New Molybdenum Epoxidation Catalyst Derived From Nanoporous MCM-41 Supported Glycine Schiff-Base

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Abstract

Covalent grafting of the nanoporous molecular sieve MCM-41 with 3-aminopropyl trimethoxysilane and acetyl acetone (acac) successively gave modified MCM-41 (acacAmpMCM-41). Reaction of the resulted material with glycine afforded the corresponding supported glycine Schiff base ligand and subsequent reaction with [bis(acetylacetonato)dioxomolybdenum(VI)] was lead to molybdenum complex supported on MCM-41 through propyl chain spacer. Characterization of the resulting material was carried out with FT-IR, atomic absorption spectroscopy, powder X-ray diffraction and BET nitrogen sorption methods. The XRD and BET analyses revealed that textural properties of support were preserved during the grafting experiments. The resulted material successfully catalyzed the epoxidation of olefins with *tert*-butyl hydroperoxide to the corresponding epoxides.

1. Introduction

In recent years epoxidation of olefins in the presence of high valent molybdenum and tungsten compounds with oxo ligands have attracted considerable academic and industrial interests [1-12]. These compounds are known to catalyze various industrially valuable processes such as olefin epoxidation and alcohol oxidation. Recent developments in green chemistry have introduced

a number of compelling requirements that should be met in the development of practical catalysts [1-3]. Since from environmental and economical point of view, the use of heterogeneous catalysts offers several advantages, such as easy separation of the products, possibility of recovery and repeated use and designing continuous processes, there is a considerable academic and industrial interest in the heterogenization of well-defined homogeneous catalysts [4-7]. One of the main

methods for transforming a homogeneous catalyst to heterogeneous one is the anchoring of the active catalytic site on a solid having a large surface area.

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) [8]. Since the discovery of nanoporous molecular sieve MCM-41 by Mobil group in 1992 [9], great efforts have been devoted to utilization of this type of support in heterogenization of some transition metal catalysts [4-7, 10-15]. This type of support has several advantages such as retaining a rigid exposed surface area in comparison to conventional polymer beads typically swell and shrink variably in different media, or consisting of ordered array of hexagonal channels with a pore diameter in the mesoporous region, which permits a lower diffusional resistance for the reactant molecules to access the metal active sites located within the channels.

Amino acid Schiff bases prepared by condensation of amine group of amino acid with a carbonyl group of aldehyde or ketone are interesting ligands and there are a few reports on the catalytic application of this type of Schiff base complexes [16-18]. However, there are few reports on the preparation and investigation of catalytic activity of heterogeneous catalysts based on supported amino acid Schiff bases [19-20].

Here, preparation, characterization and investigation of catalytic activities of a supported molybdenum complex of Schiff base ligand derived from glycine on the surface of nanoporous MCM-41 is investigated. The prepared heterogenized catalyst successfully catalyzed the epoxidation of olefins with good activities and selectivities.

2. Experimental

2.1. Instrumentation

Infrared spectra were recorded using Perkin-Elmer Spectrum RXI FT-IR spectrometer. Powder X-ray diffraction data were collected with a SIEFERT XRD 3003 PTS diffractometer using Cu Kα radiation. Scanning electron micrographs (SEM) of the samples were taken with ZEISS-DSM 960A microscope with attached camera. 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 using Quanta chrome Nova 2200, Version 7.11 Analyzer.

2.2. Preparation of supported glycine Schiff base ligand

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 (1g) was then added under dry nitrogen atmosphere. The resultant mixture was refluxed for 24 hours. After separation the resultant material was soxhlet extracted with dichloromethane 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 [22].

The supported glycine Schiff base ligand was prepared according to the standard method used for preparation of Schiff bases [23, 24]. To a mixture of activated acacAmpMCM-41 (1.5 g) in 25 ml absolute ethanol was added 3 mmol of glycine. The mixture was refluxed for 24 hours

under dry nitrogen atmosphere to afford MCM-41 supported glycine Schiff base glyacacAmpMCM-41. The solid was filtered, dried and then soxhlet extracted with methanol to remove the unreacted glycine and dried under vacuum at 423 K overnight.

