

Sol–gel synthesis, characterization and catalytic property of silicas modified with oxomolybdenum complexes

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Abstract

Active solid oxidation catalysts can be obtained by incorporating dioxomolybdenum(VI) species derived from $\text{MoO}_2\text{Cl}_2(\text{OPMePh}_2)_2$ into silica matrices via a sol–gel method. The supported catalyst has been characterized by elemental analysis, XRD, N_2 -physisorption, FT-IR, FT-Raman, UV–vis and solid-state MAS NMR spectroscopy, and a pathway for the reaction between $\text{MoO}_2\text{Cl}_2(\text{OPMePh}_2)_2$ and tetraethoxysilane (TEOS) is suggested. The molybdenum catalyst was tested in the epoxidation of cyclohexene in the presence of *tert*-butyl hydroperoxide (TBHP). The conversion of cyclohexene and the selectivity to the epoxide were very high and increased further on raising the reaction temperature.

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1. Introduction

Over the past three decades, direct oxidation of olefins using environmentally benign oxidants such as hydrogen peroxide, oxygen and alkyl hydroperoxides in the presence of high-valent transition-metal catalysts [1] has emerged as a very promising approach to the production of epoxides. Transition-metals used as catalysts include rhenium [2], titanium [3], vanadium [4,5], molybdenum [6–13], selenium and platinum [14]. In the case of molybdenum-containing complexes, oxomolybdenum species have been particularly widely investigated because of their high activity for selective oxidation [6–13]. Recently, considerable effort has been directed towards the heterogenization of molybdenum onto different supports, such as silica [15] or polymers [16–25], due to the well known advantages of heterogeneous cata-

lysts over homogeneous analogues. Compared to polymer supports, inorganic ones do not swell or dissolve in organic solvents, and show better mechanical and thermal stabilities. Various mono- or bidentate ligands have been used to functionalize a silica surface so that covalent bonds can be formed between the catalytically active site and the support. Molybdenum-containing silicates [26] and molybdenum-incorporation in the framework of MCM-41 [27–31] or MCM-48 [29,32] have been reported, and some truly heterogeneous catalysts were obtained by such means. Sol–gel technologies have been used to prepare amorphous silicates [33–35]. These silicates containing molybdenum [36–39] display high activity in the epoxidation of alkenes and the oxidation of alcohols.

We have previously reported [40,41] that easily prepared molybdenum(VI) containing complexes such as $\text{MoO}_2\text{X}_2(\text{OPR}_3)_2$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$; $\text{OPR}_3 = \text{OPMePh}_2, \text{OPPh}_3$) exhibit high catalytic activities for the epoxidation of cyclohexene. The electronic and steric environment of the molyb-

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denum center can be adjusted by changing either X or R. However, halogen-containing by-products and the phosphine oxide ligand were detected in the reaction system, which indicates that decomposition of the catalyst occurred. As with other homogeneous catalysts, recovery of the catalysts, their separation from the reaction products, and the difficulties associated with the recycling of the catalytic species are other problems. This work concerns the preparation and characterization of supported catalysts based on these complexes obtained by sol–gel methods. Our aim of the present study is to understand the structure of the supported catalyst and visualize an active catalytic behavior of our catalyst.

2. Experimental

2.1. Materials

Dichloromethane (99%, Acros) was dried over calcium hydride and distilled under nitrogen. Most materials were obtained from commercial sources and used as received: cyclohexene (99%, Acros), cyclohexene oxide (98%, Acros), cyclooctene (95%, Acros), 1-hexene (97%, Acros), 1-octene (+99%, Acros), decane (+99%, Acros), cyclododecene (TCI-EP), 1-decene (TCI-EP), *tert*-butyl hydroperoxide (TBHP, ~5.5 M in nonane, Fluka), and tetraethylorthosilicate (TEOS, Beijing Chemical Reagents Company).

