

# Synthesis and characterization of a new epoxidation catalyst by grafting *cis*-MoO<sub>2</sub>(salpr) complex to functionalized MCM-41

M. Masteri-Farahani<sup>a</sup>, F. Farzaneh<sup>b,\*</sup>, M. Ghandi<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Tehran, Tehran, Iran

<sup>b</sup> Department of Chemistry, University of Alzahra, Vanak, Tehran, Iran

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## Abstract

The mesoporous molecular sieve MCM-41 was covalently grafted with 3-chloropropyl trimethoxysilane and was then reacted with *N,N*-bis(3-salicylideneaminopropyl)amine (salpr) to afford MCM-41 containing salpr ligand, salpr/Si-MCM-41. Powder X-ray diffraction and nitrogen adsorption–desorption analyses revealed that not only the textural characteristics of the support were preserved during the grafting experiments but also the channels remained accessible despite sequential reduction in surface area, pore volume and pore size. The salpr/Si-MCM-41 material was then reacted with MoO<sub>2</sub>(acac)<sub>2</sub> to give MoO<sub>2</sub>(salpr)/Si-MCM-41 catalyst with molybdenum loading of 1.75 wt.%. The molybdenum-containing MCM-41 was shown to successfully catalyze the epoxidation of 1-hexene, 1-octene, cyclohexene and cyclooctene with tert-butylhydroperoxide (TBHP) quantitatively with 95–99% selectivity toward the corresponding epoxides under mild conditions.

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## 1. Introduction

Studies of catalytic epoxidation reactions as an important area has attracted many research groups during the past years. These have been based on the fact that these compounds are important intermediates either in laboratory researches or in industries for production in huge tonnages. Using soluble compounds of early transition metal compounds such as Mo, W, Ti and V as homogeneous catalysts for olefin epoxidations have been reported previously [1]. The fundamental role of molybdenum-based catalysts for the production of both bulk and fine chemicals has increased the researchers attentions toward this metal [1,2]. Utilization of bis(acetylacetonato)dioxo-molybdenum (VI) and two types of MoO(O<sub>2</sub>)<sub>2</sub>L<sub>1</sub>L<sub>2</sub> and MoO<sub>2</sub>X<sub>2</sub>L<sub>1</sub>L<sub>2</sub> complexes as olefin epoxidation catalysts provide successful examples [3–5]. Dioxomolybdenum (VI) complexes of tetradentate Schiff

bases [6], dichloro and dimethyldioxo Mo (VI) diazabutadiene were reported as active epoxidation catalysts [7].

Despite good results obtained with soluble Mo complexes, many attempts have been made to develop the heterogeneous systems. Grafting Mo compounds to functionalized polymer supports [8,9], preparation of amorphous Mo silicates via sol–gel method [10,11] and incorporation of Mo in the framework of silicalite are examples in this regard [12]. Micelle-templated inorganic oxides of silica and alumina have emerged in the past decade as very promising support materials owing to their unique textural properties (high surface area, pore volume and narrow pore size distribution) [13–17]. Jia and Thiel modified the micelle-templated silica MCM-41 with a bidentate pyrazolopyridine ligand and prepared a covalently anchored complex of MoO(O<sub>2</sub>)(L-L) types [18,19]. It was found that this hybrid catalyst was active for epoxidation of cyclooctene. Mo complexes of MoO<sub>2</sub>Cl<sub>2</sub>(L<sub>1</sub>)(L<sub>2</sub>) type have also been immobilized within MCM-41 functionalized with monodentate nitrile and bidentate bipyridyl ligands [20,21]. Moreover, functionalization of

\* Corresponding author. Tel.: +98 21 88258977; fax: +98 21 66404848.  
E-mail address: [faezeh\\_farzaneh@yahoo.com](mailto:faezeh_farzaneh@yahoo.com) (F. Farzaneh).

MCM-41 and MCM-48 with a bidentate 1,4-diazabutadiene ligand and complexation with molybdenum resulted in a more stable catalyst for olefin epoxidation [22].