2.3. Preparation of supported molybdenum catalyst

$MoO_2(acac)_2$ (650 mg, prepared according to the literature method [25]) was dissolved in ethanol (30ml). Supported glycine Schiff base ligand (1g, dried in vacuum oven at 423 K) was then added to this solution and the mixture was refluxed for 12 hours. After filtration, the product was dried and then soxhlet extracted with dichloromethane to remove the unreacted $MoO_2(acac)_2$. The resultant molybdenum containing material MoO_2glyacacAmpMCM-41 was 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. Catalytic epoxidations

Epoxidation of olefins such as cyclooctene, cyclohexene, 1-octene and 1-hexene with tert-butyl hydroperoxide (TBHP, 80% in di-tertiary butyl peroxide) as oxidant was carried out in a 25 ml round bottom flask equipped with a condenser and a magnetic stirrer. 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 (1g, 8.75 mmol) as internal standard. GC-MS of products were recorded using a Shimadzu-14A fitted with a capillary column (CBP5-M25).

3. Results and discussion
3.1. Preparation and spectroscopic investigation of the catalyst

The supported glycine Schiff base ligand was prepared via the reaction of acacAmpMCM-41with glycine. According to Scheme 1 Schiff base condensation of AmpMCM-41 (prepared with reaction of γ-aminopropyl trimethoxy silane with silanol groups of the surface of the MCM-41) with acetyl acetone resulted in acacAmpMCM-41 material [19] that contains one carbonyl group per each grafted acac ligand. Reaction of this carbonyl group with amine group of glycine gave rise to the formation of glyacacAmpMCM-41 material.

In the FT-IR spectrum of the resulting material (Figure 1) the presence of a band at 1706 cm^{-1} is attributed to the presence of COO^{-} group of glycine. Also the band around 1635 cm^{-1} indicates the presence of C=N groups. Subsequent reaction of the glyacacAmpMCM-41 with $MoO_2(acac)_2$ resulted in the preparation of supported
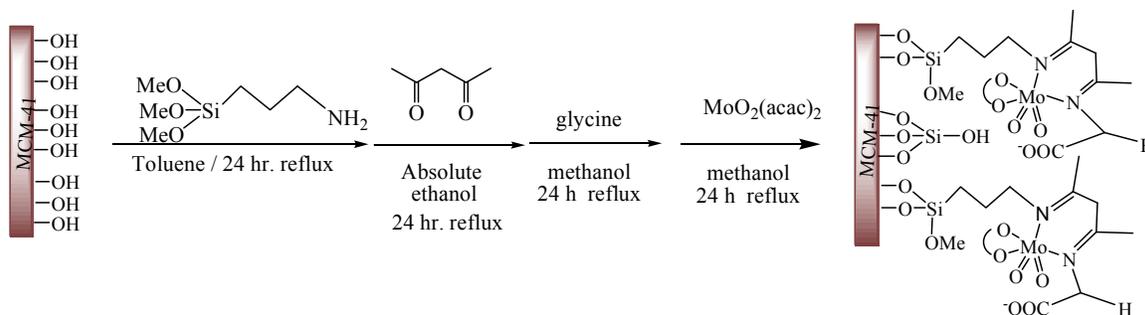
Scheme 1. Schematic illustration of MoO₂glyacacAmpMCM-41 preparation.

Table 1. Spectroscopic data of the prepared catalyst.

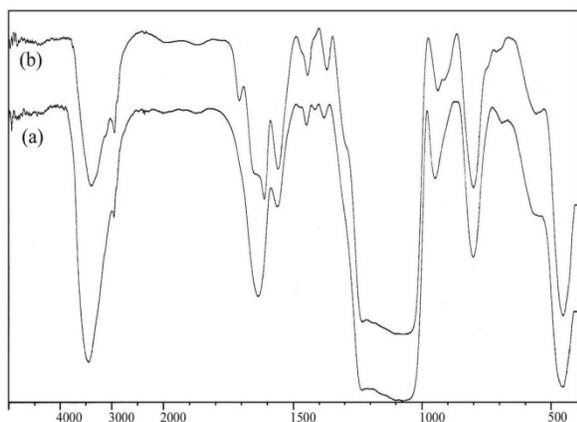| Material	$\upsilon_{Mo=O}$ (cm^{-1})	$\upsilon_{C=N}$ (cm^{-1})	Mo loading (%wt.)
glyacacAmpMCM-41	-	1635	-
MoO₂glyacacAmpMCM-41	911, 939	1612	0.71

Fig. 1. FT-IR spectra of (a) glyacacAmpMCM-141 and (b) MoO₂ glyacacAmpMCM-41.

molybdenum glycine Schiff base material MoO₂glyacacAmpMCM-41. The presence of cis-MoO₂ group was confirmed by appearance of two adjacent bands at 911 and 939 cm^{-1}, due to symmetric and asymmetric stretching vibrations of cis-MoO₂ group, in the FT-IR spectrum of this material [26]. On the other hand, the shift of the $\upsilon_{C=N}$ to lower frequencies (Table 1) is another evidence for the complexation of supported glycine Schiff base.

