

## MoO<sub>2</sub>(acac)<sub>2</sub> Supported on MCM-41: An Efficient and Reusable Catalyst for Alkene Epoxidation with *tert*-BuOOH

S. Tangestaninejad\*, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork, K. Ghani  
*Department of Chemistry, Catalysis Division, University of Isfahan, Isfahan, Iran*

(Received 12 December 2007, Accepted 9 February 2008)

This paper is dedicated to Professor H. Firouzabadi on the occasion of his 65<sup>th</sup> birthday and his honorable retirement

A new heterogeneous catalyst prepared by immobilization of MoO<sub>2</sub>(acac)<sub>2</sub> on Mobil Catalytic Material, MCM-41, is reported. This catalyst, MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41, was successfully applied for efficient epoxidation of olefins with *tert*-BuOOH in 1,2-dichloroethane as solvent. The catalyst was characterized by elemental analysis, FT-IR, UV-Vis, X-ray diffraction (XRD), and scanning electron microscopy (SEM). This catalyst can be reused several times without significant loss of its catalytic activity.

**Keywords:** Supported catalyst, Epoxidation, Molybdenyl acetylacetonate, MCM-41.

---

### INTRODUCTION

Catalytic olefin epoxidation in the liquid phase is an important topic for the synthesis of fine chemicals [1], because epoxides are valuable intermediates in organic laboratories and in industries for production of various chemicals such as polyethers, diols and aminoalcohols. Many soluble metal salts or complexes have been found to be active catalysts in this reaction during the last few decades. The application of soluble compounds of early transition metals such as Mo, W, Ti and V, as homogeneous catalysts for olefin epoxidation, has been recently reported [2]. Among the molybdenum complexes, oxomolybdenum species have been particularly investigated because of their good catalytic activity for selective oxidation [3,4].

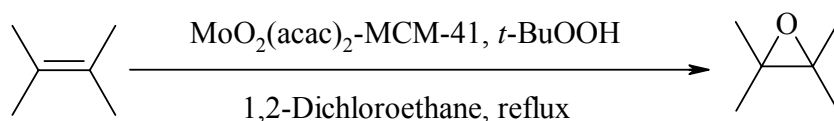
Reusable heterogeneous catalysts have attracted a great deal of interest in organic laboratories and industries [5]. Since

most of the catalysts are expensive and/or contaminate the environment, the development of efficient methods for recovery and reuse of the catalysts is a very important aspect in chemistry. An easy solution to this problem is to heterogenize the homogeneous catalysts by supporting them on solid materials. The major advantages of solid-supported catalysts are the facile recovery from the reaction mixture and possibility of reusing them. Furthermore, supporting of the catalysts efficiently increases their surface area and consequently improves their catalytic activity. Different approaches have been used in order to obtain heterogeneous molybdenum catalysis for olefin epoxidation.

In recent years, functionalized polymers and inorganic supports have been used for immobilization of the homogeneous catalysts. Sherrington group has synthesized polystyrene, polymethacrylate, polybenzimidazole and polysiloxane resins for immobilization of Mo(VI) catalysts and investigated their catalytic activity in the alkene epoxidation with *tert*-butylhydroperoxide [6-11]. Recently, we showed that molybdenum hexacarbonyl immobilized on

---

\*Corresponding author. E-mail: stanges@sci.ui.ac.ir



**Scheme 1.** Alkene epoxidation with *tert*-BuOOH catalyzed by MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41

functionalized polystyrene could be employed as an active and highly reusable catalyst for alkene epoxidation with *tert*-BuOOH [12-14]. However, compared to organic supports, inorganic ones do not swell or dissolve in organic solvents, and show better thermal and mechanical stabilities. Molybdenum compounds immobilized on functionalized inorganic supports via various mono- or bidentate-ligands have been reported for epoxidation of alkenes [15-19].

Here, we describe the immobilization of MoO<sub>2</sub>(acac)<sub>2</sub> on Mobil Catalytic Material (MCM-41), MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41, via acetylacetonate linkage and investigation of its catalytic activity in the epoxidation of alkenes with *tert*-BuOOH (Scheme 1).

