

## Immobilization of a molybdenum complex with tetradentate ligand on mesoporous material MCM-41 as catalyst for epoxidation of olefins

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### Abstract

Covalent grafting of MCM-41 with 3-chloropropyl trimethoxysilane and subsequent reaction respectively with acacdien and complexation with  $\text{MoO}_2(\text{acac})_2$  afforded  $\text{MoO}_2\text{acacdien@MCM-41}$ . X-ray diffraction and nitrogen sorption analyses revealed the preservation of the textural properties of the support as well as accessibility of the channel system despite sequential reduction in surface area, pore volume and pore size. Elemental analyses showed nearly complete complexation of the supported ligands and the presence of 0.24 mmol molybdenum per gram of the catalyst. Epoxidation of cyclooctene, 1-hexene and 1-octene in the presence of  $\text{MoO}_2\text{acacdien@MCM-41}$  with *tert*-butyl hydroperoxide (TBHP) were carried out with relatively good conversion in the mild reaction conditions.

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## 1. Introduction

The direct oxidation of hydrocarbons catalyzed by metal complexes plays an important role in organic syntheses [1-6]. Epoxidation of

unsaturated hydrocarbons is an important reaction and the use of transition metal complexes as catalysts for this reaction has received increased attention [1,7-10]. In this respect it is known that high valent d0 transition metal compounds such as

Mo(VI), W(VI) and Ti(IV) are active catalysts for the epoxidation of olefins [9-14]. Particularly, molybdenum based catalysts (*cis*-dioxo molybdenum complexes) are efficient and selective catalysts for this purpose and much attention is being paid to this type of catalysts [11-14]. Recently, heterogenization of homogeneous molybdenum catalysts have been the subject of much efforts and especially those based on nanoporous materials (for example MCM-41, MCM-48, etc) are of great interests [12, 15-18]. The main advantages of this type of catalysts is the extremely high surface area, large and defined pore sizes, easy separation and recyclability and good stability in the reaction conditions. Anchoring of the multidentate ligand, e.g. Schiff base on to the nanopores of the MCM-41 and next complexation of the resulted hybrid material with metal salts afforded new heterogenized homogeneous catalysts.

In this work, we report a new heterogeneous molybdenum catalyst based on an easily prepared tetradentate Schiff base ligand derived from acetylacetone and diethylenetriamine supported on MCM-41. Catalytic properties of the catalyst were investigated in the epoxidation of cyclooctene and 1-hexene a model olefins.

## 2. Experimental

### 2.1. Preparation of MCM-41 and chloropropyl modified MCM-41 (ClpMCM-41)

Mesoporous molecular sieve MCM-41 was prepared according to reported method [19]. 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 hour. 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 ClpMCM-41 was performed using FT-IR spectroscopy and X-ray diffraction.

### 2.2. Preparation of acacdien@MCM-41

The acacdien ligand was prepared according to the general method of preparation of Schiff bases [20]. For preparation of acacdien modified MCM-41, chloropropyl modified MCM-41 (2 g) was suspended in 90 ml of benzene and to this mixture was added excess of acacdien ligand (1 g, 3.2 mmol) and triethylamine (0.5 ml) and refluxed for 12 hours. The solid was filtered, dried and then soxhlet extracted with ethanol and dried under vacuum at 473 K. The prepared acacdien@MCM-41 material was characterized with FT-IR spectroscopy.

### 2.3. Preparation of MoO<sub>2</sub> acacdien@ MCM-41 catalyst

For preparation of MoO<sub>2</sub>acacdien modified MCM-41 (MoO<sub>2</sub>acacdien@MCM-41), excess of MoO<sub>2</sub>(acac)<sub>2</sub> (500 mg, 1.5 mmol), prepared according to literature method [21], was dissolved in ethanol (50 ml). Then acacdien modified MCM-41 (1 g, dried in vacuum oven at 473 K) was added to this solution and the mixture was refluxed for 12 hours. After filtration, the product was dried and then soxhlet extracted with a mixture of

dichloromethane and ethanol (1:1) to remove unreacted  $\text{MoO}_2(\text{acac})_2$ .  $\text{MoO}_2\text{acacdien@MCM-41}$  material was then dried under vacuum at 473 K and characterized with FT-IR spectroscopy, X-ray diffraction and BET nitrogen sorption studies.

## 2.4. Instrumentation

Infrared spectra were recorded using Perkin-Elmer Spectrum RXI 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 Quanta chrome Nova 2200, Version 7.11 Analyzer.

