

Molybdenum-Schiff Base Complex Immobilized on Magnetite Nanoparticles as a Reusable Epoxidation Catalyst

Masteri-Farahani, Majid⁺*

Faculty of Chemistry, Kharazmi University, Tehran, I.R. IRAN

Taghizadeh, Fereshteh

Faculty of Chemistry, Ardabil Branch, Islamic Azad University, Ardabil, I.R. IRAN

ABSTRACT: *The surface of magnetite nanoparticles as nano-sized solid support was modified with a molybdenum-Schiff base complex to prepare an easily separable heterogeneous catalyst for the epoxidation of olefins. Characterization techniques such as Fourier transform infrared and inductively coupled plasma optical emission spectroscopies, X-ray diffraction, vibrating sample magnetometry, scanning, and transmission electron microscopies indicated the presence of molybdenum-Schiff base complex and a magnetite core in the catalyst. The magnetite nanoparticles supported Mo catalyst exhibited high catalytic activity and selectivity toward the epoxidation of olefins and was easily recovered from the reaction mixture by magnetic separation to be utilized for subsequent reactions. The catalyst showed reusability for three times without significant loss of activity.*

KEYWORDS: *Magnetite; Molybdenum; Recoverable; Catalyst; Epoxidation.*

INTRODUCTION

Although many selective homogeneous catalysts have been developed so far, their practical uses in industrial processes are inhibited by their high costs as well as problems in their separation from the reaction mixtures. To overcome these difficulties, many various approaches have been utilized to prepare immobilized catalysts [1,2]. When used in liquid phase reactions, catalysts immobilized on solid supports have a high surface area as well as additional advantage of the facile recovery. Preferably, the solid support should possess a large surface area to increase the catalyst loading and activity. Besides making the support porous, it is also possible

to increase the surface area by reducing the particle size of the support. Owing to their high surface area and more accessibility to the reactants, nanoparticles have been considered as novel supports to prepare immobilized catalysts [3-5]. However, conventional separation methods may become ineffective for small support particle sizes. The incorporation of magnetic materials into the supports provides a solution to this problem. Among the various magnetic nanoparticles, superparamagnetic materials such as magnetite nanoparticles are of great importance. They can be readily magnetized in the presence of an external

* To whom correspondence should be addressed.

+ E-mail: mfarahani@khu.ac.ir

1021-9986/2018/6/35-42

8/\$/5.08

magnetic field. Due to this particular property, superparamagnetic materials have been widely used in various biomedical applications, such as DNA purification [6], MRI contrast enhancement [7,8], drug targeting [8,9] and catalysis [10-12].

The coordination chemistry of molybdenum (VI) has attracted great attention due to its recently found biochemical importance [13,14], as well as the involvement of Mo (VI), compounds as catalysts in some industrially important processes, such as olefin metathesis [15,16], and epoxidation of olefins [17-20]. Recently, we reported the catalytic activity of some molybdenum complexes covalently anchored onto the MCM-41 mesoporous material and magnetite nanoparticles in the selective epoxidation of olefins [21-23].

Herein, we report the design of a novel heterogenized molybdenum-Schiff base catalyst composed of a magnetite core which made the catalyst magnetically recoverable and its application in the selective epoxidation of olefins. The catalyst can be simply separated with an external magnet without additional filtration step. Thus, the process is green and solves the problems associated with mass transfer and catalyst recycling in other heterogeneous catalysts.