## EXPERIMENTAL

All materials were commercial reagent grade and obtained from Merck and Fluka. Elemental analysis was performed on a Perkin-Elmer 2400 instrument. Atomic absorption spectrometric analyses were carried out on a Shimadzu 120 spectrophotometer. Diffuse reflectance UV-Vis (DR-UV-Vis) spectra were recorded on a Shimadzu UV-265 instrument using optical grade BaSO<sub>4</sub> as reference. FT-IR spectra were obtained as potassium bromide pellets in the range 400-4000 cm<sup>-1</sup> with a Nicolet-Impact 400D instrument. Scanning electron micrographs of the catalyst and support were taken on SEM Philips XL 30. Powder X-ray diffraction data were obtained on a D<sub>8</sub> Advanced Bruker using Cu K $\alpha$  radiation. Gas chromatography experiments (GC) were performed with a Shimadzu GC-16A instrument using a 2 m column peaked with silicon DC-200 or Carbowax 20m. <sup>1</sup>H NMR spectra were recorded on a Bruker-Arance AQS 300 MHz. Conversions and yields were obtained by GC experiments and the products were identified after isolation and purification. MCM-41 was prepared according to literature [20].

### Preparation of chloropropylated MCM-41 Mesoporous molecular sieve

MCM-41 (2.0 g) was treated with 3-chloropropyltri(methoxysilane), Cl(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>, (20 ml)

in toluene (40 ml). The mixture was stirred under reflux for 24 h. Then, the solution was filtered and the solids were washed with dichloromethane and dried under vacuum for several hours at room temperature.

### Functionalization of chloropropylated MCM-41 with acetylacetone

To a mixture of chloropropylated MCM-41 (2.0 g) in DMF (40 ml), were added sodium acetylacetonate monohydrate (1.0 g) and sodium iodide (0.1 g), and the mixture was stirred at 80 °C for 24 h. The solid was filtered, washed with methanol and dried under vacuum.

### Immobilization of MoO<sub>2</sub>(acac)<sub>2</sub> on chloropropylated MCM-41 functionalized with acetylacetone

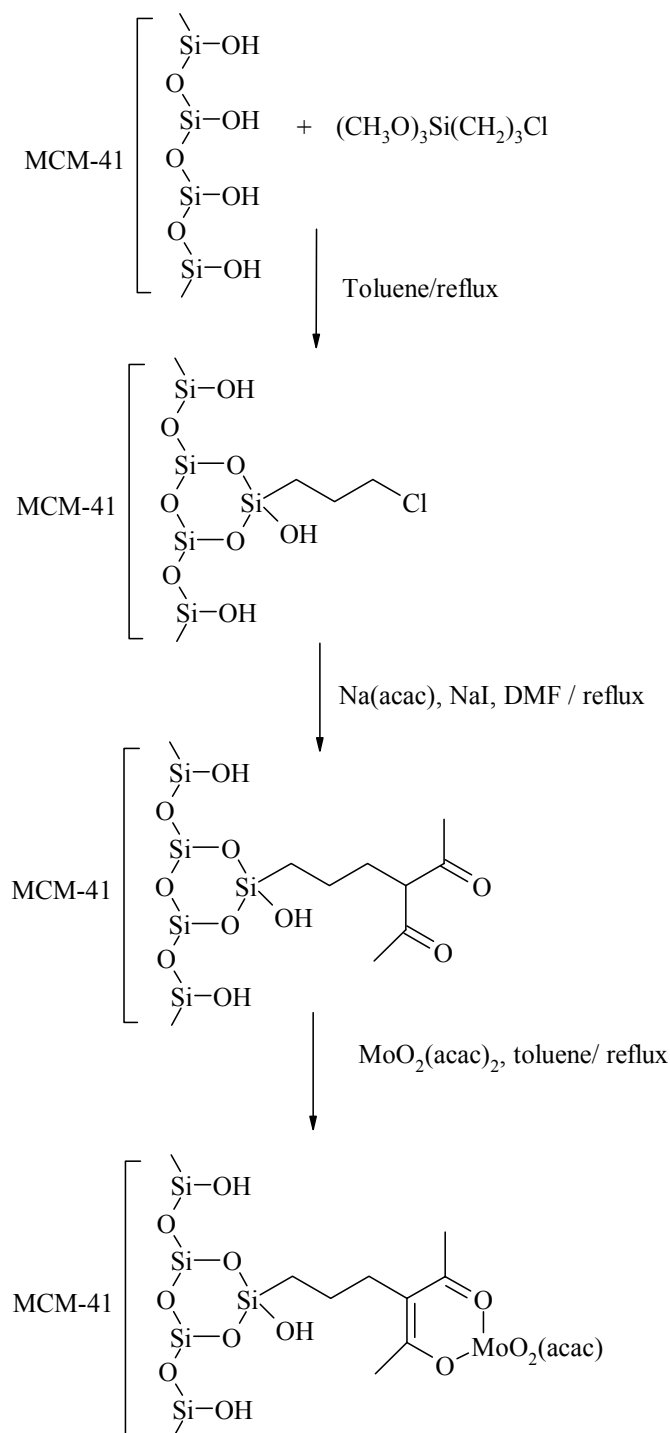
MoO<sub>2</sub>(acac)<sub>2</sub> was synthesized according to the published procedure [21]. A mixture of MoO<sub>2</sub>(acac)<sub>2</sub> (3.0 g) and acetylacetonated MCM-41 (2.0 g) in toluene (100 ml) was heated under reflux for 4 days. The beads were isolated by filtration, washed with toluene and acetone, successively, and dried under vacuum at 40 °C.

