Synthesis and characterization of molybdenum complexes with bidentate Schiff base ligands within nanoreactors of MCM-41 as epoxidation catalysts

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Abstract

The mesoporous molecular sieve MCM-41 was covalently grafted with 3-aminopropyl trimethoxysilane to give aminopropyl modified MCM-41 (AmpMCM-41). Reaction of this material with furfural, pyrrolcarbaldehyde, 2-acetylpyrrol, 2-aminoacetophenone, salicylaldehyde and acetylacetone afforded the corresponding supported Schiff base ligands. Subsequent reaction with bis(acetylacetonato)dioxomolybdenum(VI) leads to various molybdenum complexes supported on MCM-41 through propyl chain spacer. Characterization of these materials was carried out with FT-IR, atomic absorption spectroscopy, powder X-ray diffraction (XRD) and BET nitrogen adsorption–desorption methods. The XRD and BET analyses revealed that textural properties of support were preserved during the grafting experiments. The resultant materials successfully catalyzed the epoxidation of cyclooctene, cyclohexene, 1-hexene and 1-octene with *tert*-butyl hydroperoxide (TBHP) to the corresponding epoxides with 98–100% selectivities.
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1. Introduction

In recent years, great interest of many researchers has been focused on the heterogenizing of homogeneous catalysts [1–4]. This is important because while some advantages of homogeneous catalysts such as catalytic activities and selectivities are retained, other properties like easier work-up, recyclability and stability of heterogeneous systems will be obtained. Different approaches like encapsulation or immobilization of homogeneous catalysts in solid supports such as faujasite zeolites [5,6] and covalent grafting of homogeneous catalysts on reactive polymer surfaces [7] or inorganic solids [8,9] have been used. The latter is of great importance especially after the discovery of a new class of mesoporous molecular sieves such as MCM-41 and MCM-48 containing reactive silanol groups which offer large pores and great surface area to the guest metal complex with considerable stability under different reaction conditions [1–4,10–12]. Among the homogeneous catalysts, those of molybdenum types are of great interest because a variety of industrial chemical reactions especially hydrodesulphurization and oxygen transfer reactions such as epoxidation of olefins are catalyzed with these compounds [13,14]. In this manner, molybdenum present in the structure of some enzymes such as nitrogenase, nitrate reductase and aldehyde oxidase serves as a site for catalytic redox reactions [15].

Much effort has been done for immobilization of molybdenum catalysts within different supports such as silicates, zeolites and other molecular sieves [16,17]. A major drawback encountered in this regard is the instability of the molybdenum in the structure of catalysts due to leaching during reaction course. To overcome this, we recently proposed a new hybrid catalyst of molybdenum using a tetradentate Schiff base ligand supported on MCM-41 mesoporous material, salpr/MCM-41 (salpr = N,N'-bis(3-salicylidenaminopropyl)amine). Complexation of this material with molybdenum afforded a stable and active heterogeneous catalyst for epoxidation of olefins [18].

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In this paper, we report new heterogeneous systems for stabilizing molybdenum in the structure of catalysts derived from aminopropyl modified MCM-41. These systems are relatively similar to that applied for heterogenizing of palladium catalyst on silica surface by Clark and coworkers for Suzuki and Heck reactions [19,20]. They prepared a series of novel silica supported palladium catalysts bearing N–N, N–S and N–O chelating Schiff base ligands derived from reaction of aminopropyl modified silica with different aldehydes and ketones. They showed that their systems were stable under reaction conditions and catalytic activities were retained after recycling the catalysts. We have shown that our systems not only show similar stabilities, but also act as active and selective catalysts for epoxidation of olefins.

2. Experimental

2.1. Preparation of the catalysts

2.1.1. Preparation of MCM-41 and aminopropyl modified MCM-41 (AmpMCM-41)

Mesoporous molecular sieve MCM-41 was prepared according to literature method [21]. Modification of the prepared MCM-41 was carried out as follows: MCM-41 (2 g) was suspended in dry toluene (60 ml) and aminopropyl trimethoxysilane (1 g) was then added under dry nitrogen atmosphere. The resultant mixture was refluxed for 24 h. After filteration and washing with dichloromethane and ethanol, the solid was dried. The resultant material was then soxhlet extracted with a mixture of ethanol and dichloromethane (1:1) to remove the residue of silylating reagent and was then vacuum dried at 423 K. Characterization of AmpMCM-41 was performed with FT-IR spectroscopy, X-ray diffraction and BET nitrogen sorption methods.

