Mo:cyclooctene:^tBuOOH (mol/mol) = 1:130:134 (for **Mo-SG-1** and **Mo-SG-3**), or 1:1240:1280 (for **Mo-SG-2**); solvent, chloroform; reaction temperature, 61 °C.

3.2. Catalytic tests

Treatment of the hybrid silica materials **SG-1–SG-3** with $MoO(O_2)_2 \cdot (DMF)_2$ in $CHCl_3$ solution (see Scheme 1) gave the three catalysts **Mo-SG-1–Mo-SG-3**, which were tested for the epoxidation of cyclooctene with ^tBuOOH at 61 °C (see Fig. 4).

As expected, they are all active for this reaction with nearly 100% selectivity to epoxycyclooctane, which is consistent with the grafted MCM-41 system and corresponding homogeneous catalysts we previously reported [8–13]. Under the reaction conditions applied, **Mo-SG-3** showed higher reaction rates than **Mo-SG-1**, although the loading with active molybdenum sites is the same for both catalysts. The low activity of **Mo-SG-2** is due to the low loading with active molybdenum sites, which is probably caused by the very low BET surface area of the **SG-2** precursor.

For a heterogenized catalyst, the leaching of the active species into the liquid phase under operating conditions should be as low as possible [20]. To investigate this, the Mo-containing catalysts were filtered at about 45% of conversion of cyclooctene (Fig. 5).

This has to be done at the reaction temperature of 61 °C, since filtration at lower temperatures may lead to readsorption of leached homogeneous species into the solid support, which would falsify the results. For **Mo-SG-1**, there is almost no detectable subsequent conversion in the filtrate after removing the catalyst, which is a very strong evidence for a real heterogeneous catalysis. For **Mo-SG-2**, it was found that cyclooctene can be converted at a low rate in the filtrate, which means that a small part of the active species is leached from the hybrid catalyst. For **Mo-SG-3**, the epoxidation reaction is continued at a very high rate after the solid catalyst is removed, which means that leaching of active species occurs during the reaction process and thus plays an important role for the catalytic performance of this material.

These immediately lead to the question, Why do the three hybrid catalysts, prepared from the same starting materi-

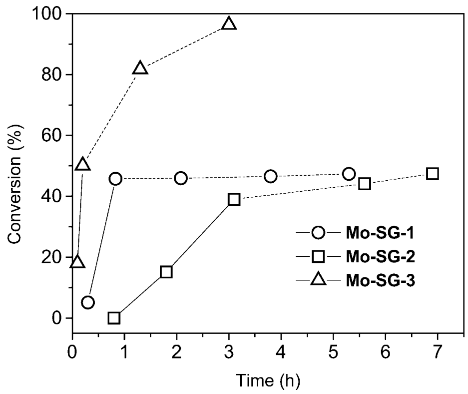


Fig. 5. Leaching experiments of three Mo-containing catalysts by continuing the reaction after the filtration of the catalysts at the reaction temperature. Dashed lines indicate the conversions after the removal of the catalysts. Reaction conditions are analogous to Fig. 4.

als (ligand **1** and TEOS), show such a different stability? In a previous work [8], we found that the grafted Mo-containing mesoporous MCM-41 catalyst, prepared from **1**, shows a very high stability against leaching during the epoxidation of cyclooctene. This can be attributed to the covalent link between the organic ligand system and the inorganic mesoporous material, and to the strong binding between the $MoO(O_2)_2$ unit and the chelating ligand as already depicted. The latter feature was examined in a series of experiments with related homogeneous oxodiperoxo molybdenum catalysts [10–13]. In the present case, only **Mo-SG-1** shows a stability similar to the grafted Mo-containing MCM-41 system. Considering the relatively low BET surface area of the sol–gel precursors of **SG-2** ($< 5\ m^2\,g^{-1}$) and **SG-3** ($43\ m^2\,g^{-1}$), it is reasonable to assume that most of the chelating sites are located in the bulk of the hybrid material and are therefore not accessible for the coordination of molybdenum species. Especially for **Mo-SG-3**, which is highly loaded with molybdenum, it seems to be plausible that a large part of the $MoO(O_2)_2$ unit does not undergo coordination with the chelate ligand.