### General procedure for epoxidation of alkenes

To a 25 ml round bottom flask equipped with a magnetic stirring bar were added 3 ml 1,2-dichloroethane, 0.5 mmol alkene, 1 mmol *tert*-BuOOH and 0.030 g catalyst, and the reaction mixture was refluxed under stirring. The reaction progress was monitored by GLC. The reaction mixture was diluted with Et<sub>2</sub>O (20 ml) and filtered. The catalyst was thoroughly washed with Et<sub>2</sub>O and the filtrates were purified on a silica-gel plate or a silica-gel column. IR and <sup>1</sup>H NMR spectral data confirmed the identities of the products. Blank experiment was performed in the presence of the oxidant and absence of the catalyst using the same experimental conditions.

### Reusability of the catalyst

The reusability of the catalyst was studied in repeated epoxidation reaction of *cis*-cyclooctene. The reactions were



**Scheme 2.** Preparation of MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41

carried out as described above. At the end of each reaction, the mixture was filtered, and the catalyst washed with 3×5 ml Et<sub>2</sub>O, dried in an oven at 60 °C and reused.

## RESULTS AND DISCUSSION

### Preparation and characterization of MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41

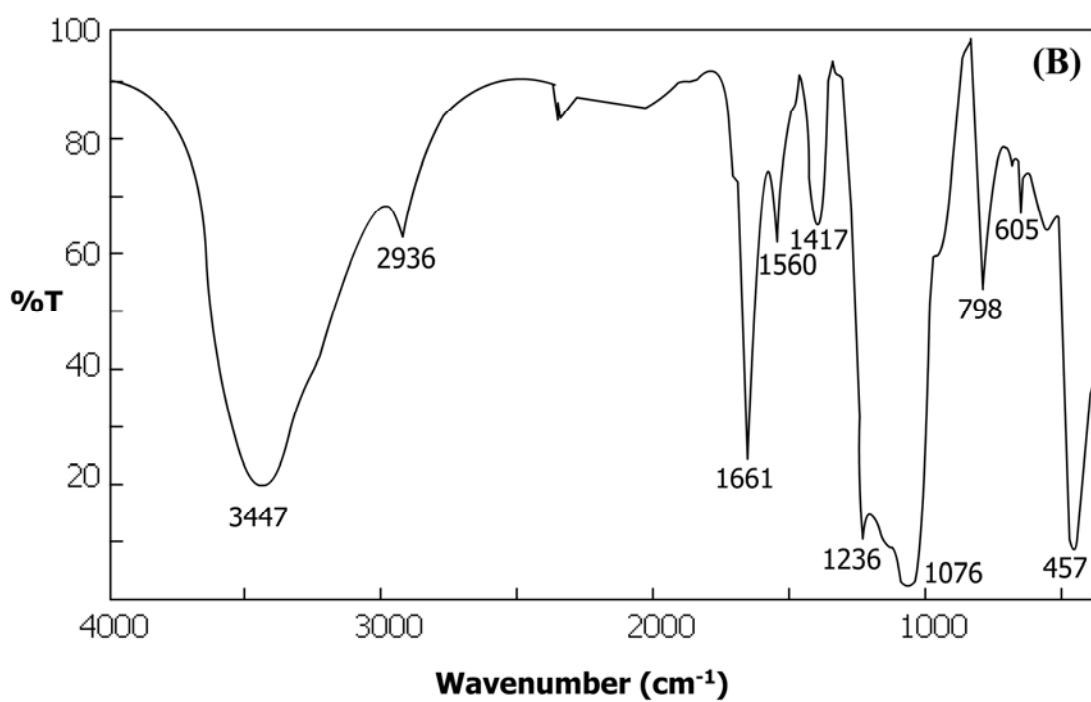
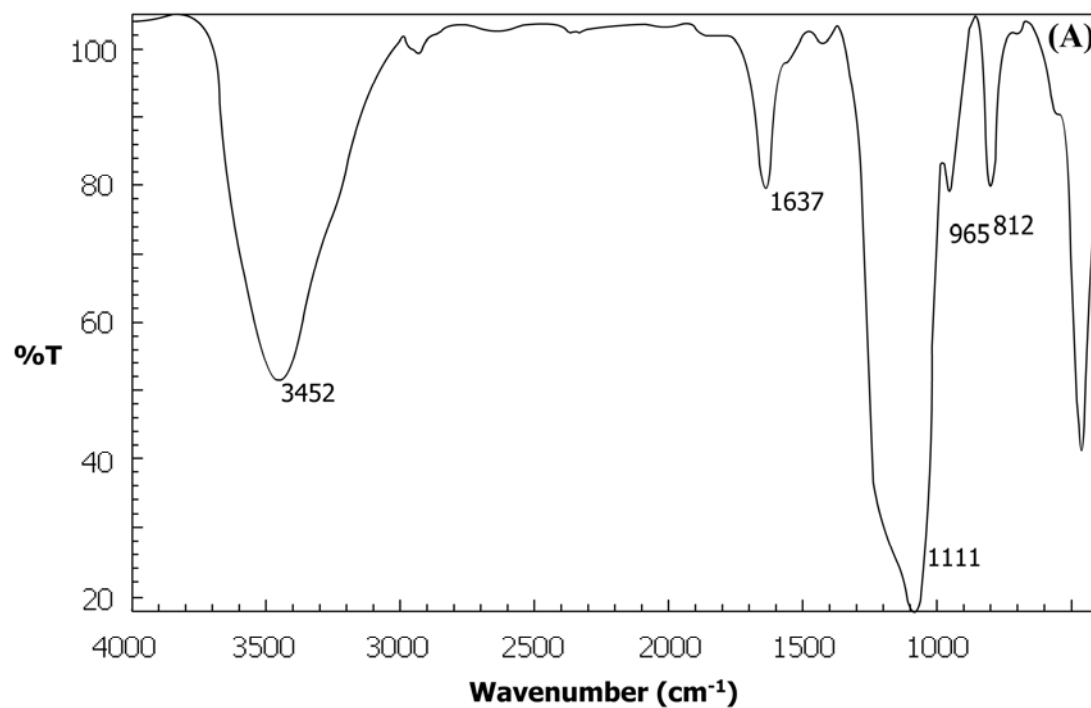
Scheme 2 shows the preparation procedure of MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41 catalyst. The catalyst was prepared using the known procedures for the surface modification of MCM-41. Chloropropyltrimethoxysilane reacts with MCM-41 surface silanol groups to afford the chloropropylated MCM-41. Subsequent reaction of this chloropropylated MCM-41 with sodium acetylacetonate in the presence of catalytic amount of NaI produced the acetylacetonated MCM-41, which was used as a support for MoO<sub>2</sub>(acac)<sub>2</sub>. Direct ligand exchange of acetylacetonated MCM-41 with MoO<sub>2</sub>(acac)<sub>2</sub> yielded the supported MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41 catalyst.