2.1.2. Preparation of supported Schiff base ligands

The various supported Schiff base ligands were prepared according to the standard method used for preparation of silica supported Schiff bases [19,20]. As a general procedure, to a mixture of activated AmpMCM-41 (1.5 g) in 25 ml absolute ethanol was added 3 mmol of aldehyde or ketone (furfural, pyrrolcarbaldehyde, 2-acetylpyrrol, 2-amino acetophenone, salicylaldehyde and acetylacetone). The mixture was refluxed for 24 h under dry nitrogen atmosphere to afford MCM-41 supported Schiff base ligands furAmpMCM-41, pycaAmpMCM-41, acpyAmpMCM-41, amacAmpMCM-41, salAmpMCM-41 and acacAmpMCM-41, respectively. The solids were filtered, dried and then soxhlet extracted with ethanol to remove the unreacted aldehyde or ketone and dried under vacuum at 423 K overnight.

2.1.3. Preparation of supported molybdenum catalysts

$MoO_2(acac)_2$ (650 mg, prepared according to the literature method [22]) was dissolved in ethanol (30 ml). Supported Schiff base ligand (1 g, dried in vacuum oven at 423 K) was then added to this solution and the mixture was refluxed for 12 h. After filteration, the product was dried and then soxhlet extracted with a mixture of dichloromethane and ethanol (1:1) to remove the unreacted $MoO_2(acac)_2$. The resultant molybdenum containing materials; MoO_2furAmpMCM-41, MoO_2pycaAmpMCM-41, MoO_2acpyAmpMCM-41 and MoO_2amacAmpMCM-41, MoO_2salAmpMCM-41 and MoO_2acacAmpMCM-41 were then dried under vacuum at 423 K and characterized with FT-IR, atomic absorption spectroscopy, X-ray diffraction and BET nitrogen sorption method.

2.2. Characterization

Infrared spectra were recorded using Shimadzu 4300 FT-IR spectrometer. Powder X-ray diffraction data were collected with a SIEFERT XRD 3003 PTS diffractometer using Cu Kα radiation. Chemical analyses of samples were carried out with Perkin-Elmer spectrometer. Nitrogen sorption studies were performed at liquid nitrogen temperature using Quanta chrome Nova 2200, Version 7.11 Analyzer.

2.3. Catalytic epoxidations

Epoxidation of cyclooctene, cyclohexene, 1-octene and 1-hexene was carried out in a 25 ml round bottom flask equipped with a condenser and a magnetic stirrer. *Tert*-butyl hydroperoxide (TBHP, 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. The mixture was refluxed for a given time. Samples were withdrawn periodically and after cooling and dilution with chloroform were analyzed using a gas chromatograph (HP, Agilent 68909N) equipped with a capillary column (HP-5) and a FID detector. The products were quantified using isooctane (1 g, 8.75 mmol,) 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 catalysts was measured using atomic absorption spectroscopy.

