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Investigation of catalytic activities of new heterogeneous molybdenum catalysts in epoxidation of olefins

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ABSTRACT

The mesoporous molecular sieve MCM-41 was covalently grafted with 3-aminopropyl trimethoxysilane and acetyl acetone (acac) successively to give modified MCM-41 (acacAmpMCM-41). Reaction of this material with amino acids, e.g. alanine, phenyl alanine, leucine, isoleucine, histidine and valine afforded the corresponding supported amino acid Schiff base ligands. Subsequent reaction with bis (acetylacetonato)dioxomolybdenum(VI) lead 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.

1. Introduction

Recently there has been increasing trends to develop environmentally friendly processes in industrial chemistry. A subject of concern is the waste minimization by using alternative reagents and catalysts. Also separation of products or catalysts from the reaction mixture is one of the major contributions to waste in a chemical process. In this respect, the use of supported catalysts has been of great interest due to easy separation and more stability of these catalysts, and many attempts have been done on their preparation [1–4].

On the other hand in recent years mesoporous silica materials especially MCM-41 have opened new opportunities for application in the field of supported catalysts due to their large well defined pore sizes and high surface areas [5–9]. Surface functionalization with organosilane reagents and then incorporation of metal complexes is one of the general methods for preparation of supported catalysts based on mesoporous materials [7,8,10–22].

Among the variety of catalytically active metal complexes the transition metals bearing Schiff base ligands are of great interest and several works devoted to investigate their catalytic activities in various catalytic organic reactions [23–28]. Schiff base ligands are able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful catalytic transformations.

A particular class of Schiff bases is amino acid Schiff bases prepared by condensation of amine group of amino acid with a carbonyl group of aldehyde or ketone. There are a few reports on the catalytic application of this type of Schiff base complexes [29–31]. Wang et al. reported the preparation of a Mn(II) phenyl alanine Schiff base and investigated the catalytic activity of the complex in the oxidation of cyclohexene [29]. Also, some oxovanadium(IV) complexes of amino acid Schiff bases were prepared by Maeda and co-workers and the catalytic activity of these complexes were investigated in sulfide oxidation [30]. However, there are few reports on the preparation and investigation of catalytic activity of heterogeneous catalysts based on supported amino acid Schiff bases [32,33].

Here, preparation, characterization and investigation of catalytic activities of molybdenum amino acid Schiff base ligands supported on the surface of MCM-41 in the epoxidation of olefins are investigated.

2. Experimental

2.1. Preparation of MCM-41 and modified MCM-41 (acacAmpMCM-41)

Mesoporous molecular sieve MCM-41 was prepared according to literature method [34]. Modification of the prepared MCM-41 was carried out as follows: MCM-41 (2 g) was suspended in

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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 filtration 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. Preparation of acacAmpMCM-41 material was performed according to [12]. To a mixture of activated AmpMCM-41 (1.5 g) in 25 ml absolute ethanol was added 3 mmol acetyl acteone. The mixture was refluxed for 24 h under dry nitrogen atmosphere to afford acacAmpMCM-41. The solid was filtered, dried and then soxhlet extracted with ethanol to remove the unreacted acac and dried under vacuum at 423 K overnight.

2.2. Preparation of supported amino acid Schiff base ligands

The various supported amino acid Schiff base ligands were prepared according to the standard method used for preparation of amino acid Schiff bases [35]. As a general procedure, to a mixture of activated acacAmpMCM-41 (1.5 g) in 25 ml absolute ethanol was added 3 mmol of amino acids, e.g. alanine, phenyl alanine, leucine, isoleucine, histidine and valine and the mixture was refluxed for 24 h under dry nitrogen atmosphere to afford MCM-41 supported amino acid Schiff base ligands alaAmpMCM-41, phenalaAmpMCM-41, leuAmpMCM-41, isoleuAmpMCM-41, hisAmpMCM-41 and valAmpMCM-41, respectively. The solids were filtered, dried and then soxhlet extracted with methanol to remove the unreacted amino acid and dried under vacuum at 423 K overnight.