In this study, we have attempted to prepare and characterize a new stable and recyclable heterogeneous catalyst of molybdenum with covalent attachment of a tetradentate Schiff base ligand, salpr, to MCM-41 and subsequent complexation of  $\text{MoO}_2(\text{acac})_2$  with supported ligand for epoxidation of olefins.

## 2. Experimental

### 2.1. Preparation of catalyst

#### 2.1.1. Preparation of MCM-41 and chloropropyl modified MCM-41 (Clp/Si-MCM-41)

Mesoporous molecular sieve MCM-41 was prepared according to reported method [23]. Modification of the prepared MCM-41 was performed as followed: MCM-41 (4 g) was suspended in dry toluene (70 ml) and then chloropropyl trimethoxysilane (4 g, Merck) was added under dry nitrogen atmosphere and the mixture was refluxed for 6 h. The solid was filtered, washed with dichloromethane and ethanol and dried. It was then Soxhlet extracted with a mixture of ethanol and dichloromethane (1:1) to remove the silylating reagent residue and was vacuum dried at 473 K. Characterization of Clp/Si-MCM-41 was performed using FT-IR spectroscopy and X-ray diffraction.

#### 2.1.2. Preparation of salpr/Si-MCM-41

The salpr ligand was prepared according to the reported method [24]. For preparation of salpr modified MCM-41 [25], Clp/Si-MCM-41 (2 g) was suspended in 90 ml of benzene and to this mixture was added excess of salpr ligand (1 g, 3.2 mmol) and triethylamine (0.5 ml) and refluxed for 12 h. The solid was filtered, dried and then Soxhlet extracted with ethanol and dried under vacuum at 473 K. The prepared salpr/Si-MCM-41 material was characterized with FT-IR spectroscopy and BET nitrogen sorption studies.

#### 2.1.3. Preparation of $\text{MoO}_2(\text{salpr})/\text{Si-MCM-41}$

For preparation of  $\text{MoO}_2(\text{salpr})$  modified MCM-41 ( $\text{MoO}_2(\text{salpr})/\text{Si-MCM-41}$ ), excess  $\text{MoO}_2(\text{acac})_2$  (500 mg, 1.5 mmol) prepared according to the literature method [26], was dissolved in ethanol (50 ml). salpr/Si-MCM-41 (1 g, dried in vacuum oven at 473 K) was then added to this solution and the mixture was refluxed for 12 h. After filtration, the product was dried and then Soxhlet extracted with a mixture of dichloromethane and ethanol (1:1) to remove unreacted  $\text{MoO}_2(\text{acac})_2$ .  $\text{MoO}_2(\text{salpr})/\text{Si-MCM-41}$  was then dried under vacuum at 473 K and characterized with FT-IR spectroscopy, X-ray diffraction and BET nitrogen sorption studies.

### 2.2. Instrumentation

Infrared spectra were recorded using Shimadzu 4300 FT-IR spectrometer. Powder X-ray diffraction (XRD) data were collected with a SIEFERT XRD 3003 PTS diffractometer using  $\text{Cu K}\alpha$  radiation. Chemical analysis of samples was carried out with Perkin-Elmer atomic absorption spectrometer. Nitrogen sorption studies were performed at liquid nitrogen temperature using Quantachrome Nova 2200, Version 7.11 Analyzer.