2.2. Characterization

Powder X-ray diffraction patterns were recorded using a Shimadzu XRD-6000 instrument under the following conditions: 40 kV, 20 mV and Cu K α radiation. The samples were step-scanned in steps of 0.02° (2θ) in the range 3–70° using a count time of 10 s/step. Infrared spectra were recorded on a Bruker Vector 22 FT-IR spectrometer using KBr pellets containing 1% of the catalyst. UV–vis spectra were obtained on a Shimadzu UV/2501PC spectrometer using the diffuse reflectance technique. FT-Raman spectra were obtained on a Nicolet Raman 950 spectrometer. Nitrogen adsorption/desorption isotherms were measured at 77 K on a Quantachrome instrument with nitrogen as the probe molecule. The samples were degassed at 393 K for 2 h before measurements. ^{31}P MAS NMR spectra were recorded at 121.49 MHz on a Bruker Avance 300 spectrometer. The metal contents were measured by the ICP technique using a Shimadzu ICPS-7500 instrument. GC–MS measurements were performed on a Shimadzu QP-2010 instrument equipped with a capillary column (30 m \times 0.25 mm \times 0.25 m) using He as the carrier gas.

2.3. Synthesis of the catalysts

$\text{MoO}_2\text{Cl}_2(\text{OPMePh}_2)_2$ was synthesized according to the published procedure [40]. The heterogeneous catalyst, SGMo-S was prepared by modifying the procedure described

by Neumann and Levin-Elad [35] for the preparation of $\text{MoO}_3\text{-SiO}_2$. In a typical preparation, TEOS (49 mmol) was dissolved in 14.7 ml ethanol, followed by addition of 98 mmol of water as a 0.1 M HCl solution. After magnetic stirring and heating at 60 °C for 2 h, the solution was cooled to room temperature. To the partially hydrolyzed TEOS was added 25 ml ethanol solution containing 1 mmol of the $\text{MoO}_2\text{Cl}_2(\text{OPMePh}_2)_2$ catalyst and another portion of 0.1 M hydrochloric acid. The pH of the final mixture was adjusted to 2 and allowed to stand in the hood until all the volatile solvent was evaporated, leaving a homogenous transparent xerogel. After washing with CH_2Cl_2 in a Soxhlet for 24 h, the xerogel was dried under air at 120 °C for 16 h to remove excess solvent and water. Heating at this temperature is known to result in only minimal changes in the xerogel. The same procedures were applied using the phosphine oxide ligand in place of the complex and the resulting product is denoted SG-OPMePh $_2$.

2.4. Catalytic experiments

The reactions were carried out without precautions to exclude moisture and oxygen, using a two-necked 25 ml round bottom flask equipped with a reflux condenser and a septum. In a typical experiment, a mixture of cyclohexene (10 mmol), TBHP (15 mmol), Mo catalyst (3.9×10^{-3} mmol) and *n*-decane (2.5 mmol) as an internal standard for the GC–MS were magnetically stirred at the required temperature for 8 h. The reactions were monitored by taking aliquots from the reaction mixtures every 30 min. The samples were analyzed by GC–MS. In order to quantify the nature of our catalyst, two parameters, namely the conversion of olefin and the selectivity to olefin epoxide, were calculated to describe the experimental results, as follows:

$$\text{Conversion (C)} = \left\{ \frac{1 - [\text{remaining olefin}]}{\sum[\text{initial olefin}]} \right\} \times 100\%$$

$$\text{Selectivity (S)} = \left\{ \frac{[\text{olefin epoxide}]}{\sum[\text{oxo products}]} \right\} \times 100\%$$

The conversion of cyclohexene and selectivity to cyclohexene epoxide was calculated using a calibration curve ($r^2 = 0.999$) obtained prior to the reaction.

3. Results and discussion

3.1. Catalyst characterization

The powder X-ray patterns of the catalyst supported on the inorganic matrix (SGMo-S) are very similar to that of the control silicate obtained from TEOS, indicating the retention of the structure after supporting the catalyst on this matrix. Elemental analysis of the resulting materials contain 1.2 mass% Mo, which is an appropriate concentration for catalytic application [26].