3. Results and discussions

3.1. Preparation of the catalysts

For preparation of catalysts, the surface hydroxyl groups of MCM-41 were first reacted with the methoxy groups of aminopropyl trimethoxysilane. In this grafting reaction mainly two methoxy groups of the silylating agent were replaced by silanol groups of the surface [23]. The aminopropyl groups were then reacted with different aldehydes and ketones to form various bidentate Schiff base ligands supported on MCM-41 surface through propyl chain spacer (Scheme 1). In this reaction, amine groups of AmpMCM-41 and carbonyl groups of aldehyde or ketone are condensed to afford imine groups that act as nitrogen donor in resultant supported Schiff base ligands. Depending on substrate used, two types of N,O- and N,N-donor ligands are obtained. Utilization of salicylaldehyde, furfural and acetyl acetone produces bidentate N,O-donor ligands of salAmpMCM-41, furAmpMCM-41 and acacAmpMCM-41, respectively. On the other hand, using pyrrolcarbaldehyde, acetylpyrrol and
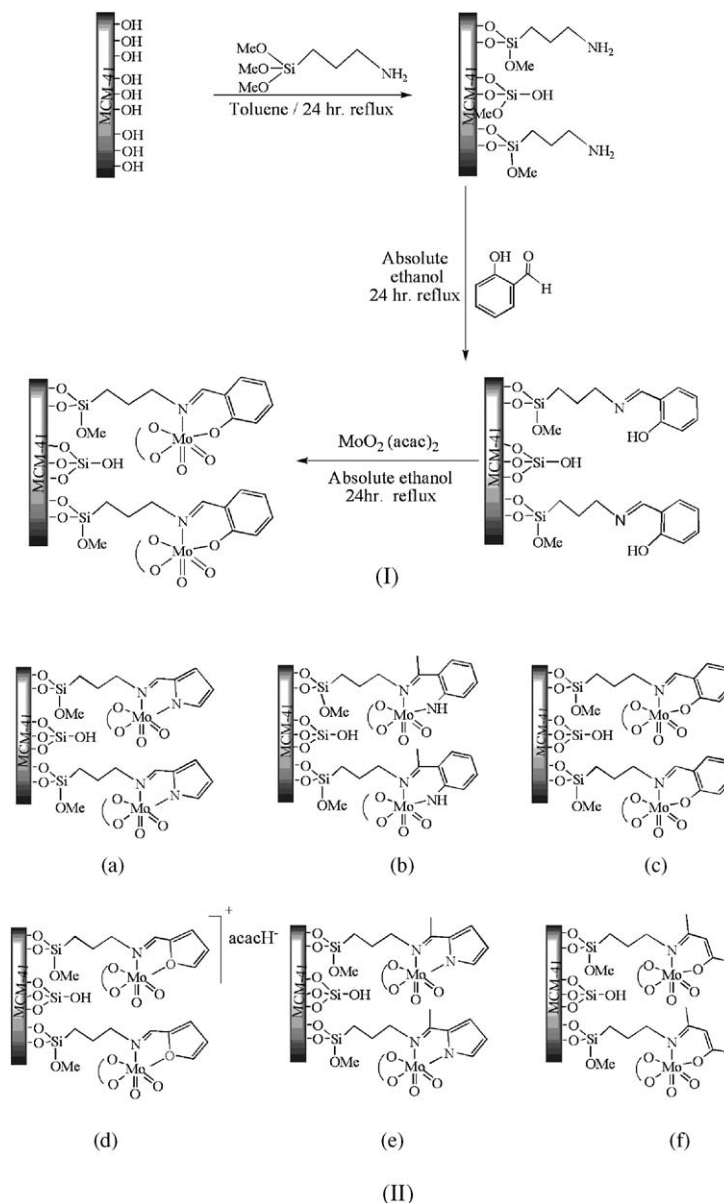
Scheme 1. (I) Preparation of catalysts from AmpMCM-41 and (II) structures of the catalysts: (a) MoO$_2$pycaAmpMCM-41, (b) MoO$_2$amacAmpMCM-41, (c) MoO$_2$salAmpMCM-41, (d) MoO$_2$furAmpMCM-41, (e) MoO$_2$acpyAmpMCM-41, and (f) MoO$_2$acacAmpMCM-41.

2-aminoacetophenone affords bidentate N,N-donor ligands of pycaAmpMCM-41, acpyAmpMCM-41 and amacAmpMCM-41, respectively. Reaction of the supported Schiff base ligands with MoO$_2$(acac)$_2$ in refluxing absolute ethanol forms the corresponding supported molybdenum complexes on MCM-41 surface (Scheme 1). The remaining unreacted MoO$_2$(acac)$_2$ have been removed by soxhlet extraction. Thus the active sites of catalyst have specific physicochemical stability since the molybdenums are covalently bonded to MCM-41 surface.

Table 1
FT-IR and molybdenum content data of prepared catalysts

Material	$\upsilon_{Mo=O}$ (cm^{-1})	$\upsilon_{C=N}$ (cm^{-1})[a]	Mo loading (wt.%)
MoO$_2$amacAmpMCM-41	900, 935	1610(1637)	0.67
MoO$_2$acpyAmpMCM-41	896, 943	1610(1635)	0.65
MoO$_2$pycaAmpMCM-41	901, 941	1634(1637)	0.76
MoO$_2$acacAmpMCM-41	914, 943	1612(1612)	0.67
MoO$_2$salAmpMCM-41	903, 939	1620(1637)	0.70
MoO$_2$furAmpMCM-41	916, 941	1610(1647)	0.58

[a] The numbers in parentheses are $\upsilon_{C=N}$ of uncomplexed ligands.