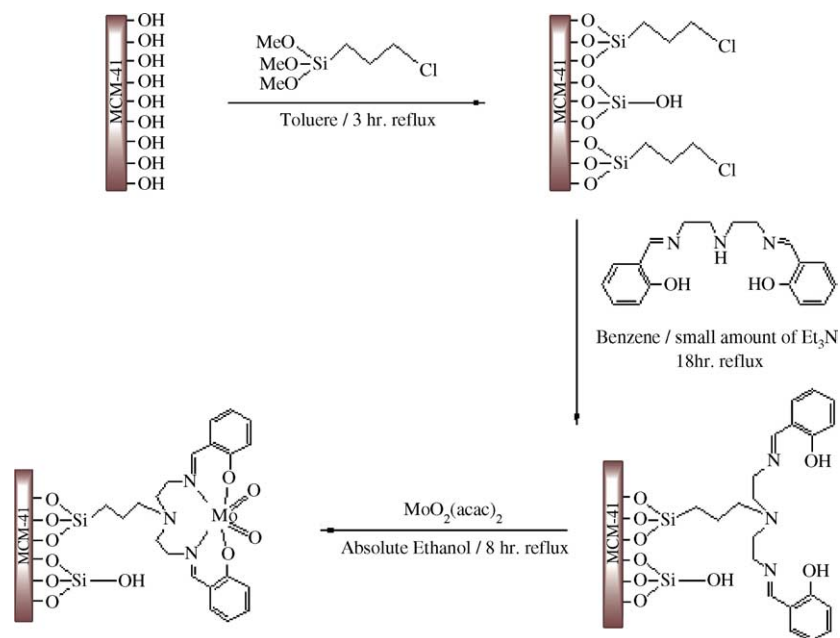
### 2.3. Catalytic epoxidation

Epoxidation of olefins such as cyclohexene, cyclooctene, 1-hexene and 1-octene purchased from Merck was carried out in a 25 ml round-bottomed flask equipped with a condenser and a magnetic stirrer. *Tert*-butylhydroperoxide (TBHP) (obtained from Merck as 80% in di-tertiary butyl peroxide) was used as oxidant. In a typical procedure, to a mixture of catalyst (200 mg) and olefin (8 mmol) in chloroform (20 ml) was added TBHP (1.6 ml, 14.4 mmol) under nitrogen atmosphere and the mixture was refluxed for appropriate time. Samples were withdrawn periodically and after dilution with chloroform and cooling were analyzed using a gas chromatograph (HP, Agilent 68909N) equipped with a capillary column (HP-5) and a FID detector. Products were quantified using isooctane (1 g, 8.75 mmol, Merck) as internal standard. GC-MS of products were recorded using a Shimadzu-14A fitted with a capillary column (CBP5-M25). The molybdenum content of recycled catalyst was measured with above mentioned atomic absorption spectrometer after dissolution of the solid in hydrogen fluoride solution.

## 3. Results and discussions

### 3.1. Preparation of the catalyst

The catalyst was prepared using the standard reaction for the surface modification of mesoporous materials i.e. reaction of surface silanol groups of MCM-41 with alkoxy silanes (in this work, chloropropyl trimethoxysilane) and subsequent reaction with chelate ligand, salpr. In this reaction, the chloro group of Si-MCM-41 is replaced with the secondary amine group of salpr ligand. The ligand supported MCM-41 then reacts with  $\text{MoO}_2(\text{acac})_2$  to afford a heterogenized homogeneous catalyst i.e.  $\text{MoO}_2(\text{salpr})/\text{Si-MCM-41}$  (Scheme 1). That the multidentate schiff base, salpr, was bound to the surface of modified MCM-41 was confirmed by FT-IR spectroscopy and nitrogen sorption studies. In the FT-IR spectrum of  $\text{MoO}_2(\text{salpr})/\text{Si-MCM-41}$  (Fig. 1(a)), a new band at  $1635\text{ cm}^{-1}$  is assigned to C=N stretching vibration of salpr ligand [24], and some weak bands at  $1400\text{--}1500\text{ cm}^{-1}$  belong to stretching vibrations of aromatic rings which are not observed in either MCM-41 or Si-MCM-41. Upon reaction of salpr



Scheme 1. Schematic illustration of  $\text{MoO}_2(\text{salpr})/\text{Si-MCM-41}$  preparation in three steps.