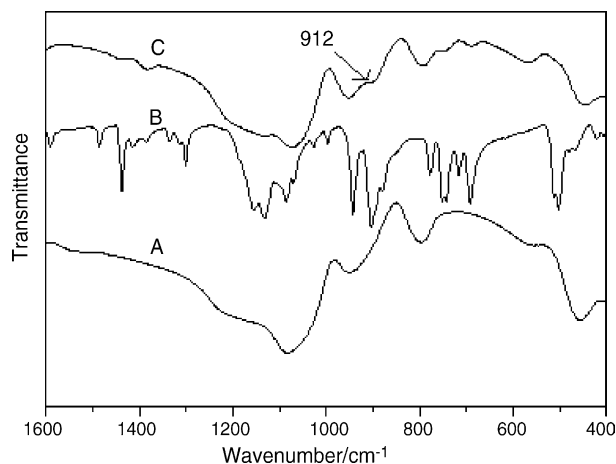


Fig. 1. FT-IR spectra of: (A) blank silicate; (B) $\text{MoO}_2\text{Cl}_2(\text{OPMePh}_2)_2$ for comparison; and (C) SGMo-S.

3.1.1. FT-IR

The FT-IR spectrum of the supported catalyst (Fig. 1B) shows bands characteristic of the silicate structure, which is dominated by absorptions at 457, 553, 799 and 1081 cm^{-1} due to Si–O–Si bending and stretching vibrations. These bands are only slightly shifted compared to those of the unmodified silicate (Fig. 1A). A band at 953 cm^{-1} is attributed to surface Si–OH vibrations [42] and is probably superimposed on absorptions due to Si–O–Mo bonds. The presence of bands at 744, 718, 693 cm^{-1} , which can be attributed to C–H bending vibrations of phenyl groups in SGMo-S is an indication of the formation of a Mo-supported catalyst. A weak band at 912 cm^{-1} is only present in the spectrum of the supported catalyst and appears in the range of Mo–O vibrations [43]. This band was previously described [33] as a characteristic feature of Mo atoms supported in silicate matrices.

3.1.2. UV–vis spectroscopy

UV–vis spectroscopy was employed in the diffuse reflectance mode for the supported catalyst together with the control silicate for comparison. For the Mo-containing species, the nature of the ligands plays a central role in determining intensity and energy of the electronic spectra [44]. Moreover, the dispersion of Mo-atoms, the Mo-atoms support interaction and the local Mo symmetry all influence the UV–vis spectra [45]. The supported catalyst exhibits four absorption bands in the 250–280 nm region (Fig. 2B) which are also observed in the spectrum of the free complex (Fig. 2C), which can be attributed to ligand–Mo charge transfer bands. Most striking is the large difference in the spectrum between SGMo-S and the control silicate (Fig. 2A) which clearly indicates that the Mo-containing moiety has been anchored in the inorganic matrix.

3.1.3. Nitrogen physisorption

Nitrogen adsorption–desorption isotherm of SGMo-S recorded at 77 K is shown in Fig. 3, which is characteristic of

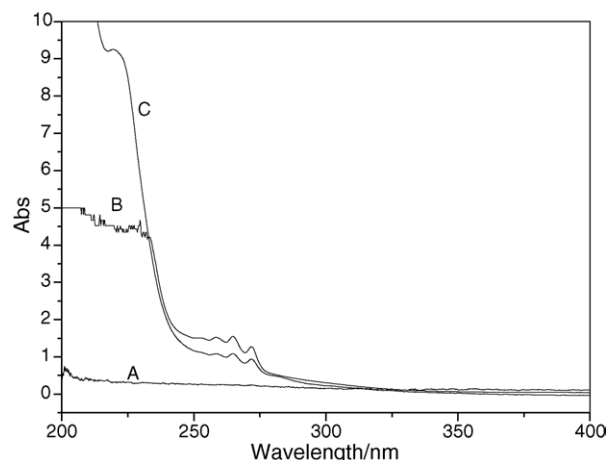


Fig. 2. UV–vis spectra of: (A) blank silicate; (B) SGMo-S; and (C) $\text{MoO}_2\text{Cl}_2(\text{OPMePh}_2)_2$ for comparison.

type I according to IUPAC classification [46]. The pores are smooth and cylindrical as indicated by the lack of hysteresis in its desorption branches. A surface area of $328.3\text{ m}^2/\text{g}$ and the modal pore size of 5.8 nm were computed using the Horvath–Kawazoe method.