MCM-41 was characterized by FT-IR spectroscopy, diffuse reflectance UV-Vis spectroscopy (DR UV-Vis), X-Ray diffraction (XRD) and scanning electron microscopy (SEM). The FT-IR spectrum of MCM-41 is shown in Fig. 1A. When this compound was acetylacetonated, the C=O stretching vibration of acetylacetonate ligand was observed at 1661 cm<sup>-1</sup> (Fig. 1B). After treatment of acetylacetonated MCM-41 with MoO<sub>2</sub>(acac)<sub>2</sub>, this band at 1661 cm<sup>-1</sup> shifted to 1544 cm<sup>-1</sup>. The appearance of bands in 1300-1500 cm<sup>-1</sup> region suggested that MoO<sub>2</sub>(acac)<sub>2</sub> has been attached to acetylacetonated MCM-41 (Fig. 1C). The presence of bands in the range of 900-1000 cm<sup>-1</sup> in the supported catalyst is due to Mo=O vibrations.

The powder XRD pattern of chloropropylated MCM-41 and MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41 are shown in Fig. 2. In the XRD pattern of chloropropylated MCM-41, four diffraction peaks are observed in 2θ=2-8°, indexed assuming a hexagonal cell as (100), (110), (200) and (210) (Fig. 2A).

In the XRD pattern of MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41, the 100 reflection is only present the shift to lower angle (Fig. 2B). The lattice parameters, which were calculated using the d<sub>100</sub>, were 40.14 Å (d<sub>100</sub> = 34.78 Å, 2θ= 2.59°) and 45.09 Å (d<sub>100</sub>=39.05 Å, 2θ=2.26°) for chloropropylated MCM-41 and MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41, respectively. The lattice parameter for MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41 increases because the functionalization of MCM-41 results in an expansion of the hexagonal unit cell.