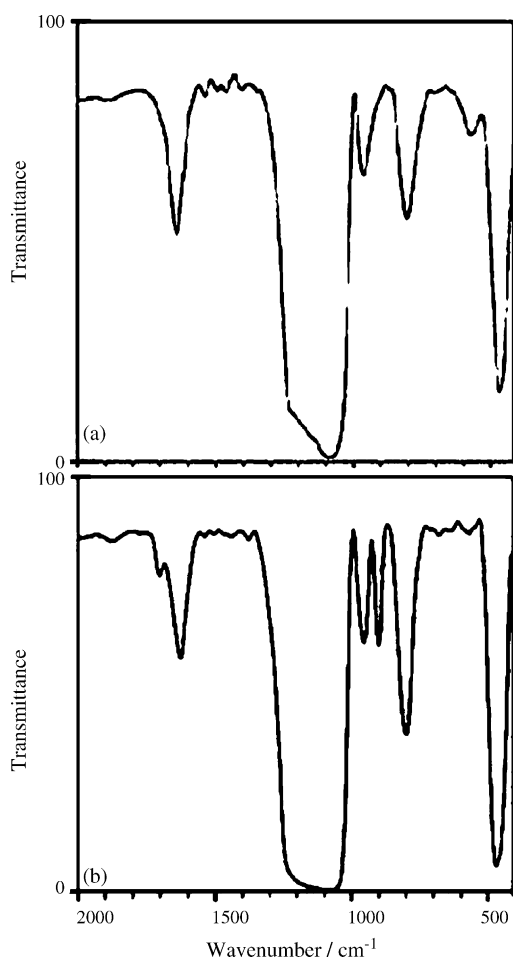


Fig. 1. FT-IR spectra of: (a)  $\text{salpr}/\text{Si-MCM-41}$  and (b)  $\text{MoO}_2(\text{salpr})/\text{Si-MCM-41}$ .

ligand with  $\text{MoO}_2(\text{acac})_2$ , the band located at  $1635\text{ cm}^{-1}$  is shifted to lower frequency ( $1620\text{ cm}^{-1}$ ) (Fig. 1(b)) indicating complexation of C=N group of supported ligand with molybdenum. The appearance of two adjacent bands at  $902$  and  $947\text{ cm}^{-1}$  in the FT-IR spectrum of complexed material is also characteristics of the presence of *cis*- $\text{MoO}_2$  group [27] and formation of  $\text{MoO}_2\text{-salpr}/\text{Si-MCM-41}$  material. Atomic absorption spectroscopy showed 1.75 wt.% of molybdenum in the  $\text{MoO}_2\text{-salpr}/\text{Si-MCM-41}$  catalyst. This quantity was obtained after 24 h soxhlet extraction of product obtained from reaction of  $\text{MoO}_2(\text{acac})_2$  with  $\text{salpr}/\text{Si-MCM-41}$ . Thus any impregnated molybdenum in this material is negligible.

### 3.2. X-ray diffraction studies

Textural properties of resulted molybdenum catalyst were investigated with XRD. X-ray diffraction patterns of prepared MCM-41, Clp-MCM-41 and  $\text{MoO}_2\text{-salpr}/\text{Si-MCM-41}$  are presented in Fig. 2(a)–(c). X-ray diffraction pattern of unmodified MCM-41 (Fig. 2(a)) consists of a strong reflection at  $2\theta = 2.71^\circ$  assigned to the 100 reflection and three weaker reflection at higher angles that can be assigned to the 110, 200 and 210 reflections of a hexagonal unit cell. The hexagonal unit cell parameter,  $a_0$  (or lattice parameter), a measure of spacing between the hexagonal layers is calculated as the  $d_{100}(2/\sqrt{3})$ . For the unmodified MCM-41, this parameter is  $37.6\text{ \AA}$  (Table 1). The XRD pattern for the chloropropyl modified MCM-41 (Fig. 2(b)) also shows the strong (100) reflection as well as two weak reflections (110 and 200) at higher angles. Compared to MCM-41, the intensities of peaks decrease and shift to lower angles (higher  $d$ -values). The lattice parameter for this material is  $38.06\text{ \AA}$