It was reported that silica and oxodiperoxo molybdenum species can interact to form surface peroxo species, and organosilanols can be used to model the silica-supported oxodiperoxo metal species [21]. In our work, we have also confirmed that $MoO(O_2)_2$ species can be absorbed by porous silica gels or mesoporous MCM-41 materials directly even without introducing any organic ligand previously. The absorbed molybdenum species could not be removed by Soxhlet extraction with $CHCl_3$, which means that the metal-supported system is stable under the preparation conditions. However, it was found that such Mo-containing materials are not stable under the reaction conditions of the cyclooctene epoxidation, where they are treated with high polar and protic reagents like ^{t}BuOOH or ^{t}BuOH. Similar results have recently been reported by Buffon and co-workers [7]. They found that $MoO_2(acac)_2/SiO_2$ catalysts prepared by a sol–gel procedure are unstable toward leaching during the olefin epoxidation. The recyclablity of this catalyst could be improved when 3-(triethoxysilyl)propylethylenediamine and 1,4-bis(triethoxysilyl)benzene were incorporated during the preparation process. Therefore, in our opinion, the poor stability of **Mo-SG-2** and **Mo-SG-3** against leaching is due to the presence of $MoO(O_2)_2$ species interacting with surface silanol groups (or similar groups) of the hybrid silica-based materials. On the other side, very high stability of **Mo-SG-1** against leaching under the epoxidation conditions proves that all $MoO(O_2)_2$ units are coordinated to the chelate ligand. For this material, the ratio of molybdenum to ligand **1** is 0.5:1.0, which can be calculated according to the content of ligand **1** and the loading of molybdenum. It means that at least half of the chelate ligands in **SG-1** are accessible owing to the larger pore volume and higher BET surface area of this material. Besides, for **Mo-SG-1**, the chelate ligands should be mainly located on the internal surface of the mesoporous system instead of a location on the external surface for other two catalysts. We believe that the presence of mesoporous channels may also play a positive role for the stability of the hybrid catalyst.

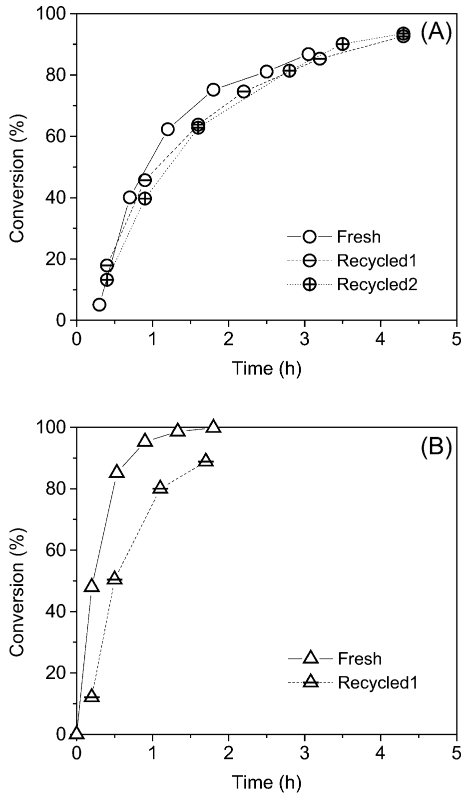


Fig. 6. Recyclablity studies for (A) **Mo-SG-1** and (B) **Mo-SG-3**. Reaction conditions are analogous to Fig. 4.

The recyclability of **Mo-SG-1** and **Mo-SG-3** was studied by using the catalysts in a second and/or third reaction run (Fig. 6). Before reused, the catalyst was separated from the reaction mixture by filtration at the reaction temperature, washed with $CHCl_3$, and dried at room temperature.

The catalytic properties of the recycled **Mo-SG-1** catalyst did not change significantly compared with the fresh sample (Fig. 6A), indicating the excellent stability and recyclability of these systems. For **Mo-SG-3** (Fig. 6B), an obvious decrease in activity was observed in the second run, which can be explained due to the loss of a part of active Mo species during the first run.

4. Conclusion

Hybrid organic-inorganic materials containing the chelate ligand (3-triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]-acetamide (**1**) were synthesized successfully by sol–gel copolymerization with TEOS. Heterogeneous epoxidation catalysts can be obtained after introducing oxodiperoxo molybdenum species $MoO(O_2)_2$ into the hybrid sol–gel materials. The Mo-containing material, prepared from a sol–gel precursor with a higher BET specific surface, is active and truly heterogeneous catalyst for the liquid phase epoxidation of cyclooctene with ^{t}BuOOH as the oxygen source. The very high stability against leaching can be mainly attributed to the higher accessibilities of the chelate ligands in the hybrid material and thus can coordinate with $MoO(O_2)_2$ species to form stable heterogeneous epoxidation catalysts. As the fundamental properties of the synthesized sol–gel materials are greatly influenced by many factors, we believe that more suitable hybrid materials (e.g., large pore volume and high BET surface) containing such kinds of chelate ligands for the application in catalysis can be obtained in a high yield by improving preparation methods and conditions of the sol–gel process.

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