EXPERIMENTAL SECTION

Preparation of the Mo-Schiff base-SCMNPs catalyst

All solvents and reagents were purchased from Merck Corporation and used without further purification. The Schiff base ligand was synthesized according to the literature method [24]. Aminopropyl-modified silica coated magnetite nanoparticles (Amp-SCMNPs) were synthesized according to our previous work [23]. For the immobilization of Schiff base ligand on the surface of silica coated magnetite nanoparticles, vacuum dried Amp-SCMNPs (1 g) were suspended in 30 ml of ethanol. Then, the Schiff base ligand (2 mmol) was added to this mixture and refluxed for 8h. The product, Schiff base-SCMNPs, was separated with a permanent magnet, washed with ethanol and vacuum dried. The prepared Schiff base-SCMNPs (1.0 g, dried in a vacuum oven at 353K) was dispersed in 30 mL ethanol with sonication. To this mixture was added a solution of $\text{MoO}_2(\text{acac})_2$ (2 mmol, prepared according to literature method [25]) dissolved in 20 mL ethanol. The mixture was refluxed for 24 h under

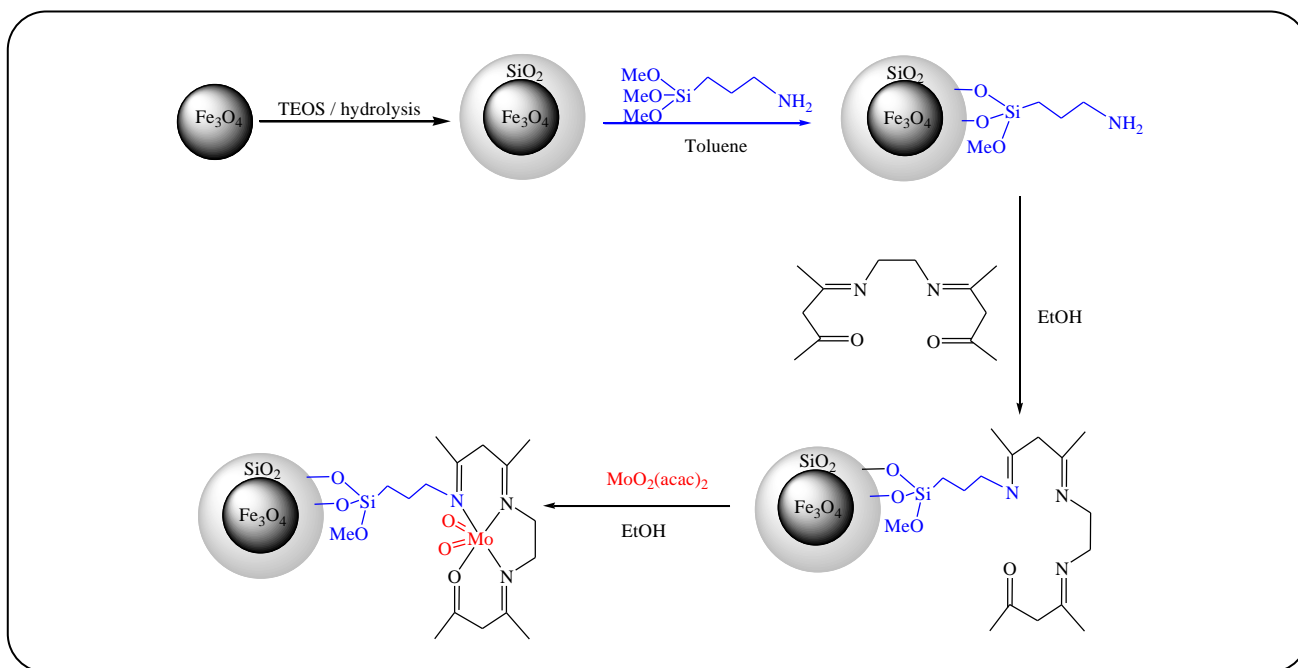
nitrogen atmosphere. The product was separated with a permanent magnet and washed with ethanol. The obtained Mo-Schiff base-SCMNPs was soxhlet extracted with ethanol to remove unreacted reagents and was dried under vacuum at 353 K.