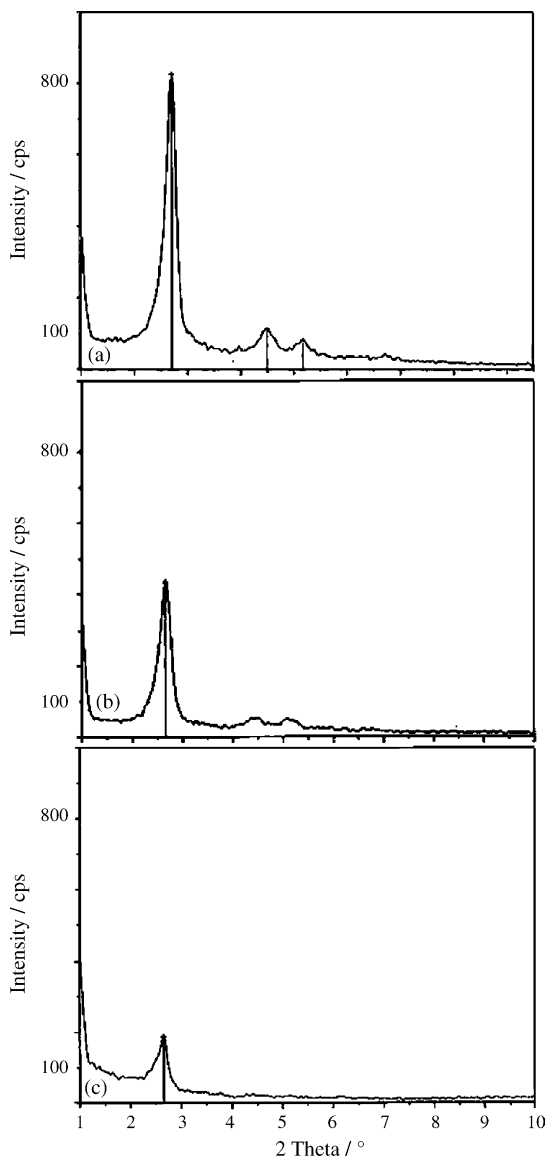


Fig. 2. X-ray diffraction pattern: (a) MCM-41, (b) Clp/Si-MCM-41 and (c) MoO<sub>2</sub>(salpr)/Si-MCM-41.

(Table 1) and increases with respect to MCM-41 indicating expansion of unit cell due to incorporation of chloropropyl groups within MCM-41. In the XRD pattern of supported molybdenum catalyst, MoO<sub>2</sub>-salpr/Si-MCM-41 (Fig. 2(c)), the 100 reflection is only present and shifts to lower angle (or higher *d*-value). The lattice parameter for this material is 38.3 Å (Table 1) and increases with respect to MCM-41 and ClpMCM-41 due to the incorporation of bulky group MoO<sub>2</sub>-

Table 1  
Texture parameters of samples taken from XRD studies

Solid	2θ (°)	<i>d</i> -Value (Å)	Lattice parameter (Å) <sup>a</sup>
MCM-41	2.71	32.57	37.61
ClpMCM-41	2.68	33	38.06
MoO <sub>2</sub> -(salpr)/Si-MCM-41	2.66	33.17	38.30

<sup>a</sup> Determined by equation:  $a_0 = d_{100}(2/\sqrt{3})$ .

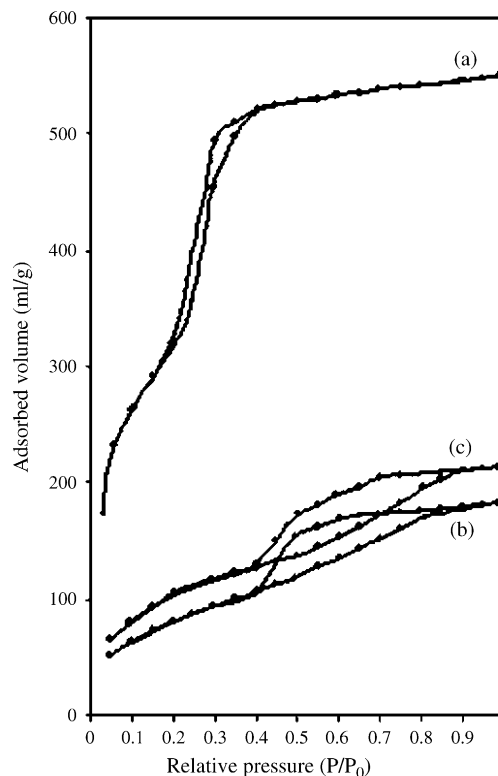


Fig. 3. Nitrogen sorption isotherm of: (a) MCM-41, (b) salpr/Si-MCM-41 (c) MoO<sub>2</sub>(salpr)/Si-MCM-41.

salpr and expansion of unit cell. Lower intensity of the peak 100 for MoO<sub>2</sub>-salpr/Si-MCM-41 is likely due to decrease of surface uniformity in this material with respect to MCM-41 and Si-MCM-41.