2.3. Preparation of supported molybdenum catalysts

$MoO_2(acac)_2$ (650 mg, prepared according to the literature method [36]) was dissolved in ethanol (30 ml). Supported amino acid 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 filtration, 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_2alaAmpMCM-41, MoO_2phenalaAmpMCM-41, MoO_2leuAmpMCM-41, MoO_2isoleuAmpMCM-41, MoO_2hisAmpMCM-41 and MoO_2valAmpMCM-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.

2.4. Characterization

Infrared spectra were recorded using Perkin-Elmer Spectrum RXI FT-IR spectrometer, with a resolution of 4 cm^{-1} and 32 scans, using pellets of the materials diluted with KBr. Powder X-ray diffraction data were collected with a SIEFERT XRD 3003 PTS diffractometer using Cu Kα radiation in the range $2\theta = 1–10^\circ$ with a step size of 0.05° and dwell time of 5 s per point. Chemical analyses of samples were carried out with VARIAN VISTA-MPX ICP-AES atomic absorption spectrometer. Nitrogen sorption studies were performed at liquid nitrogen temperature (77 K) using Quanta chrome Nova 2200, Version 7.11 Analyzer. Before the adsorption experiments the samples were outgassed under nitrogen gas during 3 h at 393 K.

2.5. 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 (100 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 6890N) 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.

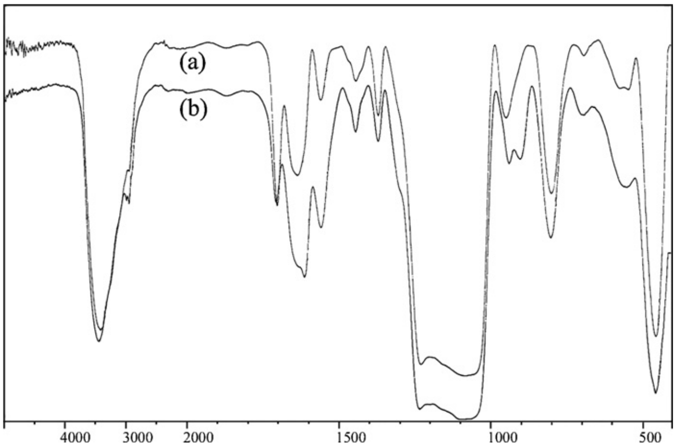


Fig. 1. The typical FT-IR spectra of (a) phenalaAmpMCM-41 and (b) MoO_2, phenalaAmpMCM-41 materials.