3.1.4. ^{31}P MAS NMR spectroscopy

The ^{31}P MAS NMR spectrum of SGMo-S displays three resonances at 41, 46 and 59 ppm (Fig. 4). For comparison, the ^{31}P MAS NMR spectra for complex $\text{MoO}_2\text{Cl}_2(\text{OPMePh}_2)_2$, SG-OPMePh₂ and OPMePh₂ were also obtained, and they display a single resonance at about 47, 35 and 30 ppm, respectively. In the preparation of SGMo-S, extensive washing with CH_2Cl_2 should have removed any surface absorbed OPMePh₂ from the material. The fact that SG-OPMePh₂ was processed in an identical manner would suggest that the polymer can somehow incorporate phosphine oxide, presumably by means of a Si–OP linkage. In the synthesis of SGMo-S, it

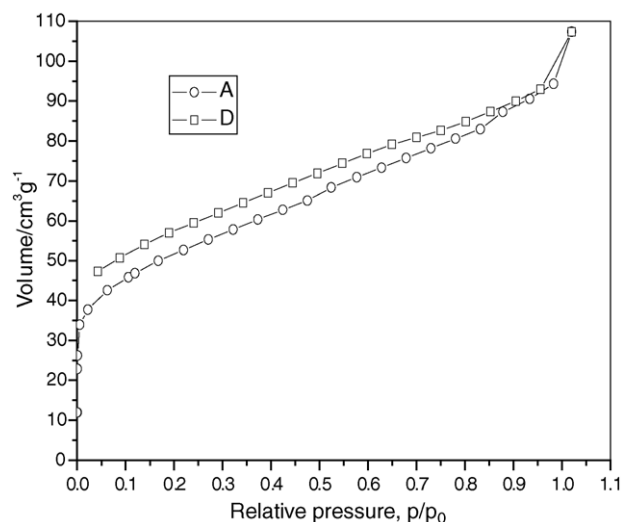


Fig. 3. Nitrogen adsorption–desorption isotherm of SGMo-S.

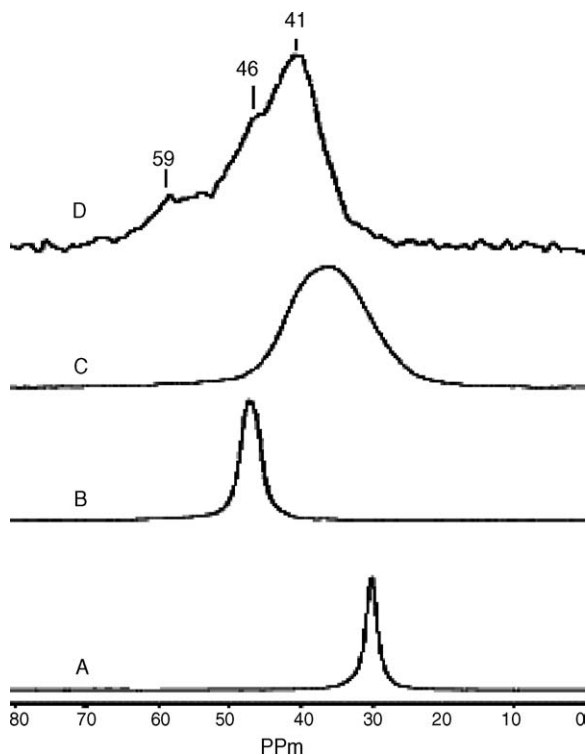


Fig. 4. ^{31}P CP MAS NMR spectra of: (A) OPMePh $_2$; (B) MoO $_2\text{Cl}_2(\text{OPMePh}_2)_2$; (C) SG-OPMePh $_2$; and (D) SGMo-S.