Atomic absorption spectroscopy showed the 0.71 %wt molybdenum content of the material (Table1). Since determination of the molybdenum content was carried out after soxhlet extraction of the prepared materials thus any contribution from physically adsorbed species on the surface should be negligible.

3.2. Textural properties of the catalyst

The powder x-ray diffraction (XRD) pattern of MoO₂glyacacAmpMCM-41 exhibits only one peak due to the < 1 0 0 > reflection in 34.74 Å (Figure 2 and Table 2). The reduction of the scattering contrast between the silica walls and the pore filling material resulted in loss of the other reflections of parent MCM-41 and decreasing the intensity of < 1 0 0 > reflection. Also, compared to MCM-41 the increase in lattice parameter of this material indicates the unit cell expansion due to the incorporation of molybdenum complex within MCM-41.
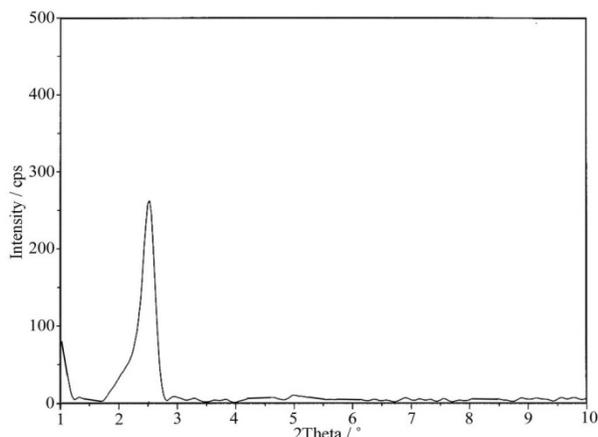
Table 2. Texture parameters of samples taken from XRD studies.

Solid	$2\theta/^o$	d value (Å)	Lattice parameter[a] (Å)
MCM-41	2.71	32.57	37.61
AmpMCM-41	2.65	33.26	38.41
MoO$_2$glyacacAmpMCM-41	2.54	34.74	40.11

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

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

Solid	BET specific surface area ($m^2.g^{-1}$)	Total pore volume (ml. g^{-1})	Average pore diameter (Å)
MCM-41	1211	0.851	28.2
AmpMCM-41	753	0.35	19
MoO$_2$glyacacAmpMCM-41	477	0.22	17.85

Fig. 2. X-ray diffraction pattern of MoO$_2$glyacacAmpMVM-41.

Nitrogen sorption isotherms of the prepared materials are shown in Figure 3. All of these materials show type IV isotherms (according to IUPAC classification) typical of mesoporous materials. As indicated in these isotherms after each functionalization the amount of physisorbed nitrogen decreased and a decrease in the S_{BET}, pore volume and average pore diameter was observed (Table 3). Also, the inflection points of the isotherms are shifted to lower values, as expected for smaller pores. As expected, this indicates the presence of molybdenum complex tethered to the pore walls and partially blocking the adsorption of nitrogen molecules.

The morphology and microstructure of the obtained material was further investigated by scanning electron microscopy (SEM). Figure 4 shows the SEM image of MoO$_2$glyacacAmpMCM-41. This image clearly shows that obtained materials have ellipsoidal morphologies and monodispersed.