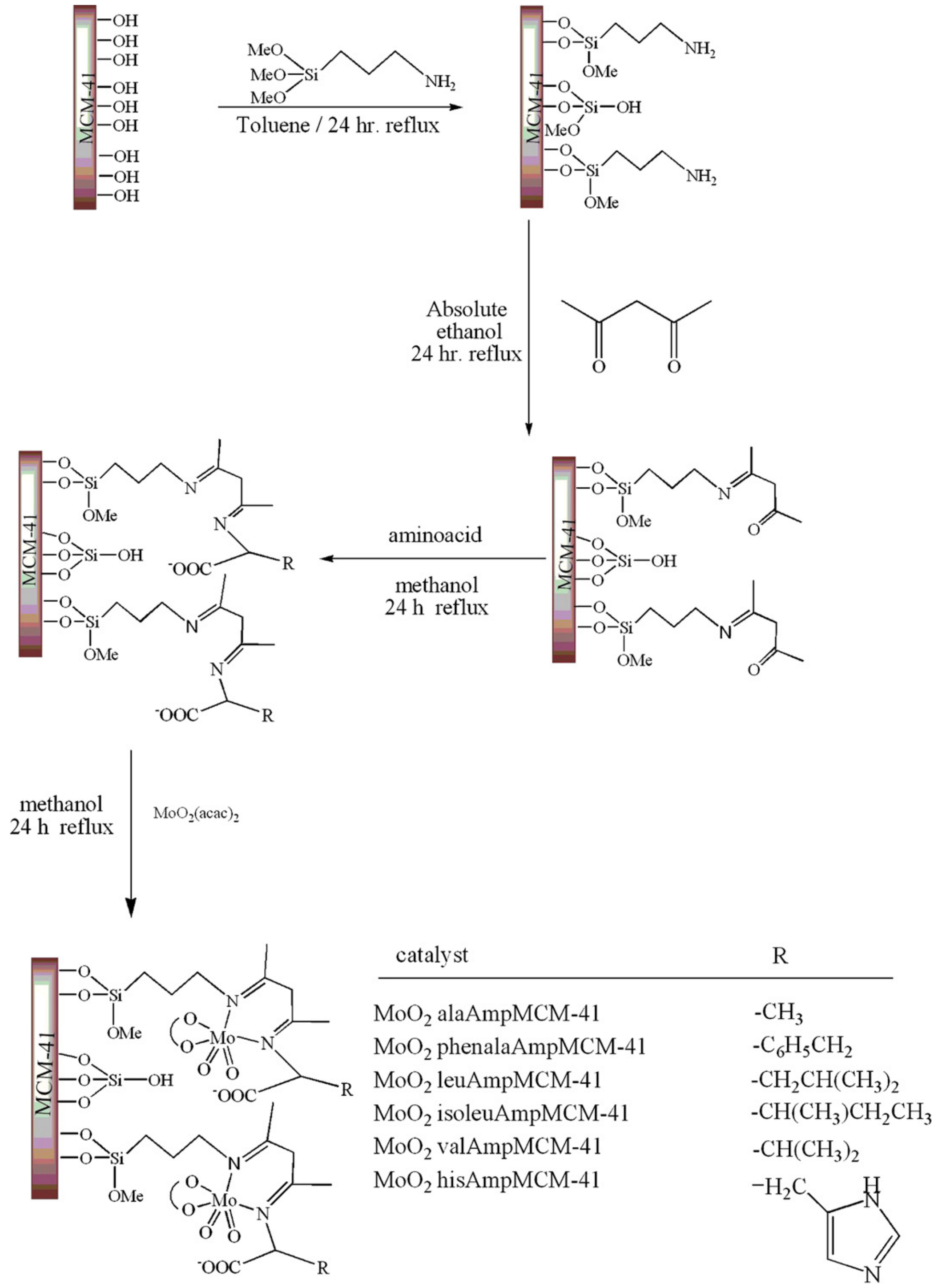
3. Results and discussion

3.1. Preparation and spectroscopic characterization of the catalysts

In the first step MCM-41 was functionalized with aminopropyl groups. Schiff base condensation of the amine groups with one of the carbonyl groups of acetyl acetone afforded a supported bidentate Schiff base ligand [12]. In the next step condensation reaction of amino acids with remaining carbonyl groups lead to the formation of an N, N bidentate Schiff base ligands containing amino acids. For assurance the resulting materials were soxhlet extracted with methanol to remove any unreacted amino acid.

FT-IR spectra showed bands about 1708 and 1635 cm^{-1} assigned to stretching vibrations of COO^- groups of amino acids and C=N bonds, respectively (as typically shown for phenalaAmpMCM-41 in Fig. 1). On the other hand, the bands around 1206, 1060 and 795 cm^{-1} are assigned to stretching vibrations of the mesoporous framework (Si–O–Si). Also, the bands around 2950 and 2850 cm^{-1} arise due to C–H stretching vibrations. The presence of these bands after the functionalization process confirms the presence of the amino acid Schiff base ligand on the MCM-41 samples.

In the last step complexation of the amino acid Schiff base ligands with $MoO_2(acac)_2$ resulted in the preparation of supported molybdenum amino acid Schiff base materials (Scheme 1). In the FT-IR spectra two adjacent band in the range of 890–950 cm^{-1} (Table 1) show the presence of cis-MoO_2 group in the resulted materials [37]. On the other hand, the stretching frequency of C=N group, $\nu_{C=N}$, shifted to lower frequency indicating the involvement of this group in complexation with molybdenum.



Scheme 1. Preparation of the catalysts from acacAmpMCM-41.