is likely that some phosphine oxide dissociated and reacted with the polymer. Therefore, the complex pattern observed in the solid state NMR spectrum for SGMo-S may be indicative of this, but lacking further proof, definitive assignments of these peaks is not possible. The peaks labeled as D in Fig. 4 may also arise from P atoms from phosphine oxide bonded to Mo which is stabilized on the polymer, as we have additional data (FT-IR and X-ray) to suggest that Mo is incorporated. Suffice it to say that the sample does not appear to contain free phosphine oxide.

3.1.5. FT-Raman spectroscopy

The FT-Raman spectra of SGMo-S and the precursor complex are given in Fig. 5. The Raman bands at about 489 and 615 cm^{-1} are characteristic of the silica support [47]. The bands at 3063, 2990 and 2926 cm^{-1} , characteristic of the C–H stretching vibrations of methyl and phenyl groups, are present in both the homogenous catalyst and SGMo-S. The band at 1586 cm^{-1} can be attributed to aromatic ring stretching.

The band at 393 cm^{-1} has been assigned to the Mo–O bending vibration [48]. It is noteworthy that a peak at 820 cm^{-1} , which has been attributed to the asymmetric stretching vibration of the Mo–O–Mo unit [49] was not observed in the spectrum of SGMo-S. This suggests that dimeric molybdenum-containing moieties were not produced during catalyst preparation. The bands at 942 and 913 cm^{-1} associated with the asymmetric and symmetric stretching vibrations of the MoO $_2$ bond [40,50] disappeared after the

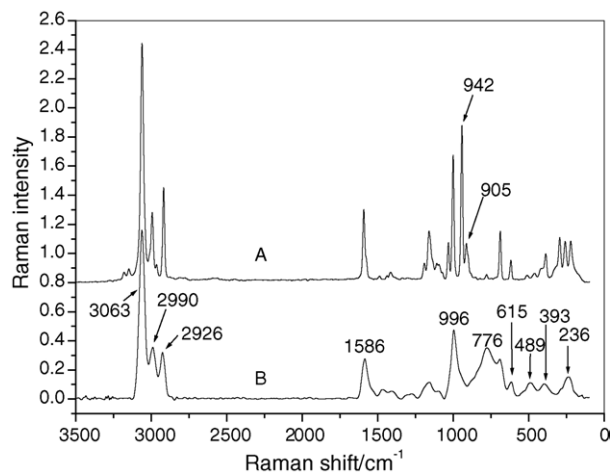


Fig. 5. FT-Raman spectra of: (A) MoO $_2\text{Cl}_2(\text{OPMePh}_2)_2$ and (B) SGMo-S.

homogeneous catalyst was immobilized on the silica however. A band at 996 cm^{-1} is observed in the spectrum of SGMo-S, which can be assigned to the symmetric stretching mode of Mo=O [51] for the silica modified Mo-containing species as has been observed for related materials [47,49,50].

3.2. Proposed reaction pathway to the heterogeneous catalyst

With regard to the possible reaction pathway between MoO $_2\text{Cl}_2(\text{OPMePh}_2)_2$ and TEOS, the following results are observed: (1) most sol–gel reactions involve nucleophilic substitutions based on an S $_N2$ mechanism at Si and hydroxylated species are formed [52,53]; (2) elemental analysis of Cl was conducted by argentometry, which confirms the presence of the chloride ligands; and (3) Mo=O [51] stretching mode is observed in the FT-Raman spectrum of SGMo-S. These results suggested that the heterogenization process might include the oxygen of TEOS initially linking to the molybdenum center with concomitant dissociation of OPMePh $_2$ from the molybdenum center, followed by hydroxylation between TEOS and the molybdenum complex, finally resulting in a molybdenum-containing silica network structure, as depicted in Fig. 6. This is also consistent with the observation of the above spectra.