## 2.5. Catalytic epoxidation of olefins

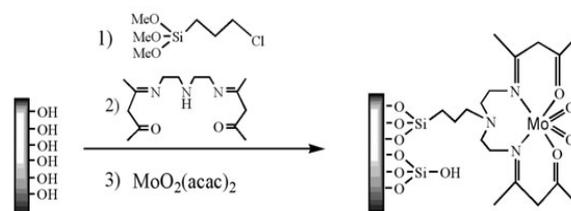
Epoxidation of olefins such as cyclooctene, 1-hexene and 1-octene purchased from Merck was carried out in a 25 ml round bottomed flask equipped with a condenser and a magnetic stirrer. Tert-butylhydroperoxide (TBHP) (obtained from Merck as 80% in di-tertiary butyl peroxide) was used as oxidant. In a typical procedure, to a mixture of catalyst (100 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 6890N) 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 discussion

### 3.1. Preparation of the $\text{MoO}_2\text{acacdien@MCM-41}$ catalyst

The hybrid mesoporous material  $\text{MoO}_2\text{acacdien@MCM-41}$  was obtained as outlined in Scheme 1. Reaction of chloropropyl modified MCM-41 with Schiff base ligand acacdien results in preparation of  $\text{acacdien@MCM-41}$  through the substitution reaction between the secondary amine of Schiff base with the chloro group.



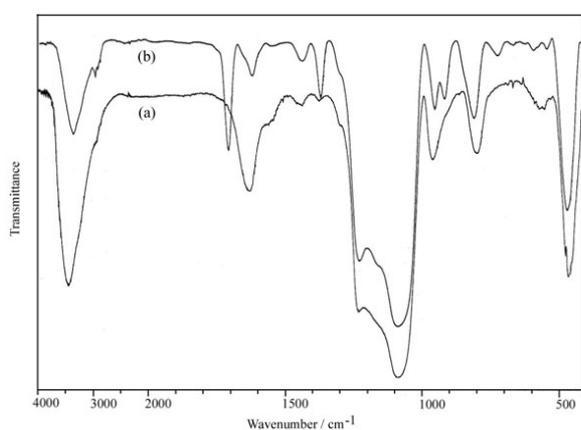
**Scheme 1.** The Schematic illustration of the preparation of  $\text{MoO}_2\text{acacdien@MCM-41}$ .

The success of chemical modification was followed with FT-IR spectroscopy (Figure 1). In the FT-IR spectrum of the resulted material the band at  $1629\text{ cm}^{-1}$  is assigned to the stretching vibration of  $\text{C}=\text{N}$  bonds and thus indicates the presence of Schiff base ligand in this material (Table 1). Subsequent reaction of the supported Schiff base with  $\text{MoO}_2(\text{acac})_2$  affords  $\text{MoO}_2\text{acacdien@MCM-41}$ . Atomic absorption spectroscopy showed that 0.12 mmol molybdenum could be accommodated per 1 g of material. In the FT-IR spectrum of this material two adjacent bands

at 910 and 956  $\text{cm}^{-1}$  (Table 1) is attributed to the presence of cis-dioxo molybdenum in this material [22].

**Table 1.** Spectroscopic data of the prepared materials.

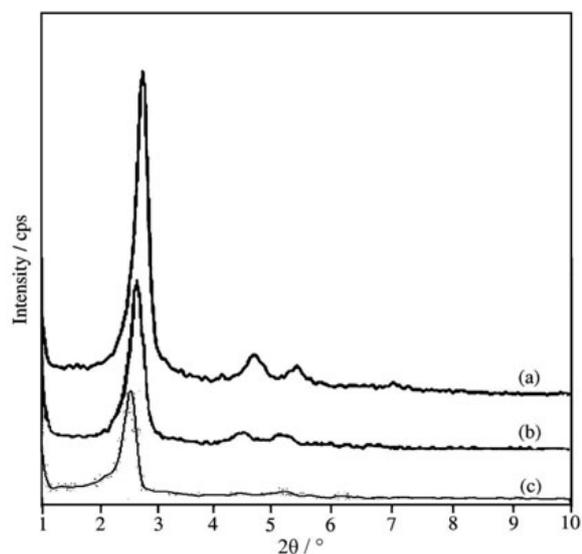
Material	$\nu_{\text{Mo=O}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{C=N}}$ ( $\text{cm}^{-1}$ )	Mo loading ( $\text{mmol.g}^{-1}$ )
acacdienMCM-41	-	1632	-
$\text{MoO}_2\text{acacdienMCM-41}$	910, 956	1626	0.12