General Procedure for the epoxidation of olefins

The prepared catalyst (0.1 g), olefin (8 mmol), tert-butylhydroperoxide (16 mmol) and chloroform (10 mL) were added in a 25 ml round-bottom flask. The mixture was allowed to reflux under nitrogen atmosphere. The reaction was monitored constantly by Gas Chromatography (GC). After completion of the reaction, the magnetic catalyst was separated by an external magnet. The reaction solution was removed from the reaction vessel by decantation while the external magnet held the catalyst inside the flask. The catalyst was then washed with methanol, separated by magnetic decantation as described above, and dried at 353 K under vacuum overnight for the recycling experiment.

Instrumentation

Fourier Transform Infra-Red (FT-IR) spectra were recorded as potassium bromide pellets in the range 400-4000 cm^{-1} using a Perkin-Elmer Spectrum RXI FT-IR spectrometer. X-Ray Diffraction (XRD) patterns were recorded on a SIEFERT XRD 3003 PTS diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda=0.154$ nm). A continuous scan mode was used for 2θ collection from 10 to 60°. Magnetic susceptibility measurements were performed using a vibrating sample magnetometer (BHV-55, Riken, Japan) in the magnetic field range of -8000 Oe to 8000 Oe at room temperature. The particle size and morphology of the materials were determined by Scanning Electron Microscopy (SEM) with ZEISS-DSM 960A microscope and transmission electronic microscopy (Philips EM 208S instrument) with an acceleration voltage of 100 kV. The TEM sample preparation was performed by dropping the dilute suspensions of the samples onto the carbon-coated copper grids and evaporation of the solvent. The analysis of epoxidation products was done by a gas chromatograph (HP, Agilent 6890N) equipped with a capillary column (HP-5) using helium as the carrier gas. GC-MS of the products was obtained using a Shimadzu-14A fitted with a capillary column (CBP5-M25).



Scheme 1: Schematic representation of the preparation of Mo-Schiff base-SCMNPs.

RESULTS AND DISCUSSIONS

The preparation of molybdenum-Schiff base supported on the surface of SCMNPs (denoted as Mo-Schiff base-SCMNPs) is shown in Scheme 1. MNPs were easily prepared by a chemical co-precipitating method, followed by a silica-coating procedure. Aminopropylsilyl modified SCMNPs were prepared according to the literature [23]. Subsequent reaction of the prepared Schiff base ligand with the AmpSCMNPs resulted in covalent tethering of this ligand onto the surface of SCMNPs. Finally, the reaction of $\text{MoO}_2(\text{acac})_2$ precursor with the supported Schiff base ligand afforded the molybdenum-Schiff base complex supported on the surface of SCMNPs. In this material, the molybdenum-Schiff base complex has been attached to the SCMNPs through the strong covalent bonds and has high chemical stability in various reaction conditions.

The prepared Mo-Schiff base-SCMNPs catalyst can be well-dispersed in both aqueous and organic solvents to form a stable suspension in the absence of a magnetic field. The high dispersion is due to the nanoscale size of the support. The high dispersion of the Mo-Schiff base-SCMNPs catalyst and easy accessibility to its active sites result in high activity in the epoxidation of olefins. Interestingly, the nanoparticles of Mo-Schiff base-SCMNPs catalyst can be aggregated using an external

magnetic field. This observation suggested that the Mo-Schiff base-SCMNPs catalyst is easy to separate from the reaction mixtures using an external magnet.

The covalent binding of the molybdenum-Schiff base complex to the surface of SCMNPs in the catalyst was confirmed by FT-IR spectroscopy. Fig. 1 shows the FT-IR spectra of SCMNPs, AmpSCMNPs, Schiff base-SCMNPs, and Mo-Schiff base-SCMNPs catalyst for comparison. The FT-IR spectra of all samples indicate two characteristic Fe-O vibrations in the range of $420\text{--}590\text{ cm}^{-1}$, and the characteristic Si-O vibrations at around $1000\text{--}1100\text{ cm}^{-1}$. The presence of aminopropyl group on the surface of AmpSCMNPs was evident from the characteristic bands at 2879 and 2933 cm^{-1} (C-H stretching vibrations) (Fig. 1b). The aminopropyl group is responsible for the covalent attachment of Schiff base ligand on the SCMNPs by forming a new imine bond, as shown in Scheme 1. After anchoring of Schiff base ligand, new bands at around 1618 and 1553 cm^{-1} appeared in the FT-IR spectrum of supported Schiff base ligand, which was the characteristic stretching vibrations of the C=N bonds (Fig. 1c). The presence of cis-MoO₂ group in Mo-Schiff base-SCMNPs catalyst was confirmed by the observation of two adjacent bands at 908 and 944 cm^{-1} in its FT-IR spectrum (Fig. 1d) [26].