Table 2
Texture parameters of samples obtained from XRD and nitrogen sorption studies

Material	BET specific surface area ($m^2 g^{-1}$)	XRD d-value (Å)	Lattice parameter (Å)
MCM-41	1211	32.57	37.61
AmpMCM-41	753	32.26	38.41
MoO_2amacAmpMCM-41	658	33.71	38.92
MoO_2acpyAmpMCM-41	643	34.63	40
MoO_2pycaAmpMCM-41	601	34.94	40.34
MoO_2acacAmpMCM-41	560	35.82	41.36
MoO_2salAmpMCM-41	539	35.18	40.62
MoO_2furAmpMCM-41	484	35.23	40.68

3.2. Spectroscopic characterization of the catalysts

In the FT-IR spectra of the prepared supported Schiff base ligands, the C=N stretching vibrations are observed in the range of 1610–1645 cm^{-1} (Table 1). These C=N bands upon complexation with MoO_2(acac)$_2$ shift to the lower frequencies in some different supported molybdenum complexes. The observation of two adjacent bands at 896–916 and 935–943 cm^{-1} in FT-IR spectra (Table 1) is characteristic of *cis*-MoO_2 group [24,25]. Since these bands are not present in FT-IR spectra of MCM-41 and AmpMCM-41, it can clearly be concluded that molybdenum complexes are successfully tethered onto the MCM-41 surface as *cis*-MoO_2 complexed supported bidentate Schiff base ligand. The exemplary FT-IR spectra of MoO_2acpyAmpMCM-41 and its supported ligand acpyAmpMCM-41 are presented in Fig. 1.

Molybdenum contents of the prepared catalysts were determined by atomic absorption spectroscopy. The obtained results were in the range of 0.58–0.76 wt.% for different catalysts. Any contribution from physically adsorbed molybdenum species on surface must be negligible since determinations were carried out after soxhlet extraction of the prepared catalysts.
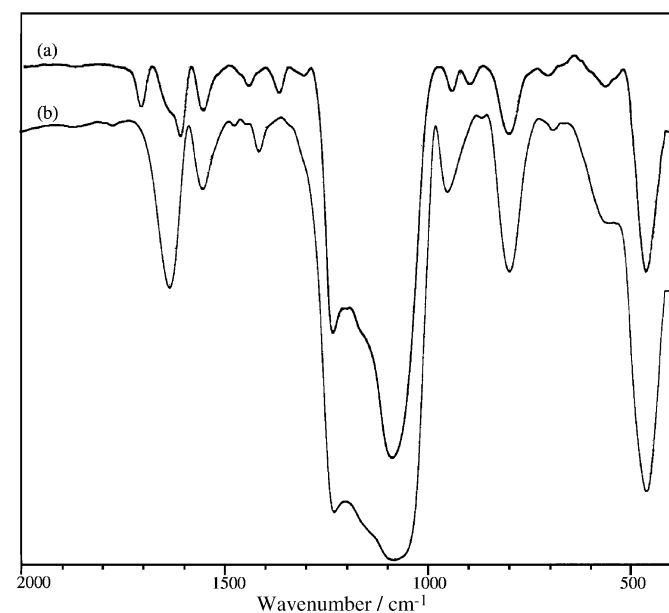
3.3. Textural properties of the catalysts