### 3.3. Nitrogen sorption studies

Nitrogen sorption isotherms of MCM-41, salpr/Si-MCM-41 and MoO<sub>2</sub>-salpr/Si-MCM-41 are shown in Fig. 3(a)–(c). These materials all show the type IV isotherms in the IUPAC classification with the appearance of hysteresis loop resulted from capillary condensation of nitrogen gas in mesopores. For unmodified MCM-41, the step corresponding to capillary condensation appears in the relative pressure ranges 0.2–0.4 (Fig. 3(a)). The specific surface area and total pore volume of prepared MCM-41 are 1211 m<sup>2</sup> g<sup>-1</sup> and 0.852 cm<sup>3</sup> g<sup>-1</sup>, respectively (Table 2). The isotherms of salpr/Si-MCM-41 and MoO<sub>2</sub>-salpr/Si-MCM-41 (Fig. 3(b) and (c)) show a lower

Table 2  
Texture parameters of samples taken from nitrogen sorption studies

Solid	BET specific surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (ml g <sup>-1</sup> )	Average pore diameter (Å)
MCM-41	1211	0.851	28.2
Salpr/Si-MCM-41	305.2	0.183	24
MoO <sub>2</sub> (salpr)/Si-MCM-41	385	0.214	22.2

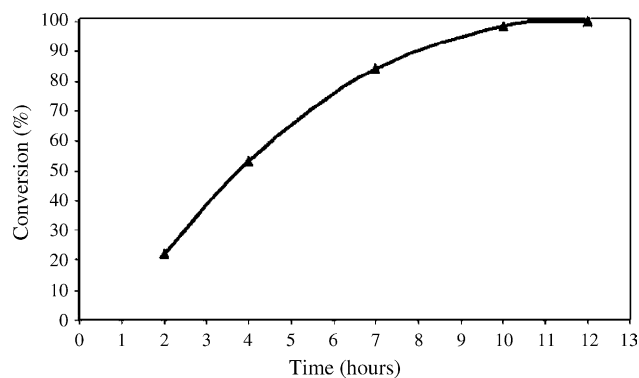


Fig. 4. Plot of cyclooctene conversion vs. reaction time.

nitrogen uptake pointing out to a decrease of specific surface area and pore volume (Table 2) due to incorporation of salpr and MoO<sub>2</sub>-salpr group in MCM-41. An interesting object in comparing BET results of salpr/Si-MCM-41 and MoO<sub>2</sub>-salpr/Si-MCM-41 is that the surface area of MoO<sub>2</sub>-salpr/Si-MCM-41 is higher than salpr/Si-MCM-41 (Table 2). This is explained with contraction of aromatic arms of salpr ligands due to complexation of salpr/Si-MCM-41 with molybdenum (Scheme 1). We also observed a broader hysteresis loops for these materials (Fig. 3(b) and (c)) with respect to MCM-41 because of a probable decrease of uniformity in pore size.

### 3.4. Catalytic activity

The catalytic activity of the prepared MoO<sub>2</sub>-salpr/Si-MCM-41 was evaluated through epoxidation of the aforementioned olefins. The optimum reaction time for cyclooctene was obtained from the study of olefin conversion percentage at different times (Fig. 4). 1-Octene and 1-hexene oxidations were carried out at twenty hours in order to obtain similar conversion percentages. The con-

Table 3

Results of epoxidations of some olefins with TBHP in the presence of MoO<sub>2</sub>(salpr)/Si-MCM-41

Olefin	Time (h)	Conversion (%) <sup>a</sup>	Selectivity (%) <sup>b</sup>	TOF <sup>c</sup>
Cyclooctene	12	99	99	59
Cyclohexene	12	95	99	53
1-Octene	20	90	98	20
1-Hexene	20	70	99	16
Cyclooctene <sup>d</sup>	12	93	99	55
Cyclooctene <sup>e</sup>	12	14	41	–
Cyclooctene <sup>f</sup>	12	21	51	–

<sup>a</sup> Calculated with use of isooctane as internal standard.