3.3. Catalytic activity and stability of the catalyst

The catalytic activity of the prepared MoO$_2$glyacacAmpMCM-41 was investigated in the epoxidation of some olefins such as cyclooctene, cyclohexene, 1-octene and 1-hexene with tert-BuOOH. Table 4 shows the conversions and selectivities as well as turnover frequencies (TOFs) (mmol of product formed per mmol of molybdenum in catalyst). The results with parent MCM-41 and blank (no catalyst) are also included in this table to make the comparison more convenient.
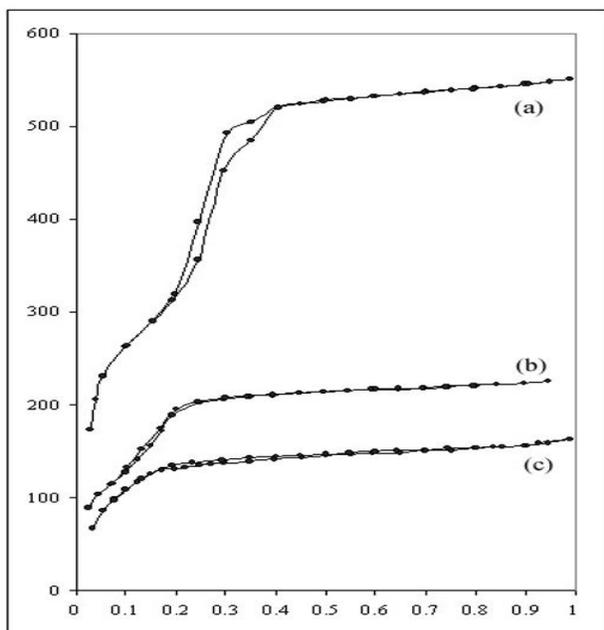
Fig. 3. Nitrogen sorption isotherms of (a) MCM-41, (b) AmpMCM-41 and (c) MoO$_2$glyacacAmpMCM-41.
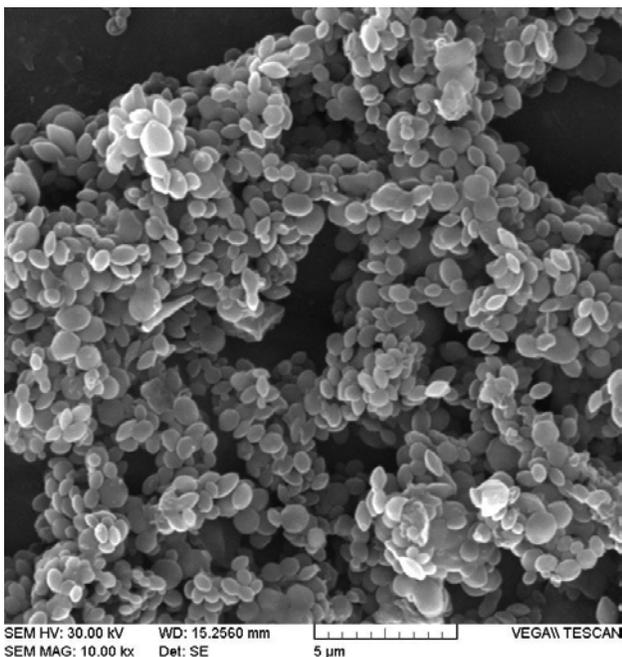

Fig. 4. SEM image of MoO$_2$glyacacAmpMCM-41 material.

Considering the results shows that the order of reactivity of olefins in epoxidation reaction is as follows:

cyclooctene > cyclohexene > 1-hexene >1-octene.

As seen in this series increasing the electronic density on the C=C double bond results in increasing the reactivity of the olefin. This observation is explained by considering the mechanism of epoxidation in the presence of molybdenum catalysts reported in previous works [27]. On the basis of this proposed mechanism in the first step tert-BuOOH attacks on the molybdenum center and produce alkyl peroxo molybdenum intermediate. The peroxidic oxygen in this species has electrophilic character and direct transfer of this oxygen atom to the olefin offers the epoxide as the major product of the reaction. 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. The other byproducts probably are produced by ring opening of the formed epoxide.

The stability of the MoO$_2$glyacacAmpMCM-41 catalyst was studied by determination of metal content after filtering the reaction mixture using atomic absorption spectroscopy. The molybdenum content of recovered catalyst was shown to be 0.69 %wt with little change with respect to initial catalyst.

On the other hand, to examine whether epoxidation was clearly performed within the pores or in solution phase, cyclooctene was allowed to be epoxidized with the same conditions in the presence of the catalyst for 2 hours. The reaction mixture was then filtered and the filtrate was refluxed for 7 hours. The results are presented in Table 4. As seen, conversion has increased slowly. Moreover, selectivity toward the formation of epoxides has

slightly decreased. This might has been the result of epoxide ring opening reaction. Since no molybdenum was detected in filtrate solution, it can be concluded that molybdenum catalyst is stable under the epoxidation reaction condition. Thus, it can be deduced that the catalytic epoxidation is truly heterogeneous in nature.

4. Conclusion

Functionalization of MCM-41 with a glycine Schiff base ligand and subsequent complexation with molybdenum affords a truly new heterogenized molybdenum catalyst which is active in catalytic epoxidation of olefins in the presence of tert-BuOOH.