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_2alaacacAmpMCM-41	904,939	1614 (1635)	0.60
MoO_2phenalaAmpMCM-41	901,937	1612 (1634)	0.49
MoO_2leuacacAmpMCM-41	910,939	1610 (1637)	0.51
MoO_2isoleuacacAmpMCM-41	912,939	1608 (1636)	0.63
MoO_2hisacacAmpMCM-41	908,939	1608 (1637)	0.53
MoO_2valacacAmpMCM-41	910,939	1608 (1635)	0.45

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

Atomic absorption spectroscopy showed the molybdenum content of the prepared materials (Table 1). This provides another evidence for the presence of supported molybdenum complex.

3.2. Textural properties of the catalysts

X-ray diffractometry confirmed the retention of MCM-41 structure during functionalization with molybdenum amino acid Schiff base complexes. The powder X-ray diffraction patterns of the complexes grafted on MCM-41 show a single peak around $2\theta = 2–3^\circ$ (not shown here), corresponding to the (1 0 0) plane of the hexagonal

Table 2
Texture parameters of samples obtained from XRD.

Material	2θ (°)	XRD d_{100} value (Å)	Lattice parameter[a] (Å)
MCM-41	2.71	32.6	37.6
AmpMCM-41	2.65	33.3	38.4
MoO_2alaacacAmpMCM-41	2.62	33.7	38.9
MoO_2phenalaacacAmpMCM-41	2.60	34.0	39.2
MoO_2leuacacAmpMCM-41	2.55	34.6	39.9
MoO_2isoleuacacAmpMCM-41	2.46	35.8	41.3
MoO_2hisacacAmpMCM-41	2.51	35.2	40.6
MoO_2valacacAmpMCM-41	2.51	35.2	40.6

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

unit cell. The absence of higher angle peaks in the XRD patterns of functionalized materials (corresponding to (1 1 0), (2 0 0) and (2 1 0) planes) indicates the contrast matching due to incorporation of the complexes into the pores of MCM-41 material. Also the position of the reflection shifted to lower angle (or higher *d*-value) that indicates the expansion of unit cell parameter as a result of incorporation of the complexes within the pores of MCM-41 (Table 2).

The low temperature N_2 adsorption/desorption analyses was performed in order to investigate the textural properties of the resulted materials such as surface area, pore volume and pore diameter, after incorporation of molybdenum amino acid Schiff base complexes. For the parent MCM-41 (not shown) and functionalized materials the isotherms are of type IV according to the IUPAC classification representing the mesoporous cylindrical pores (Fig. 2). The appearance of a hysteresis loop in the isotherm represents capillary condensation of nitrogen gas inside the mesopores. The inflection point shifted to lower relative pressures and the volume of nitrogen adsorbed decreased upon functionalization and molybdenum complex incorporation, which is indicative of reduction in the pore size.

After functionalization and molybdenum incorporation a decrease in the surface area (S_{BET}), pore volume and average pore diameter was observed (Table 3). As expected, this indicates the presence of molybdenum complex tethered to the pore walls and partially blocking the adsorption of nitrogen molecules. The order of increasing surface area is as follows:

MoO_2alaAmpMCM-41 > MoO_2isoleuAmpMCM-41 > MoO_2leuAmpMCM-41 > MoO_2valAmpMCM-41 > MoO_2hisAmpMCM-41 > MoO_2phenalaAmpMCM-41.

This trend in increasing surface area is relatively consistent with the steric demand of the side chains of amino acid groups. As the side chain is more bulky the corresponding surface area was decreased.