**Fig. 1.** The FT-IR spectra of (a) acacdien@MCM-41 and (b)  $\text{MoO}_2\text{acacdien@MCM-41}$  materials.

### 3.2. Textural characterization of the $\text{MoO}_2\text{acacdien@MCM-41}$ catalyst

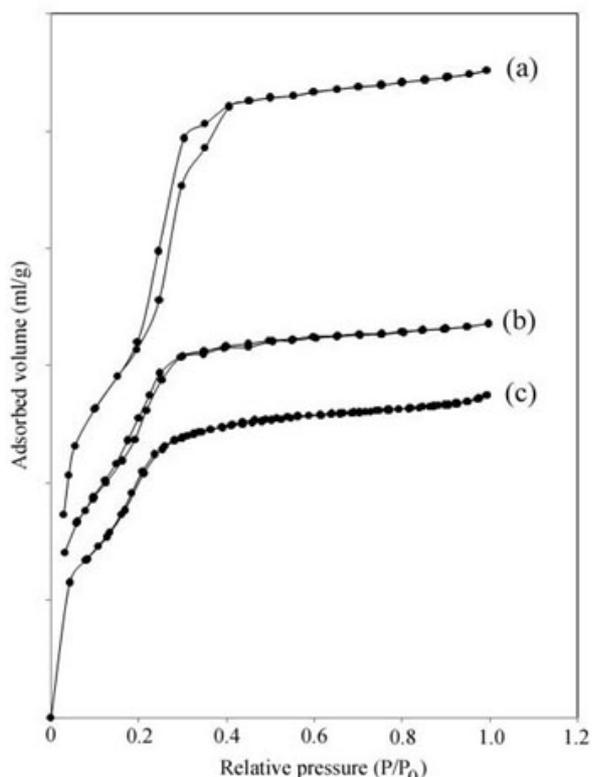
In the XRD pattern of the  $\text{MoO}_2\text{acacdien@MCM-41}$  (Fig. 2) the prominent diffraction peak  $\langle 1\ 0\ 0 \rangle$  of the MCM-41 is observed clearly, but the other peaks decrease to a very low level and are thus nearly undetectable. This suggests the presence of periodic arrangement of hexagonal geometry channels in all the three hybrid materials. The reduction in diffraction intensity upon loading of molybdenum complex can be assigned to a decrease of mesoscopic order of the material or contrast matching resulting from the presence of the organic moieties inside the pores of the material.



**Fig. 2.** XRD patterns of: (a) MCM-41 (b) ClpMCM-41 and (c)  $\text{MoO}_2\text{acacdien@MCM-41}$  materials.

Nitrogen sorption analysis provides another evidence for confirming the mesoporous structure and incorporation of the molybdenum complex into the pores of MCM-41. Fig. 3a-c show the nitrogen sorption isotherms of MCM-41, ClpMCM-41 and  $\text{MoO}_2\text{acacdien@MCM-41}$  as well as pore size distribution profiles, respectively. All the three materials exhibit type IV isotherms according to IUPAC, which is characteristic for mesoporous materials [23].

As seen, the uptake of  $\text{N}_2$  for  $\text{MoO}_2\text{acacdien@MCM-41}$  is lower and the maximum of pore size distribution was shifted to lower value. Relevant data of the materials is shown in Table 2. With incorporation of the complex the value of specific surface area (SBET), total pore volume ( $V_p$ ) and average pore diameter was decreased.



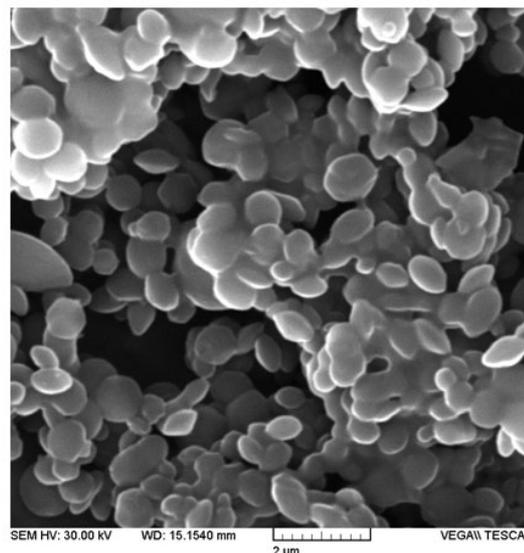
**Fig. 3.** Nitrogen sorption isotherms of: (a) MCM-41 (b) acacdien@MCM-41 and (c) MoO<sub>2</sub>acacdien@MCM-41 materials.