Lower intensity of the 100 for the supported catalyst is attributed to filling the pore of the MCM-41 due to functionalization. Diffuse reflectance UV-Vis spectroscopy was employed for comparison of chloropropylated MCM-41 and



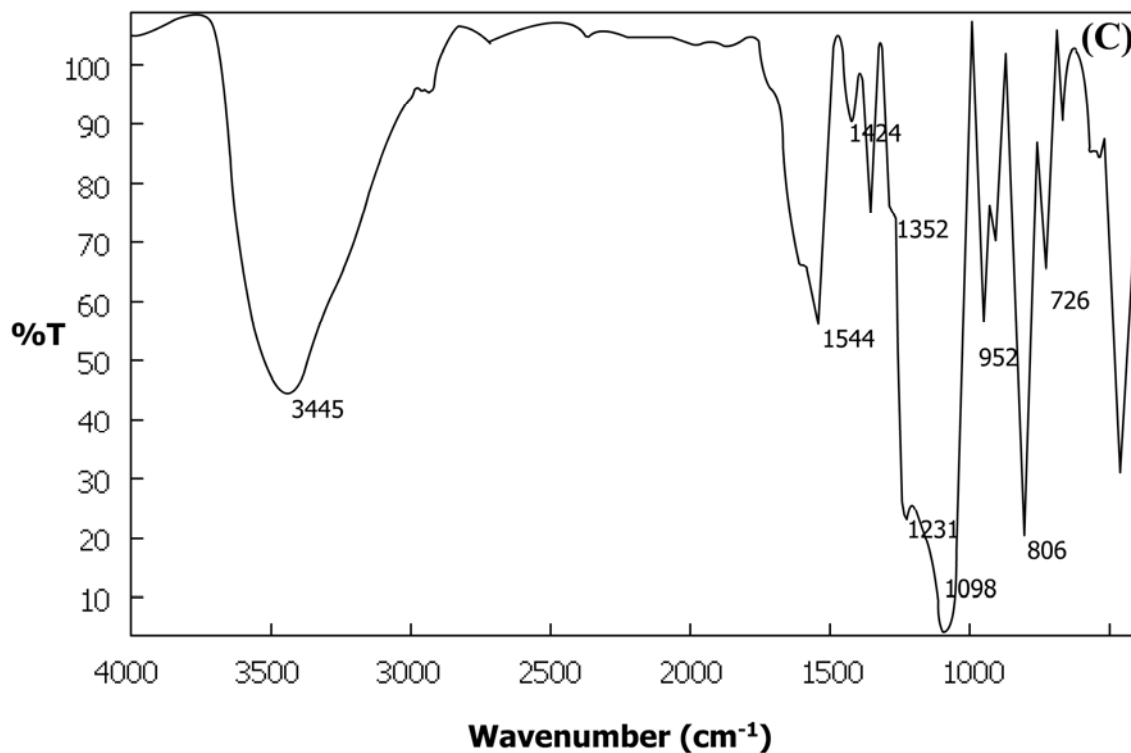


Fig 1. FT-IR spectra of MCM-41 (A), acetylacetonated MCM-41 (B) and MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41 (C)

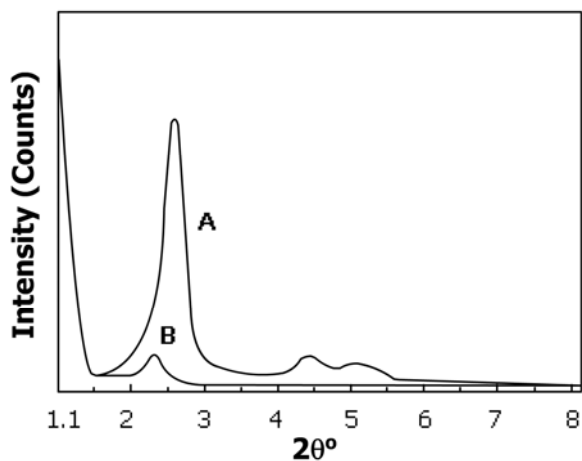


Fig 2. The XRD pattern of: (A) MCM-41; and (B) MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41