3.3. Epoxidation of olefins with TBHP as oxidant

SGMo-S was tested as a catalyst for the epoxidation of cyclohexene with $t\text{BuOOH}$ as the oxygen source at a reaction temperature of 55 $^\circ\text{C}$. SGMo-S shows high activity and selectivity to cyclohexene oxide (see Fig. 7). The conversion of the substrate increases, and the selectivity to the epoxide is consistent at around 85%. It can be also seen that the reaction rate decreases as time elapsed.

In order to determine the optimal reaction conditions we investigated the effect of varying the reaction temperature. The kinetic and selectivity profiles for SGMo-S at different

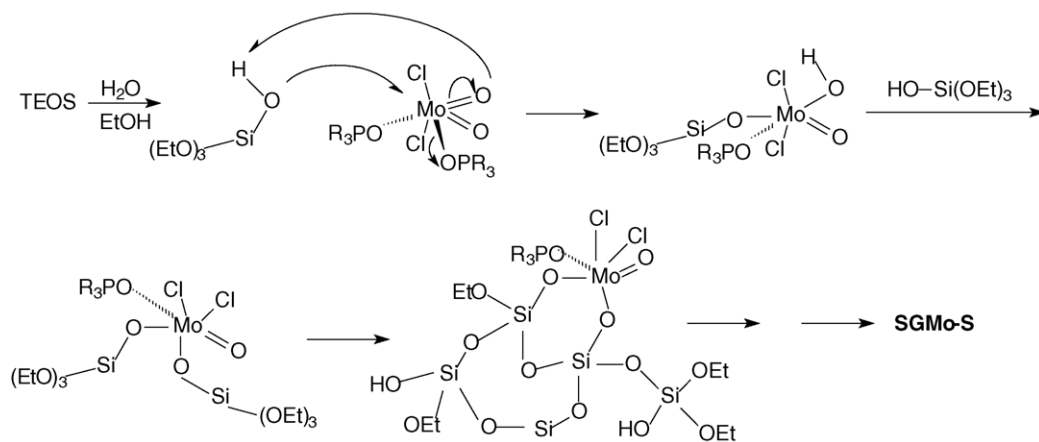
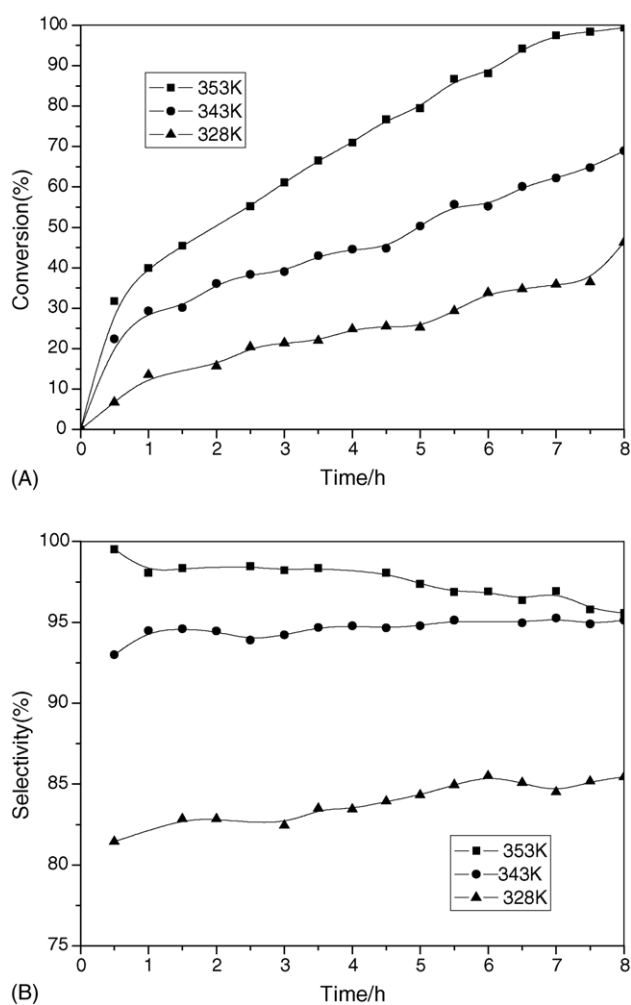
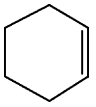
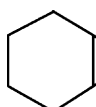
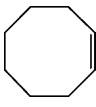
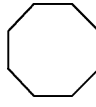
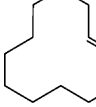
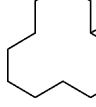
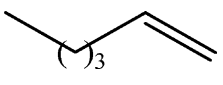
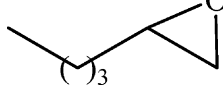
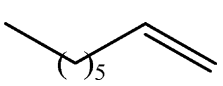
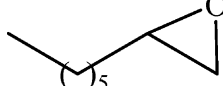
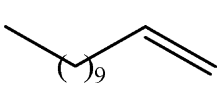
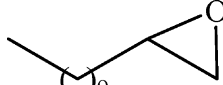
Fig. 6. Suggested reaction pathway between $\text{MoO}_2\text{Cl}_2(\text{OPR}_3)_2$ and TEOS.