Table 1: Elemental analysis of the prepared nanomaterials.

Sample	N content (mmol/g)	Mo content (mmol/g)
Amp-SCMNPs	0.41	-
Schiff base-SCMNPs	0.67	-
Mo-Schiff base-SCMNPs	0.60	0.13
Mo-Schiff base-SCMNPs ^a	0.57	0.11

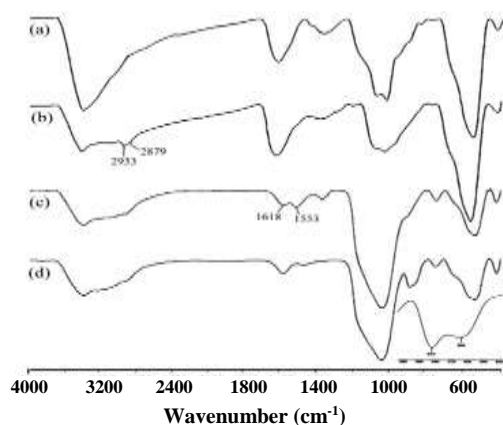
^a reused catalyst

Fig. 1: FT-IR spectra of (a) SCMNPs, (b) Amp-SCMNPs, (c) Schiff base-SCMNPs, and (d) Mo-Schiff base-SCMNPs.

The quantity of supported Schiff base ligand was determined by elemental analysis of the samples and the results are given in Table 1. Molybdenum content of the soxhlet extracted Mo-Schiff base-SCMNPs was found to be 0.13 mmol/g from the inductively coupled plasma-optical emission spectroscopy (ICP-OES) which further established the immobilization of molybdenum complex on the surface of SCMNPs.

Fig. 2 exhibits the powder X-Ray Diffraction (XRD) pattern of the prepared Mo-Schiff base-SCMNPs catalyst. This pattern shows the typical peaks at 30.1°, 35.4°, 43.1°, 53.6°, 56.9°, and 62.6°, which corresponded to the (200), (311), (411), (422), (511), and (440) reflections of pure Fe₃O₄ with a reverse spinel structure (JCPDS No.19-0629). The observation of these characteristic peaks suggested that the surface modification did not significantly affect the phase composition of magnetite nanoparticles. Moreover, the XRD pattern of Mo-Schiff base-SCMNPs catalysts did not show any distinct diffraction peak corresponding to the crystalline molybdenum Schiff base complex which confirmed the high dispersion of the complex on the surface of SCMNPs.

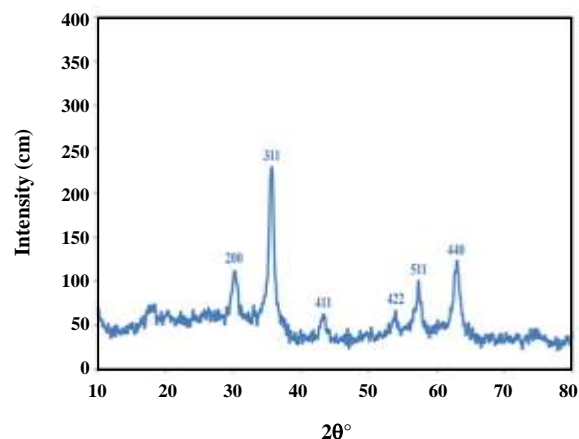


Fig. 2: XRD pattern of the prepared Mo-Schiff base-SCMNPs.

Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) analyses were used to obtain information on the particle size and morphology of the prepared Mo-Schiff base-SCMNPs catalyst. The typical TEM and SEM images are shown in Fig. 3. Particles with an approximately spherical shape and average diameter of ca. 20 nm were observed in these images. Transmission Electron Microscopy (TEM) images showed slight aggregation of MNPs after immobilization.

As the superparamagnetic property of the catalyst is crucial for its use in catalytic reactions, the magnetic behavior of MNPs, Amp-SCMNPs, and Mo-Schiff base-SCMNPs were studied by using VSM analysis. As can be seen in Fig. 4, their magnetization curves exhibited no hysteresis loop and indicated superparamagnetic properties. The saturation magnetization of the nanomaterials decreases continuously from 60 emu/g in MNPs to 38 emu/g in Mo-Schiff base-SCMNPs with surface functionalization of the magnetite core. Regardless of the decrease in the magnetization in comparison with parent MNPs, the Mo-Schiff base-SCMNPs are magnetically separable by using an external

Table 2: Results of catalytic epoxidation of some olefins with TBHP in presence of Mo-Schiff base-SCMNPs.

Run No.	Olefins	Time(h)	Conversion (%)	Selectivity (%)
1	1-Hexene	8	42	>99
		24	79	>99
2	1-Octene	8	29	>99
		24	59	>99
3	1-Decene	8	22	>99
		24	52	>99
4	Cyclooctene	8	99	>99
		24	99	>99
5	Cyclohexene	8	83	>99
		24	92	>99

Reaction conditions: Catalyst (50 mg), Olefin (4 mmol), TBHP (0.75ml), Refluxing Chloroform (5ml).

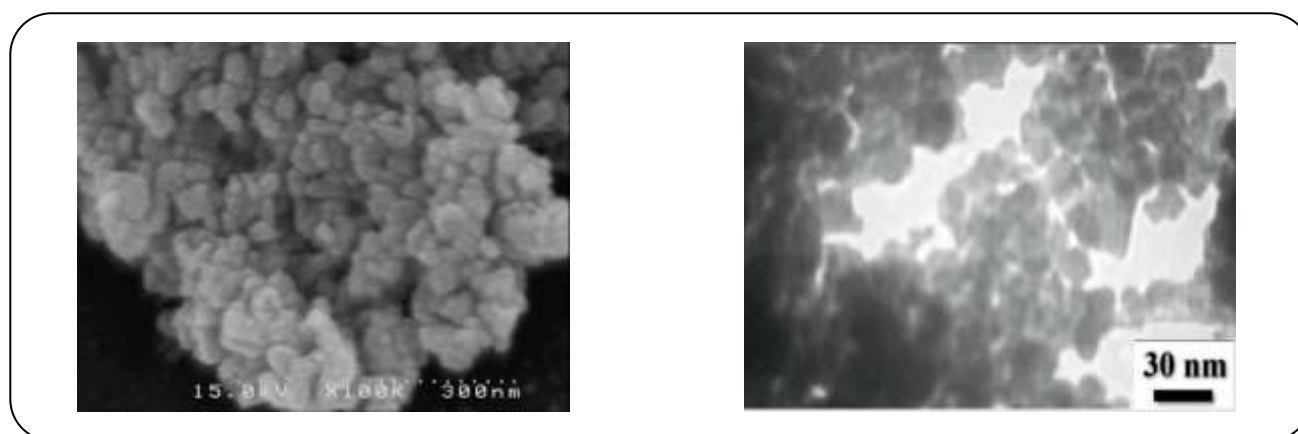


Fig. 3: The SEM (top) and TEM (bottom) images of prepared Mo-Schiff base-SCMNPs.