Table 4. Results of catalytic epoxidation of some olefins with TBHP in the presence of MoO_2glyacacaAmpMCM-41

Run number	Substrate	Time (h)	Conversion [a] (%)	Epoxide (%)	TOF [b] (h^{-1})
1	cyclooctene	2	54	>99.9	146
2		4	89	>99.9	
3		7	99	>99.9	
4		9	99.9	>99.9	
5[c]		7	57	94	
6[d]		12	14	41	
7[e]		12	21	51	
8	cyclohexene	2	17	>99.9	46
9		4	68	97	
10		9	85	>99	
11		24	97	>99	
12	1-hexene	2	12	>99.5	32
13		4	18	>99	
14		9	29	>99	
15		24	72	>99	
16	1-octene	2	5	95	14
17		4	10	>99	
18		9	26	>98	
19		24	53	>98	

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

[a] Calculated using isooctane as internal standard

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

[c] Catalytic test after filtration of the catalyst after 2 hours.

[d] Reaction was carried out without catalyst.

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

References

[1] J.H. Clark, D.J. Macquarrie, Chem. Soc. Rev. 25 (1996) 303-310.

[2] J.H. Clark, Pure Appl. Chem. 73 (2001) 103-111.

[3] P.T. Anastas, M.M. Kirchhoff, T.C. Williamson, Appl. Catal. A: 221 (2001) 3-13.

[4] A. Choplin, F. Quignard, Coord. Chem. Rev. 178-180 (1998) 1679-1702.

[5] M.H. Valkenberg, W.F. Holderich, Cat. Rev. 44 (2002) 321-374.

[6] D. Trong On, D. Desplantier-Giscard, C. Danumah, S. Kaliaguine, Appl. Catal. A. 222 (2001) 299-357.

[7] A. Taguchi, F. Schuth, Micropor. Mesopor. Mater. 77 (2004) 1-45.

[8] F. Di Renzo, H. Cambon, R. Dutarte, Micropor. Mater. 10 (1997) 283-286.

[9] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schenker, J. Am. Chem. Soc. 114 (1992) 10834-10843.

[10] B. De Clerck, F. Lefebvre, F. Verpoort, Appl. Catal. A 247 (2003) 345-364.

[11] C. Baleizao, B. Gigante, M. Sabater, H. Garcia, A. Corma, Appl. Catal. A 228 (2002) 279-288.

[12] S.H. Lau, V. Caps, K.W. Yeung, K.Y. Wong, S.C. Tsang, Micropor. Mesopor. Mater. 32 (1999) 279-285.

[13] M. Masteri-Farahani, F. Farzaneh, M. Ghandi, Catal. Commun. 8 (2007) 6-10.

[14] M. Masteri-Farahani, F. Farzaneh, M. Ghandi, J. Mol. Catal. A: 243 (2006) 170-175.

[15] S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpour-Baltork, K. Ghani, Catal. Commun. 10 (2009) 853-858.

[16] R.M. Wang, C.J. Hao, Y.P. Wang, J. Mol. Catal. A: 147 (1999) 173-178.

[17] R. Ando, H. Inden, M. Sugino, H. Ono, D. Sakaeda, T. Yagyu, M. Maeda, Inorg. Chim. Acta, 357 (2004) 1337-1344.

[18] X.W. Liu, N. Tang, Y.H. Chang, M.Y. Tan, Tetrahedron: Asymmetry, 15 (2004) 1269-1273.

[19] J. Zhao, J. Han, Y. Zhang, J. Mol. Catal. A: 231 (2005) 129-135.

[20] M. Masteri-Farahani, J. Mol. Catal. A: 316 (2010) 45-51.

[21] Q. Cai, W.Y. Lin, F.S. Xiao, W.Q. Pang, J. Micropor. Mesopor. Mater. 32 (1999) 1-15.

[22] M. Masteri-Farahani, F. Farzaneh, M. Ghandi, J. Mol. Catal. A: 248 (2006) 53-60.

[23] W.E. Estes, W.E. Hatfield, Inorg. Chem. 17 (1978) 3226-3231.

[24] M.J. O'Donnel, R.L. Polt, J. Org. Chem. 47 (1982) 2663-2666.

[25] G J. Chen, J.W. Mc Donald, W.E. Newton, Inorg.Chem. 15 (1976) 2612-2615.

[26] J. Topich, Inorg. Chem. 20 (1981) 3704-3707.

[27] R.A. Sheldon, J. Van doorn, J. Catal. 31 (1973) 427-437.