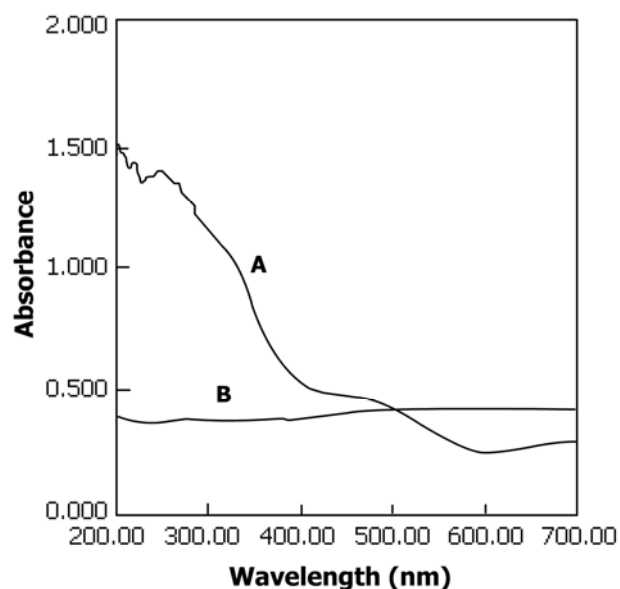
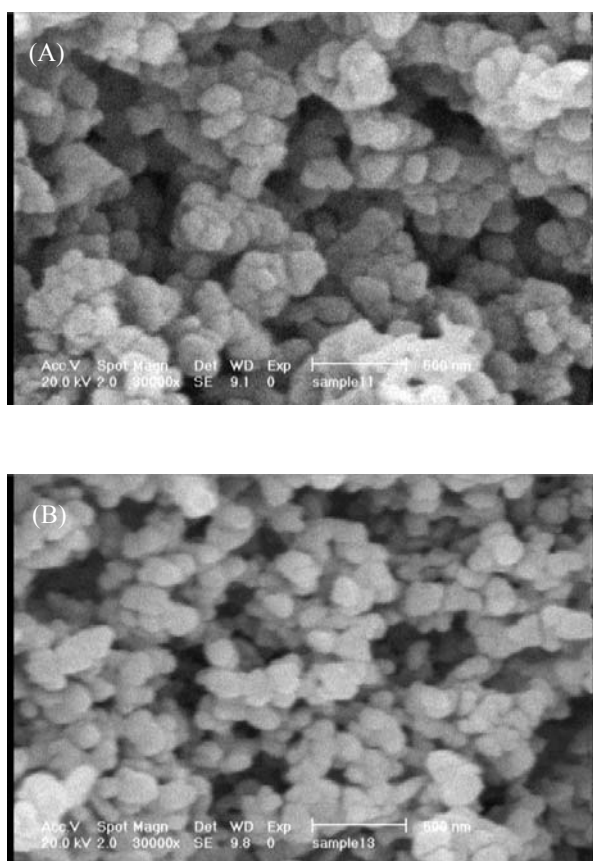


Fig 3. DR UV-Vis spectra of: (A) MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41; and (B) MCM-4

MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41. In the Mo-containing species, the nature of the ligands has an important role in intensity and

energy of the electronic spectra [22].  $\text{MoO}_2(\text{acac})_2\text{-MCM-41}$  exhibits absorption bands in the 200-350 nm region (Fig. 3A) attributed to ligand–Mo charge transfer bands, which are not observed in the spectrum of the MCM-41 (Fig. 3B). Fig. 4 shows the SEMs of acetylacetonated MCM-41 and  $\text{MoO}_2(\text{acac})_2\text{-MCM-41}$ . Scanning was done at 0-500 nm length across the materials. Comparison of images indicates that the smooth and flat surface of the acetylacetonated MCM-41 altered upon anchoring of the  $\text{MoO}_2(\text{acac})_2$ .



**Fig 4.** SEM of Acetylacetonated MCM-41 (A), SEM of  $\text{MoO}_2(\text{acac})_2\text{-MCM-41}$  (B)

The metal loading of  $\text{MoO}_2(\text{acac})_2\text{-MCM-41}$  catalyst, which was determined by neutron activation analysis (NAA), was obtained 0.99 mmol/ g.

### The effect of solvent on the epoxidation of cyclooctene with *tert*-BuOOH catalyzed by $\text{MoO}_2(\text{acac})_2\text{-MCM-41}$

First, the effect of different solvents on the catalytic activity of the resulting catalyst was investigated in the epoxidation of *cis*-cyclooctene in the presence of *tert*-butylhydroperoxide. Among the 1,2-dichloroethane, dichloromethane, chloroform, carbon tetrachloride, acetonitrile, acetone and methanol, 1,2-dichloroethane was chosen as reaction media because the highest epoxide yield was observed (Table1).

### The effect of different oxidants on the epoxidation of cyclooctene catalyzed by $\text{MoO}_2(\text{acac})_2\text{-MCM-41}$

We also investigated the ability of different oxygen donors such as *tert*-BuOOH,  $\text{NaIO}_4$ ,  $\text{H}_2\text{O}_2$ , urea hydrogen peroxide (UHP) and  $\text{KHSO}_5$  in the oxidation of *cis*-cyclooctene and TBHP was chosen as oxygen donor (Table 2).