Textural properties of resultant molybdenum catalysts were investigated with X-ray diffraction and BET adsorption–desorption analyses. The results are given in Table 2. X-ray diffraction patterns of MCM-41 and AmpMCM-41 are shown in Fig. 2, respectively. In the X-ray diffraction pattern of unmodified MCM-41 (Fig. 2a), the strong reflection at $2\theta = 2.71$ belongs to $\langle 1\,0\,0 \rangle$ reflection and three weaker reflections at higher angles arise from $\langle 1\,1\,0 \rangle$, $\langle 2\,0\,0 \rangle$ and $\langle 2\,1\,0 \rangle$ reflections of a hexagonal unit cell. The hexagonal unit cell parameter a_0 (or lattice parameter), a measure of spacing present between the hexagonal layers is calculated as $d_{1\,0\,0}(2/\sqrt{3})$. This parameter for unmodified MCM-41 is 37.06 Å (Table 2). The XRD pattern of the AmpMCM-41 (Fig. 2b) only shows the 1 0 0 reflection with lower intensity and the other reflections have been disappeared partly due to a decrease in the mesoscopic order of the materials and mainly due to the contrast matching between the silicate framework and organic moieties located inside the MCM-41 channels [26]. Also the position of this reflection shifted to lower angle (or higher d-value) that indicates the expansion of unit cell parameter due to the incorporation of aminopropyl groups within MCM-41 (Table 2).

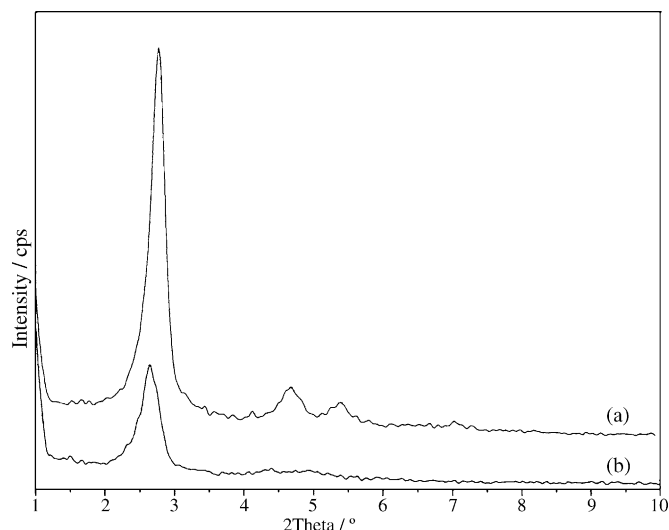X-ray diffraction patterns of the catalysts prepared from N,O-donor ligands and those prepared from N,N-donor

Fig. 1. FT-IR spectra of (a) MoO_2acpy AmpMCM-41 and (b) it supported acpy AmpMCm-41.

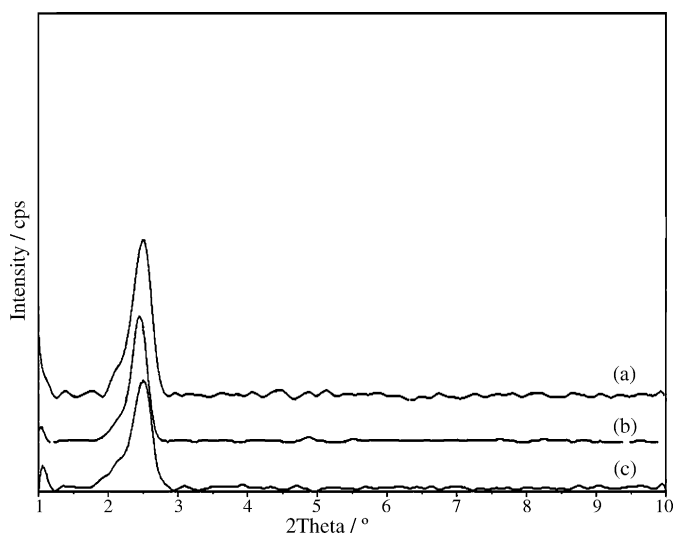Fig. 2. X-ray diffraction patterns of (a) MCM-41 and (b) AmpMCM-41.