Fig. 7. (A) Kinetic and (B) selectivity profiles for the epoxidation of cyclohexene with SGMo-S at different temperature.

temperatures are shown in Fig. 7A and B, respectively. The conversion of cyclohexene increases significantly as the reaction temperature is raised. Interestingly, the selectivity also increases with an increase in reaction temperature. Accord-

ing to GC-MS results, 2-cyclohexen-1-one is the only by-product for all catalytic runs at different temperatures. While the same epoxidation catalyzed by the homogeneous catalyst $\text{MoO}_2\text{Cl}_2(\text{OPMePh}_2)_2$ with $t\text{BOOH}$ quickly reaches the maximum conversion at 83% in an hour and does not proceed further [41].

Table 1
Conversion and selectivity data for epoxidation of representative olefins using SG-Mo catalyst

Olefin	Conversion (%)	Product [selectivity (%)]
	99	 (96)
	99	 (99)
	85	 (99)
	99	 (99)
	77	 (99)
	70	 (100)

Reaction conditions were as follows: reaction time and temperature were 8 h and 80 °C, respectively. Olefin (10 mmol), TBHP (15 mmol), Mo catalyst (3.9×10^{-3} mmol) and *n*-decane (2.5 mmol) as an internal standard for GC-MS analysis.

The catalytic behavior of SGMo-S in the epoxidation of cycloolefins and terminal alkenes was also tested with TBHP as the oxygen source (Table 1). For cycloolefins, similar quantitative olefin conversions within 8 h are observed for cyclohexene and cyclooctene, and somewhat lower conversion for cyclododecene.

The epoxide selectivities for the three cycloolefins are $\geq 96\%$ in each case. The difference in olefin reactivity is presumably due to hindered access of the larger cycloolefin to the active sites of the catalyst. SGMo-S is also active for the epoxidation of terminal alkenes, which are known to be difficult to epoxidize. The reactivities of 1-octene and 1-decene are similar, whilst that of 1-hexene is considerable higher. The epoxide yield increases as the chain length of the olefin decreases and this can also be attributed to less steric hindrance. In all runs the selectivity to the corresponding epoxides is almost 100%. These results clearly indicate the olefin size and the accessibility of the active sites in the heterogeneous catalyst affect the catalytic reactions.

4. Conclusions

FT-IR and UV-vis spectra, etc. confirmed that molybdenum-containing silicates can be prepared via a simple sol-gel process. A possible reaction pathway was proposed based on elemental analysis, ^{31}P MAS NMR and UV-Raman spectroscopy results. Under certain conditions, high catalytic yields and selectivity for the epoxidation of cyclo- and terminal olefins may be obtained. Increasing the reaction temperature is a useful way to increase selectivity.

Acknowledgements

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