<sup>b</sup> Selectivity toward the formation of epoxide.

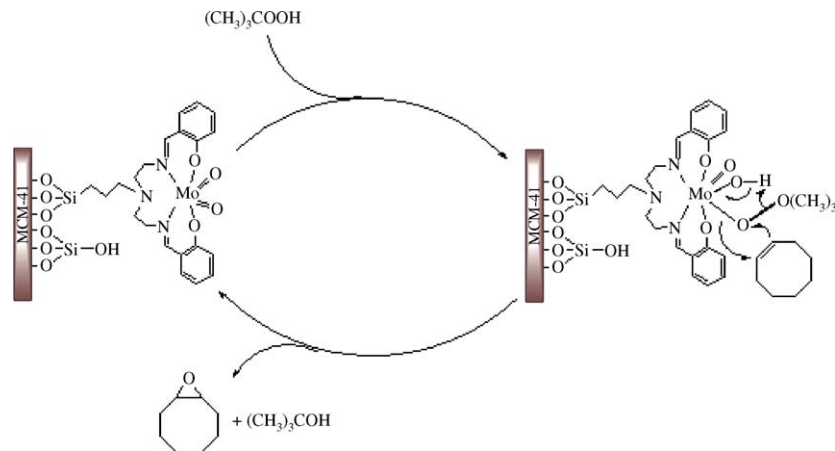
<sup>c</sup> Turn over frequency: mmol product per mmol metal per hour, calculated at the initial 4 h of reactions except for the linear olefins (20 h reaction).

<sup>d</sup> Catalytic test with recycled catalyst.

<sup>e</sup> Reaction was carried out without catalyst.

<sup>f</sup> Reaction was carried out in the presence of MCM-41.

versions and selectivities as well as turnover frequencies (TOFs) (mmol of product formed per mmol of molybdenum in catalyst) are given in Table 3. We have included the tests with blank (without catalyst) and MCM-41 (without complex) in Table 3, in order to make the comparison more convenient. As seen, the conversion percentages of cyclooctene has drastically increase from 14 (blank) and 21 (MCM-41) to 99 in the presence of MoO<sub>2</sub>(salpr)/Si-MCM-41 catalyst. It is evident that compared to linear olefins, cyclohexene and cyclooctene show higher reactivity and TOF although similar selectivities toward the corresponding epoxides are obtained. The different behavior between linear and cyclic alkenes might be inferred if one considers the reaction mechanism. On the basis of our previously reported mechanism [12], epoxidation of cyclohexene and *trans*-2-hexene-1-ol with TBHP catalyzed by molybdenum-incorporated silicalite proceed through the peroxo intermediate and concerted oxygen atom transfer to the olefin [7,28]. Based on the experimental and theoretical investigations reported very recently, epoxidation of some olefins in the presence of



Scheme 2. Mechanism of epoxidation of cyclooctene with TBHP in presence of MoO<sub>2</sub>(salpr)/MCM-41.

bis(halogeno)dioxomolybdenum(VI)–diimine complexes as catalyst was indicated to involve the transfer of a TBHP proton to the terminal oxygen atom of one of the MoO groups and coordination of t-BuOO<sup>-</sup> to the Lewis acidic metal center and formation of the peroxy intermediate in the first step [28]. With the similar mechanism depicted in Scheme 2, it can be seen that the approach of either cyclohexene or cyclooctene to the catalyst center take place faster with respect to the linear 1-hexene and 1-octene olefins with terminal double bonds since in cyclic olefins, the internal double bonds located between secondary carbons enjoy richer electron densities. Moreover, while the *cis*-double bond either in cyclohexene or cyclooctene bears bonds consisting of CH<sub>2</sub> groups and therefore feels less steric crowding in approaching to metal center, the 1-hexene and 1-octene with alkyl chain in the vicinity of double bond suffer more steric repulsion near the oxidation center.