Fig. 3. X-ray diffraction patterns of (a) MoO_2salAmpMCM-41, (b) MoO_2furAmpMCM-41, and (c) MoO_2acacAmpMCM-41.
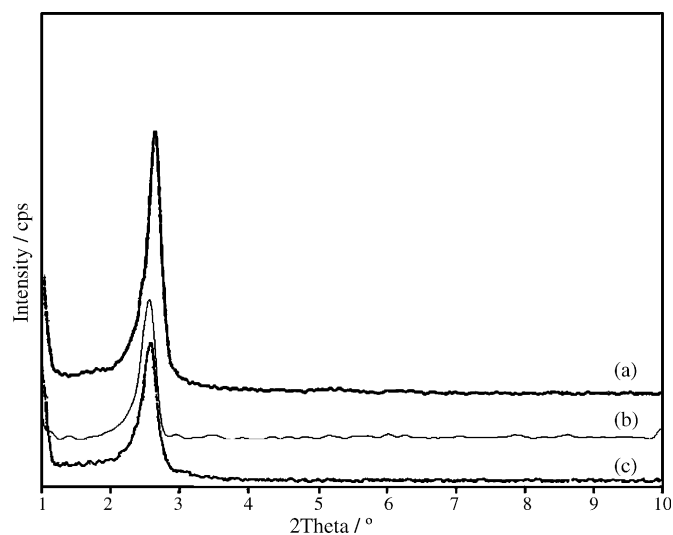

Fig. 4. X-ray diffraction patterns of (a) MoO_2amacAmpMCM-41, (b) MoO_2acpyAmpMCM-41, and (c) MoO_2pycaAmpMCM-41.

ligands are shown in Figs 3a–c and 4a–c, respectively. In both cases, the incorporation of molybdenum catalysts results in shifting the ⟨1 0 0⟩ reflection to lower angles (or higher d-values) with respect to that of MCM-41 and AmpMCM-41. As a result, this indicates further unit cell expansion in comparison with AmpMCM-41. The increasing order of unit cell parameters (Table 2) in these catalysts is arranged as MoO_2amacAmpMCM-41 < MoO_2acpyAmpMCM-41 < MoO_2

pycaAmpMCM-41 < MoO_2salAmpMCM-41 < MoO_2furAmp-MCM-41 < MoO_2acacAmpMCM-41.

It is interesting to note that catalysts containing N,N-donor ligands show lower unit cell parameters. Compared to catalysts containing N,O-donor ligands, the observation of lower unit cell parameter in this case can not easily been explained.

Mesoporous texture of the prepared catalysts was controlled by nitrogen sorption analyses. The specific surface areas of

Table 3

Results of catalytic epoxidation of some olefins with TBHP in the presence of catalysts prepared from ligands containing five-membered rings

Catalyst	Run number	Substrate	Time (h)	Conversion[a] (%)	Epoxide (%)	TOF[b] (h^{-1})
MoO_2furAmpMCM-41	1	Cyclooctene	4	79	99	263
	2		7	89	99	170
	3	Cyclohexene	4	45	98	150
	4		7	67	98	128
	5	1-Hexene	7	42	98	80
	6		10	52	98	69
	7	1-Octene	7	20	100	38
	8		10	30	100	40
MoO_2pycaAmpMCM-41	9	Cyclooctene	4	92	98	233
	10		7	100	99	145
	11	Cyclohexene	4	69	95	175
	12		7	94	99	136
	13	1-Hexene	7	46	100	67
	14		10	55	100	56
	15	1-Octene	7	34	100	49
	16		10	48	100	49
MoO_2acpyAmpMCM-41	17	Cyclooctene	4	98	99	284
	18		7	100	99	290
	19	Cyclohexene	4	88	98	255
	20		7	99	98	164
	21	1-Hexene	7	70	100	116
	22		10	80	100	93
	23	1-Octene	7	50	100	83
	24		10	68	100	79

[a] Calculated using isooctane as internal standard.

[b] Calculated as mmol of product formed per mmol of molybdenum in catalyst per time.

Table 4
Results of catalytic epoxidation of some olefins with TBHP in the presence of catalysts prepared from ligands containing six-membered rings

Catalyst	Run number	Substrate	Time (h)	Conversion (%)	Selectivity (%)	TOF (h^{-1})
MoO$_2$amacAmpMCM-41	1	Cyclooctene	4	96	98	274
	2		7	100	98	163
	3	Cyclohexene	4	70	98	200
	4		7	98	99	160
	5	1-Hexene	7	54	100	88
	6		10	77	100	88
	7	1-Octene	7	41	100	67
	8		10	59	100	68
MoO$_2$salAmpMCM-41	9	Cyclooctene	4	79	99	216
	10		7	96	98	150
	11	Cyclohexene	4	69	98	137
	12		7	87	98	99
	13	1-Hexene	7	43	100	60
	14		10	53	100	52
	15	1-Octene	7	21	100	45
	16		10	40	100	44