**Table 2.** Texture parameters of samples taken from XRD and nitrogen sorption studies.

Material	XRD d value (Å)	Lattice parameter <sup>a</sup> (Å)	BET specific surface area (m <sup>2</sup> .g <sup>-1</sup> )	Pore volume (ml.g <sup>-1</sup> )	Average Pore diameter (Å)
MCM-41	32.57	37.6	1211	0.851	28.2
Clp MCM-41	33	38.1	1060	0.47	18
MoO <sub>2</sub> AcacdienMCM-41	33.7	38.9	892	0.41	17

<sup>a</sup> Determined by equation:  $a = d100 (2/\sqrt{3})$

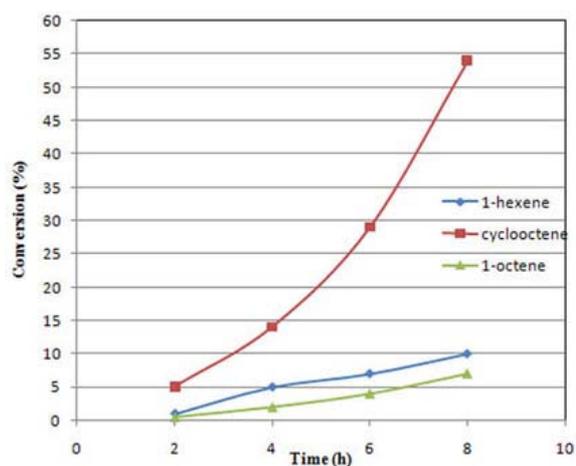
The morphologies and microstructure of the obtained products were further investigated by scanning electron microscopy (SEM). Figure 4 shows the typical SEM image of MoO<sub>2</sub>acacdien@MCM-41 material. This image clearly shows that obtained materials have ellipsoidal morphologies and monodispersed.



**Fig. 4.** Typical SEM image of MoO<sub>2</sub>acacdien@MCM-41 material.

### 3.4. Catalytic activity

The catalytic activity of the MoO<sub>2</sub>acacdien@MCM-41 was investigated through the epoxidation of olefins in the presence of TBHP and results are given in Table 3.



**Fig. 5.** Time-coursed results of catalytic epoxidation of olefins.

The catalyst showed good activity and gave the corresponding epoxide as only product. As the

time-course showed (Fig. 5), the catalyst exhibited higher catalytic activity in the early reaction period and after 10 h retains constant. On the other hand, the terminal olefins showed lower reactivities that is not surprising as indicated in previous works [7, 28] that catalytic activity towards the oxidation of internal C=C double bonds is higher than of terminal ones, which is due to higher electronic density of the former.

**Table 3.** Results of catalytic epoxidation of some olefins with TBHP in presence of MoO<sub>2</sub>acacdien@MCM-41 catalyst.

Olefin	Time (hours)	Conversion (%)	Selectivity (%) <sup>a</sup>	TOF (h <sup>-1</sup> ) <sup>b</sup>
Cyclooctene	8	54	99	45
	24 <sup>c</sup>	57	95	-
1-octene	8	7	97	5.8
	24 <sup>c</sup>	8	95	-
1-hexene	8	10	98	8.3
	24 <sup>c</sup>	15	94	-
Cyclooctene <sup>d</sup>	12	14	41	-
Cyclooctene <sup>e</sup>	12	21	51	-

Reaction conditions: catalyst (100 mg), olefin (8 mmol), TBHP (1.6 ml, 14.4 mmol), refluxing chloroform (20 ml).

<sup>a</sup> Selectivity toward the corresponding epoxide.

<sup>b</sup> Calculated as mmol of product formed per mmol of molybdenum in the catalyst per hour.

<sup>c</sup> Reaction progress after 16 hours of catalyst separation.

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

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

#### 4. Conclusion

Our work has revealed that incorporation of a multidentate Schiff base ligand such as acacdien into large pores of mesoporous material MCM-41 and subsequent treatment with MoO<sub>2</sub>(acac)<sub>2</sub> affords a new truly heterogeneous molybdenum catalyst for epoxidation of olefins with high selectivity and stability.

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