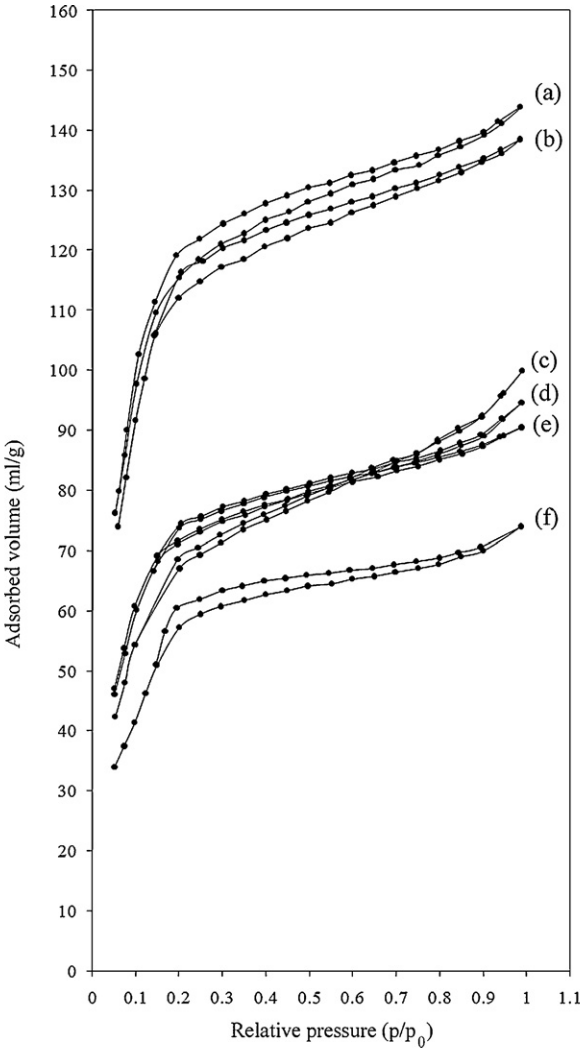


Fig. 2. Nitrogen sorption isotherms of MCM-41 supported (a) MoO_2ala, (b) MoO_2isoleu, (c) MoO_2his, (d) MoO_2leu, (e) MoO_2val and (f) MoO_2phenala acacAmp Schiff base materials.

3.3. *Catalytic epoxidation of olefins*

The catalytic activities of the prepared MCM-41 supported molybdenum amino acid Schiff bases were investigated in the epoxidation of cyclooctene, cyclohexene, 1-octene and 1-hexene with tert-butyl hydroperoxide and the relevant data as well as turn over frequencies (TOF's) are presented in Table 4. As expected all catalysts are active for epoxidation reaction with nearly 100% of selectivity to epoxides. Blank experiments, performed without catalysts or with purely MCM-41, showed a very low cyclooctene conversion and epoxide selectivity even after 12 h reaction.

In order to investigate the effect of the catalysts on the rate of reactions samples were withdrawn periodically and analyzed with GC. The plots of the conversions of cyclooctene at different times were studied and are shown in Fig. 3. The time dependent curves obtained for the catalysts show that initially the reaction is

Table 3
Texture parameters of samples obtained from nitrogen sorption studies.

Material	Average pore diameter (Å)	Total pore volume (ml g^{-1})	BET specific surface area ($m^2\ g^{-1}$)
MCM-41	28.2	0.851	1211
AmpMCM-41	19.0	0.35	753
MoO_2alaacacAmpMCM-41	18.0	0.19	413
MoO_2phenalaacacAmpMCM-41	17.3	0.09	216
MoO_2leuacacAmpMCM-41	18.1	0.12	256
MoO_2isoleuacacAmpMCM-41	17.9	0.18	403
MoO_2hisacacAmpMCM-41	17.5	0.11	244
MoO_2valacacAmpMCM-41	18.0	0.12	255

Table 4
Results of catalytic epoxidation of some olefins with TBHP in the presence of catalysts.