### Catalytic alkene epoxidation with *tert*-BuOOH in the presence of $\text{MoO}_2(\text{acac})_2\text{-MCM-41}$

The ability of this catalytic system was investigated in the oxidation of different alkenes. The obtained results in the presence of  $\text{MoO}_2(\text{acac})_2\text{-MCM-41}$  showed that this catalyst is an efficient catalyst in the epoxidation of a wide range of alkenes including cyclic and linear alkenes. All products obtained in 100% selectivity.

**Table 1.** The effect of solvent on the epoxidation of *cis*-cyclooctene with *tert*-BuOOH under reflux condition<sup>a</sup>

Solvent	Epoxide(%) <sup>b</sup>	Time(h)
$\text{CH}_2\text{Cl}_2$	5	1
$\text{CHCl}_3$	14	1
$\text{CCl}_4$	76	1
$\text{CH}_3\text{CN}$	No reaction	1
$(\text{CH}_3)_2\text{CO}$	No reaction	1
$\text{CH}_3\text{OH}$	2	1
1,2-DCE	93	1

<sup>a</sup>Reaction conditions: *cis*-cyclooctene (0.5 mmol), *tert*-BuOOH (1 mmol), catalyst (0.03 g, 0.03 mmol), solvent (3 ml).

<sup>b</sup>GLC yield based on the starting cyclooctene.

MoO<sub>2</sub>(acac)<sub>2</sub> Supported on MCM-41

**Table 2.** The effect of oxidant on the epoxidation of *cis*-cyclooctene under reflux condition <sup>a</sup>

Solvent <sup>b</sup>	Oxidant	Time (h)	Epoxide (%) <sup>c</sup>
1,2-DCE/H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub> <sup>d</sup>	1	2
	NaIO <sub>4</sub> <sup>d</sup>	1	No reaction
	KHSO <sub>5</sub> <sup>d</sup>	1	No reaction
CH <sub>3</sub> CN/H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>	1	6
	NaIO <sub>4</sub>	1	No reaction
1,2-DCE	UHP	1	No reaction
	TBHP	1	93



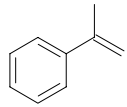
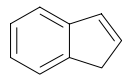
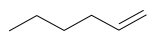
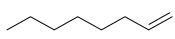
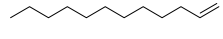
<sup>a</sup> Reaction conditions: *cis*-cyclooctene (0.5 mmol), oxidant (1 mmol), catalyst (0.03 g, 0.03 mmol).

<sup>b</sup> A 3:1 mixture of organic solvent: water was used.

<sup>c</sup> GLC yield based on the starting cyclooctene.

<sup>d</sup> Tetrabutylammonium bromide (0.01 g) was used.

**Table 3.** Epoxidation of alkenes with *tert*-BuOOH catalyzed by MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41 under reflux conditions

Entry	Alkene	Conversion (%)	Epoxide selectivity <sup>b</sup>	Time(h)	TOF (h <sup>-1</sup> )
1		93	100	1	15.5
2		90	100	1.5	10
3		94	100	12	2.6
4		64	100	12	1.8
5		94	100	6	5.2
6		91	100	8	3.8
7		89	100	14	2.1

<sup>a</sup> Reaction conditions: alkene (0.5 mmol), *tert*-BuOOH (1 mmol), catalyst (0.03 g, 0.03 mmol) and 1,2-dichloroethane (3 ml).

<sup>b</sup> GLC yield based on the starting alkene.

1-Hexene, 1-octene and 1-dodecene as linear alkenes were epoxidized efficiently by this catalyst in high yields. Cyclic olefins such as cyclohexene and cyclooctene were also epoxidized in high yields.

### Catalyst reuse and stability

The reusability of supported catalysts is one of the most important benefits which make them useful for commercial applications. The recovery and reusability of the supported

**Table 4.** Investigation of catalyst reuse and stability in the epoxidation of *cis*-cyclooctene with *tert*-BuOOH under reflux conditions<sup>a</sup>

Run	Epoxide (%) <sup>b</sup>	Time(h)	Mo leached (%) <sup>c</sup>
1	93	1	1.5
2	91	1	0
3	91	1	0
4	91	1	0
5	91	1	0

<sup>a</sup> Reaction conditions: alkene (0.5 mmol), *tert*-BuOOH (1 mmol), catalyst (0.03 g, 0.03 mmol) and 1,2-dichloroethane (3 ml).

<sup>b</sup>GLC yield based on the starting alkene.

<sup>c</sup>Determined by AAS.

MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41 catalyst was investigated in the sequential epoxidation of *cis*-cyclooctene with *tert*-BuOOH. At the end of reaction, the catalyst was separated by simple filtration, washed with acetone and dried before using in the next run. The filtrates were used for determining the catalyst leaching. The amount of catalyst leached in filtrates was determined by AAS. The results showed that only small amounts of Mo catalyst was leached after the first run and no Mo was detected after the second run in the reaction mixture (Table 4). Also, the catalytic behavior of the separated liquid was tested by addition of fresh olefin to the filtrates after each run. The oxidation reaction under the same reaction conditions, as with the catalyst, showed that the obtained results are the same as the blank experiments. The amount of Mo in the recovered catalyst was determined by NAA after each consecutive run. The results showed that the Mo content of the recovered catalyst remains constant. This fact confirmed the strong coordination of Mo towards acac ligand.

## CONCLUSION

We immobilized molybdenyl acetylacetonate catalyst on MCM-41 via acetylacetonate linkage and found that this supported catalyst was active in epoxidation of alkenes, such as linear and cyclic alkenes. The heterogeneous MoO<sub>2</sub>(acac)<sub>2</sub>-MCM-41 is a reusable catalyst and can be reused five consecutive times with significant loss of its activity.

## ACKNOWLEDGEMENT

We are thankful to the Center of Excellence of Chemistry of University of Isfahan (CECUI) for financial support of this work.

## REFERENCES

- [1] M. Beller, C. Bolm, *Transition Metals for Fine Chemicals and Organic Synthesis*, Wiley-VCH, Weinheim, Vol. 2 (1998) 261.
- [2] K.A. Jorgensen, *Chem. Rev.* 89 (1989) 431.
- [3] W.R. Thiel, T. Preimer, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1737.
- [4] F.E. Kuhn, A.D. Lopes, A.M. Santos, E. Herdweck, J.J. Haider and C.C. Romao, *J. Mol. Catal. A: Chem.* 151 (2000) 147.
- [5] A. Corma, M. Domine, J.L. Jorda, M.T. Navarro, F. Rey, J. Perez-Pariente, J. Tsuji, B. Mc Culloch and L.T. Nemeth, *Chem. Commun.* (1998) 2211.
- [6] D.C. Sherrington, S. Simpson, *J. Catal.* 131 (1991) 115.
- [7] D.C. Sherrington, S. Simpson, *React. Polym.* 19 (1993) 13.
- [8] M.M. Miller, D.C. Sherrington and S. Simpson, *J. Chem. Soc. Perkin Trans. 2* (1994) 2091.
- [9] M.M. Miller, D.C. Sherrington, *J. Catal.* 152 (1995) 368.
- [10] M.M. Miller, D.C. Sherrington, *J. Catal.* 152 (1995) 377.



MoO<sub>2</sub>(acac)<sub>2</sub> Supported on MCM-41

- [11] J.H. Ahn, D.C. Sherrington, *J. Chem. Soc. Chem. Commun.* (1996) 229.
- [12] G. Grivani, S. Tangestaninejad, M.H. Habibi and V. Mirkhani, *Catal. Commun.* 6 (2005) 375.
- [13] G. Grivani, S. Tangestaninejad, M.H. Habibi, V. Mirkhani and M. Moghadam, *Appl. Catal. A: Gen.* 299 (2006) 131.
- [14] S. Tangestaninejad, M.H. Habibi, V. Mirkhani, M. Moghadam and G. Grivani, *Inorg. Chem. Commun.* 9 (2006) 575.
- [15] M. Jia, W.R. Thiel, *Chem. Commun.* (2002) 2392.
- [16] M. Jia, A. Siefert, W.R. Thiel, *Chem. Mater.* 15 (2003) 2174.
- [17] D. Nunes, A.A. Valente, M. Pillinger, A.C. Fernandes, C.C. Romao, J. Rocha and I.S. Concalves, *J. Mater. Chem.* 12 (2002) 1735.
- [18] C.C.D. Nunes, M. Pillinger, A.A. Valente, A.D. Lopes and I.S. Gonçalves, *Inorg. Chem. Commun.* 6 (2003) 1228.
- [19] M. Masteri-Farahani, F. Farzaneh and M. Ghandi, *J. Mol. Catal. A: Chem.* 243 (2006) 170.
- [20] Q. Cai, W.Y. Lin, F.S. Xiao and W.Q. Pang, *J. Micropor. Mater.* 32 (1999) 1.
- [21] G.J. Chen, J.W. Mc Donald and W.E. Newton, *Inorg. Chem.* 15 (1976) 2612.
- [22] M.D. Hopkins, W.P. Schaefer, M.J. Bronikowski, W.H. Woodruff, V.M. Miskowski, R.F. Dallinger & H.B. Gray, *J. Am. Chem. Soc.* 109 (1987) 408.