Table 5
Results of catalytic epoxidation of some olefins with TBHP in the presence of catalyst prepared from acac ligand

Catalyst	Run number	Substrate	Time (h)	Conversion (%)	Selectivity (%)	TOF (h^{-1})
MoO$_2$acacAmpMCM-41	1	Cyclooctene	4	97	99	235
	2		7	99	99	138
	3	Cyclohexene	4	90	98	186
	4		7	97	98	114
	5	1-Hexene	7	51	98	85
	6		10	59	98	68
	7	1-Octene	7	22	100	53
	8		10	43	98	50

MCM-41, AmpMCM-41 and the prepared catalysts are given in Table 2. These results reveal that incorporation of molybdenum catalyst lead to specific surface area reduction of prepared materials. The order of increasing specific surface area is as MoO$_2$furAmpMCM-41 < MoO$_2$salAmpMCM-41 < MoO$_2$acacAmpMCM-41 < MoO$_2$pycaAmpMCM-41 < MoO$_2$acpyAmpMCM-41 < MoO$_2$amacAmpMCM-41. This trend is almost inversed with respect to that observed in unit cell parameters of the catalysts. It can be deduced that decrease of unit cell parameter is equal to increase of specific surface area of the catalysts and vice versa.

Despite of decreasing specific surface area of the prepared catalysts, the remaining space in pores is still so large that many of the organic substrates can enter into the channels. We subsequently used these materials as catalysts for epoxidation of some olefins.

3.4. Catalytic tests

Catalytic activities of the prepared molybdenum catalysts were investigated in the epoxidation of cyclooctene, cyclohexene, 1-octene and 1-hexene with TBHP. The resultant conversions, selectivities and turnover frequencies (TOFs) are given in Tables 3–5. Due to higher reactivity of cyclic olefins and lower reactivity of terminal olefins, we have selected the reaction times in the range 4–7 h for cyclic olefins and 7–11 h for terminal ones to allow the slower reactions proceed to comparable transformations.

Inspection of the results reveals that both olefin and catalyst structures affect the catalyst activity. Based on the epoxidation mechanism suggested earlier [27,28], higher electron donating ability of olefin double bond is expected to facilitate the reaction rate. As seen in Tables 3–5, the order of increasing reactivities based on either conversions or TOFs are as cyclooctene > cyclohexene > 1-hexene > 1-octene. To explain this trend, two determining parameters of electronic and steric effects should be taken into consideration. The higher electronic density of the double bond is expected to show more epoxidation reactivity. Therefore, cyclooctene and cyclohexene with double bonds driven from secondary carbons should exhibit more activities in comparison with 1-hexene and 1-octene which contain double bonds between secondary and primary carbons. On the other hand, cyclooctene is more reactive than cyclohexene due to the presence of more electron donating (CH$_2$)$_6$ cyclic bridge connected to the double bond. That 1-octene is epoxidized slower than 1-hexene can be inferred since larger hexyl group connected to double bond sterically hinders it in approaching to the catalyst metal center with respect to 1-hexene which its double bond carries a smaller butyl group.

Another trend encountered in Tables 3–5 is that for a given substrate, catalytic activity and TOF increase as MoO$_2$acpy-AmpMCM-41 > MoO$_2$amacAmpMCM-41 > MoO$_2$acacAmp-
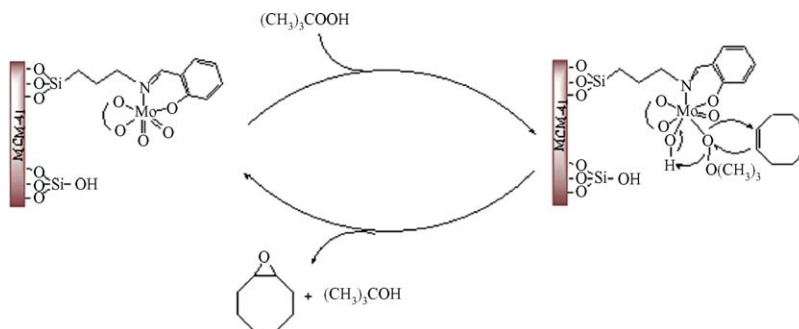
Scheme 2. Mechanism of epoxidation of the cyclooctene with TBHP in presence of MoO$_2$salAmpMCM-41.