Catalyst	Run number	Substrate	Time (h)	Conversion[a] (%)	Epoxide (%)	TOF[b] (h^{-1})
MoO_2alaacacAmpMCM-41	1	Cyclooctene	9	87	99	124
	2	Cyclooctene[c]	2	18	100	115
		Cyclooctene[d]	7	21	97	–
	3	Cyclohexene	9	30	98	43
	4	1-Hexene	9	20	98	28
	5	1-Octene	9	18	100	26
MoO_2phenalaacacAmpMCM-41	6	Cyclooctene	9	99	99	172
	7	Cyclooctene[c]	2	68	100	376
		Cyclooctene[d]	7	50	98	–
		Cyclooctene[e]	9	94	99	163
	8	Cyclohexene	9	87	99	152
	9	1-Hexene	9	80	100	139
	10	1-Octene	9	57	100	99
MoO_2leuacacAmpMCM-41	11	Cyclooctene	9	87	99	146
	12	Cyclooctene[c]	2	8	98	60
		Cyclooctene[d]	7	11	96	–
	13	Cyclohexene	9	86	98	144
	14	1-Hexene	9	38	100	64
	15	1-Octene	9	23	100	38
MoO_2isoleuacacAmpMCM-41	16	Cyclooctene	9	75	99	102
	17	Cyclooctene[c]	2	17	100	104
		Cyclooctene[d]	7	20	97	–
	18	Cyclohexene	9	59	98	80
	19	1-Hexene	9	46	100	62
	20	1-Octene	9	25	99	34
MoO_2hisacacAmpMCM-41	21	Cyclooctene	9	73	99	118
	22	Cyclooctene[c]	2	26	100	188
		Cyclooctene[d]	7	27	98	–
	23	Cyclohexene	9	70	98	113
	24	1-Hexene	9	23	100	37
	25	1-Octene	9	17	98	27
MoO_2valacacAmpMCM-41	26	Cyclooctene	9	35	99	66
	27	Cyclooctene[c]	2	5	100	43
		Cyclooctene[d]	7	6	98	–
	28	Cyclohexene	9	15	98	28
	29	1-Hexene	9	10	100	19
	30	1-Octene	9	8	100	15
No molybdenum species	31	Cyclooctene[f]	12	14	41	–
	32	Cyclooctene[g]	12	21	51	–

Reaction conditions: catalyst (100 mg), olefin (8 mmol), TBHP (14.4 mmol), refluxing $CHCl_3$ (20 ml).

[a] Calculated using isooctane as internal standard.

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

[c] Catalytic activity immediately after catalyst separation (2 h).

[d] Reaction progress after 5 h of catalyst separation.

[e] Reaction was carried out in the presence of recovered catalyst.

[f] Reaction was carried out without catalyst.

[g] Reaction was carried out in the presence of MCM-41.

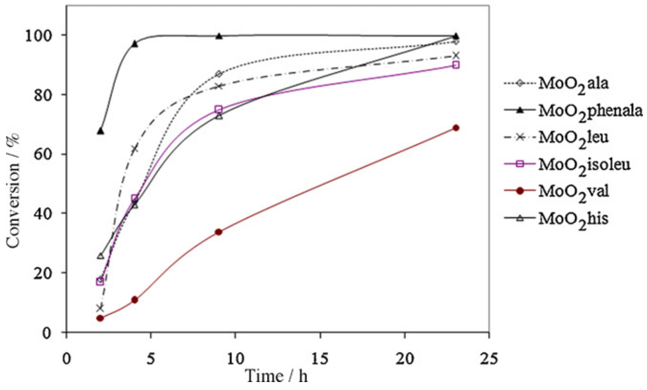
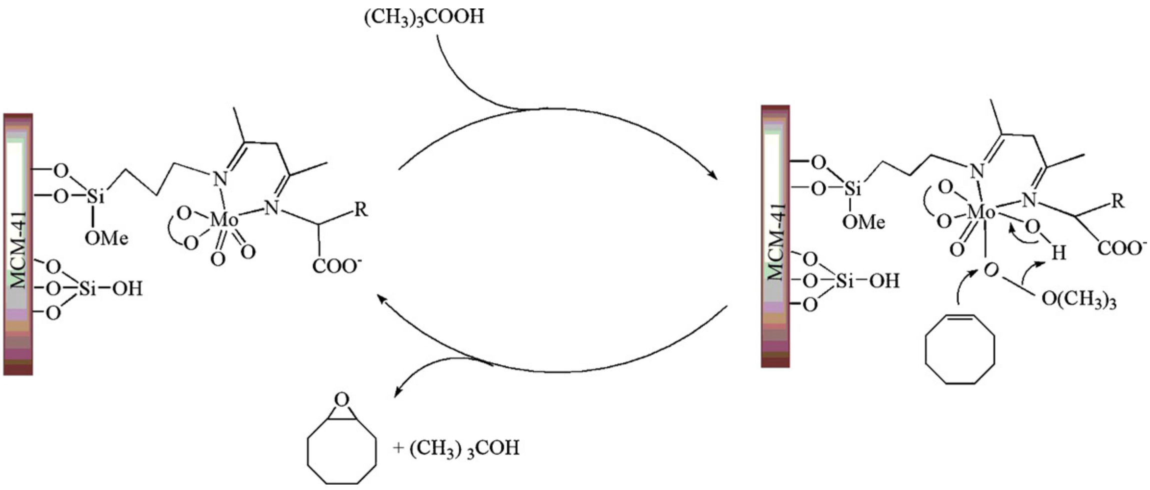