The stability of the MoO<sub>2</sub>-salpr/Si-MCM-41 catalyst was studied by recycling the recovered catalyst and determination of metal content using atomic absorption spectroscopy. The molybdenum content of recovered catalyst was shown to be 1.73 wt.% with little change with respect to initial catalyst. The recovered catalyst was used again in epoxidation of cyclooctene with TBHP. As shown in the last entry of Table 3, minor decrease in conversion and TOF percentages were observed although selectivity remains unchanged. With this result and observation of no desorption, the presence of affixed Mo complex within MCM-41 is confirmed. It can be concluded that the catalytic epoxidation is truly heterogeneous in nature.

#### 4. Conclusion

Our work has revealed that incorporation of a multidentate schiff base ligand such as salpr within the large pores of mesoporous material Si-MCM-41 and subsequent treatment with MoO<sub>2</sub>(acac)<sub>2</sub> affords a new highly stable and heterogeneous molybdenum catalyst for epoxidation of olefins with high turnover frequencies and selectivities.

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#### References

- [1] K.A. Jorgensen, Chem. Rev. 89 (1989) 431.
- [2] B.S. Lane, K. Burgess, Chem. Rev. 103 (2003) 2457.
- [3] E.P. Talsi, K.V. Shalyaev, K.I. Zamaraev, J. Mol. Catal. A 83 (1993) 347.
- [4] R.H. Holm, Chem. Rev. 87 (1987) 1401.
- [5] N. Indictor, W.F. Brill, J. Org. Chem. 29 (1965) 2075.
- [6] K. Ambroziak, R. Pelech, E. Milchent, T. Dziembowska, Z. Rozwadowski, J. Mol. Catal. A 211 (2000) 9.
- [7] A.A. Valente, J. Moreira, A.D. Lopes, I.S. Goncalves, New. J. Chem. 28 (2004) 308.
- [8] St. Kotov, St. Boneva, T.S. Kolev, J. Mol. Catal. A 154 (2000) 121.
- [9] P. Reyes, G. Borda, J. Gnecco, B.L. Rivas, J. Appl. Polym. Sci. 93 (2004) 1602.
- [10] R. Neumann, M. Levin-Elad, J. Catal. 166 (1997) 206.
- [11] U. Arnold, R. Serpa da cruz, D. Madelli, J. Mol. Catal. A 165 (2001) 149.
- [12] M. Masteri-Farahani, F. Farzaneh, M. Ghandi, J. Mol. Catal. A 192 (2003) 103.
- [13] D.E. De Vos, M. Dams, B.F. Sels, P.A. Jacobs, Chem. Rev. 102 (2002) 3615.
- [14] A. Anwander, Chem. Mater. 13 (2001) 44191.
- [15] M.H. Valkenberg, W.F. Holderich, Catal. Rev. 44 (2002) 321.
- [16] A. Taguchi, F. Schuth, Micropor. Mesopor. Mater. 77 (2004) 1.
- [17] P. Mc Morn, G.J. Hutching, Chem. Soc. Rev. 33 (2004) 108.
- [18] M. Jia, W.R. Thiel, Chem. Commun. (2002) 2392.
- [19] M. Jia, A. Siefert, W.R. Thiel, Chem. Mater. 15 (2003) 2174.
- [20] C.D. Nones, M. Pillinger, A. Valente, I.S. Goncalves, J. Mater. Chem. 12 (2002) 1735.
- [21] C.D. Nones, M. Pillinger, A. Valente, I.S. Goncalves, Eur. J. Inorg. Chem. (2003) 3870.
- [22] C.D. Nones, M. Pillinger, A. Valente, I.S. Goncalves, Inorg. Chem. Commun. 6 (2003) 1228.
- [23] Q. Cai, W.Y. Lin, F.S. Xiao, W.Q. Pang, J. Micropor. Mesopor. Mater. 32 (1999) 1.
- [24] W.M. Coleman, L.T. Taylor, Inorg. Chem. 10 (1971) 2195.
- [25] P. Sutra, D. Brunel, Chem. Commun. (1996) 2485.
- [26] G.J. Chen, J.W. Mc Donald, W.E. Newton, Inorg. Chem. 15 (1976) 2612.
- [27] J. Topich, Inorg. Chem. 20 (1981) 3704.
- [28] R.A. Sheldon, J. Van doorn, J. Catal. 31 (1973) 427.