MCM-41 > MoO$_2$pycaAmpMCM-41 > MoO$_2$furAmpMCM-41 > MoO$_2$salAmpMCM-41. In order to make comparison easier, the series are located in three tables on the basis of ligands containing five-membered ring (Table 3), ligands containing six-membered ring (Table 4) and without ring ligand (Table 5). The order of catalytic activities can be explained with consideration of two factors in these series. First, the catalysts prepared from N,N-donor ligands represent higher epoxidation activities than those prepared from N,O-donor ligands (compare for instance runs 3, 4, 11, 12 with 1, 2 in Table 3 and runs 1, 2 with 9, 10 in Table 4). On the other hand, the presence of methyl group on the carbon of C=N bond increases the catalytic activity as well, for example the better results obtained from MoO$_2$acpyAmpMCM-41 (runs 17–24 in Table 3) in comparison with MoO$_2$pycaAmpMCM-41 (runs 9–16 in Table 3). The importance of this effect is so pronounced that N,O-donor type catalyst MoO$_2$acacAmpMCM-41 mostly exhibit more activity than N,N-donor type catalyst MoO$_2$pycaAmpMCM-41 (compare runs 9–16 in Table 3 with 1–8 runs in Table 5). A similar effect was observed by Clark and coworkers in Suzuki and Heck reactions catalyzed by similar heterogenized palladium catalysts [19,20].

Epoxidation mechanism can be rationalized as direct oxygen atom transfer from the metal complex derived by coordination of *t*-BuOO⁻ anion to molybdenum center to the olefin [26,27] (Scheme 2). Therefore, reaction of an olefin as a nucleophile with oxygen as an electrophile easily explains the observation that electron rich olefins react faster than electron poor olefins. On the other hand, *tert*-butanol formed as a by-product is capable of coordinating to the molybdenum center and therefore retards the reaction rate. The higher π-accepting character of the bidentate Schiff base ligands derived from functionalized aldehydes can enhance the competitive coordination of *tert*-BuOH (instead of TBHP) to the metal center and make the catalyst less reactive. On the other hand, the more electron withdrawing character of oxygen in comparison to nitrogen makes N,O-donor type catalyst more susceptible to deactivation with *tert*-BuOH and thus lowering TOFs and catalytic activities of these catalysts. Therefore, consideration of these effects in rationalization of reactions results is useful.

To examine whether epoxidation was clearly preceded within the cavities or in solution phase, cyclooctene was allowed to be epoxidized with the same conditions in the presence of six catalysts for 1.5 h. The slurries were then filtered and the fil-

Table 6

Results of epoxidation of cyclooctene with different catalysts after filtration of the catalysts after 1.5 h

Catalyst	Time (h)	Conversion (%)	Selectivity (%)
MoO$_2$furAmpMCM-41 (filtrate)	1.5	39	99
	7	43	92
MoO$_2$pycaAmpMCM-41 (filtrate)	1.5	48	98
	7	55	92
MoO$_2$acpyAmpMCM-41 (filtrate)	1.5	59	99
	7	67	89
MoO$_2$amacAmpMCM-41 (filtrate)	1.5	51	99
	7	60	90
MoO$_2$salAmpMCM-41 (filtrate)	1.5	34	99
	7	36	92
MoO$_2$acacAmpMCM-41 (filtrate)	1.5	56	98
	7	60	89

trates were refluxed for 7 h. The results are presented in Table 6. As seen, although conversions have increased slightly, no further changes are observed during 7 h. Moreover, selectivities toward the formation of epoxides have slightly decreased. This might have been the result of epoxide ring opening reactions induced by the TBHP present in reaction. Since no molybdenum was detected in filtrate solutions, it can be concluded that molybdenum catalysts are stable under the epoxidation reaction conditions.

4. Conclusion

Our work has revealed that incorporation of bidentate Schiff base ligands via reaction of aminopropyl modified MCM-41 with different aldehydes and ketones and subsequent treatment with MoO$_2$(acac)$_2$ afford a new class of heterogeneous molybdenum catalysts for oxidation of alkenes with high reactivity and selectivity toward the formation of the corresponding epoxides.

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