Fig. 3. The plots of the conversions of cyclooctene at different times in the presence of prepared molybdenum catalysts.

fast, indicating that the active oxidizing species are formed rapidly upon addition of the alkyl hydroperoxide to the reaction mixture. Then the reaction rate decreases progressively, which may result from the formation of tert-butyl alcohol in the course of the reaction (Scheme 2) which then competes with TBHP for coordination to the molybdenum center. As seen, under the reaction conditions applied, in the case of MoO_2phenalaAmpMCM-41 and MoO_2leuAmpMCM-41 the olefin conversion increased more than the others. In the case of MoO_2valAmpMCM-41 the reaction rate increases lower than others, probably due to more steric hinderance of the ligand toward the approach of olefin.

For a given substrate, catalytic activities and TOF's increase as MoO_2phenalaAmpMCM-41 > MoO_2leuAmpMCM-41 > MoO_2isoleuAmpMCM-41 > MoO_2hisAmpMCM-41 > MoO_2alaAmpMCM-41 > MoO_2valAmpMCM-41. This trend is explained with considering the fact that tert-butanol formed as a byproduct is capable of coordinating to the molybdenum center and therefore retards the reaction rate. The higher π-accepting character of the complex can enhance the competitive coordi-



Scheme 2. Proposed mechanism of epoxidation of olefins in presence of the prepared catalysts.

nation of tert-BuOH (instead of TBHP) to the metal center and make the catalyst less reactive. Increasing electron density on the molybdenum center (e.g. phenyl group in MoO_2phenalaAmpMCM-41) decreased the π-accepting character of the complex and thus the deactivation by coordinating tert-BuOH may be lowered.

The investigation of the results in Table 4 reveals another trend affecting the conversion of olefins. The order of increasing reactivities are as cyclooctene > cyclohexene > 1-hexene > 1-octene. Two determining parameters of electronic and steric effects should be taken into consideration to explain this trend. Based on the epoxidation mechanism suggested earlier [38] higher electron donating ability of olefin double bond is expected to show more epoxidation reactivity. Therefore, cyclooctene and cyclohexene with inner double bonds should exhibit more activities in comparison with 1-hexene and 1-octene which contain terminal double bonds. On the other hand, cyclooctene is more reactive than cyclohexene due to the presence of more electron donating group 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.

Stability of the prepared catalysts was investigated in separate tests in which epoxidation of cyclooctene was allowed to proceed 2 h and then reaction mixture was filtered. The filtrate was allowed to further react under the same reaction conditions. The conversions and selectivities were determined immediately (after 2 h) and also after 7 h (Table 4). It was found that after separation of the catalyst the conversion only slightly increased and then remains constant. Instead, selectivity toward formation of epoxide was decreased slightly probably as a result of epoxide ring opening reaction or decomposition of the remained TBHP and side reaction with cyclooctene.

The stability of the MoO_2phenalaAmpMCM-41 as a typical catalyst was also 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 0.45 wt% with little change with respect to initial catalyst. The recovered catalyst was used again in epoxidation of cyclooctene with TBHP. As shown in Table 4, minor decrease in conversion and TOF were observed although selectivity remains unchanged. Such observation confirms the presence of affixed Molybdenum complex within MCM-41. Thus, it can be deduced that the catalytic epoxidation is truly heterogeneous in nature.

4. Conclusion

Our work has revealed that incorporation of amino acid Schiff base ligands via reaction of acacAmpMCM-41 with different amino acids and subsequent treatment with $MoO_2(acac)_2$ affords a new class of heterogeneous molybdenum catalysts for oxidation of olefins with high activity and selectivity toward the formation of the corresponding epoxides.

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