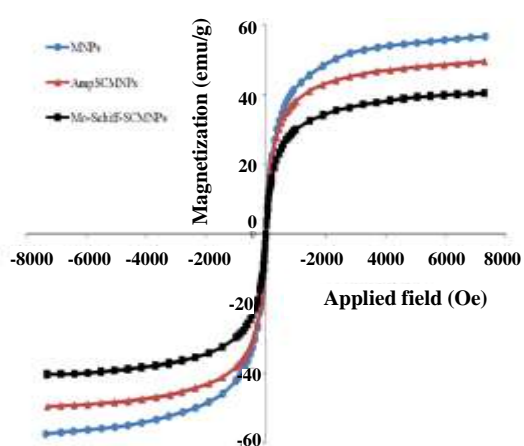


Fig. 4: Magnetization curves of (a) MNPs, (b) Amp-SCMNPs, and (c) Mo-Schiff base-SCMNPs.

magnetic field and redispersed quickly without aggregation when the magnetic field is removed.

With the easily accessible surface-attached Mo complex, the Mo-Schiff base-SCMNPs have been used for the epoxidation of olefins with high activity and selectivity. As shown in Table 2, the olefins were converted to their corresponding epoxide in the presence of tert-butylhydroperoxide with high selectivity. The olefin conversions are significantly high and comparable to those of earlier reports [20-23].

The Mo-Schiff base-SCMNPs catalyst was easily recovered by decanting the reaction mixture while attracting the modified MNPs with an external magnet. The supernatant was not active for epoxidation of olefins and thus the reaction was completely stopped by catalyst removal (Table 3). This observation indicated

Table 3: Results of the epoxidation of cyclooctene with TBHP in different conditions.

Run No.	Time (h)	Conversion (%)	Selectivity ^a (%)
1 ^b	12	14	41
2 ^c	12	16	36
3 ^d	2	72	>99
	24	75	>99

Reaction conditions: catalyst (50 mg), cyclooctene (4 mmol), TBHP (0.75 ml), refluxing chloroform (5 ml). ^aSelectivity toward epoxy cyclooctane. ^bOxidation in the absence of catalyst. ^cOxidation in the presence of SCMNP. ^dResults after separation of the catalyst.

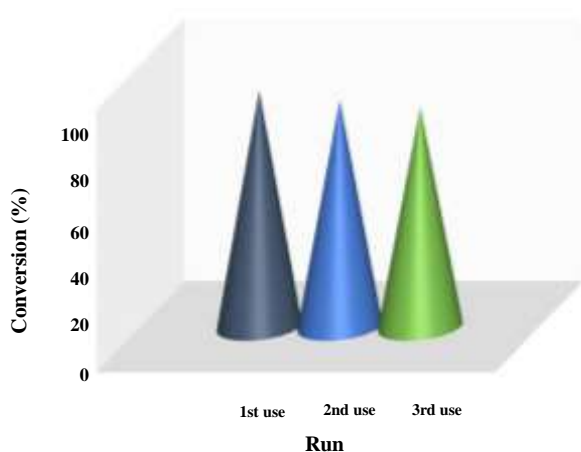


Fig. 5: Results of the epoxidation of cyclooctene with TBHP in the presence of recovered Mo-Schiff base-SCMNPs. Reaction conditions: catalyst (50 mg), olefin (4 mmol), TBHP (0.75 mL), refluxing chloroform (5 mL).

the heterogeneous nature of the Mo-Schiff base-SCMNPs catalyst system.

Besides the high catalytic efficiency in epoxidation reaction, another important property of the prepared Mo-Schiff base-SCMNPs catalyst is its easy separation using a magnetic field. Upon completion of the reaction, the Mo-Schiff base-SCMNPs catalyst can be quantitatively recovered from the reaction mixture using an external magnetic field. The organic phase was then separated from the catalyst by decantation. The Mo-Schiff base-SCMNPs catalyst was reused for the epoxidation of cyclooctene. Fig. 5 shows the results of the recovery and reusability of Mo-Schiff base-SCMNPs catalyst in the epoxidation of cyclooctene. The catalyst can be recycled for up to three times with no appreciable decrease in conversion and selectivity, which demonstrated that the prepared catalyst possessed good stability and reusability.

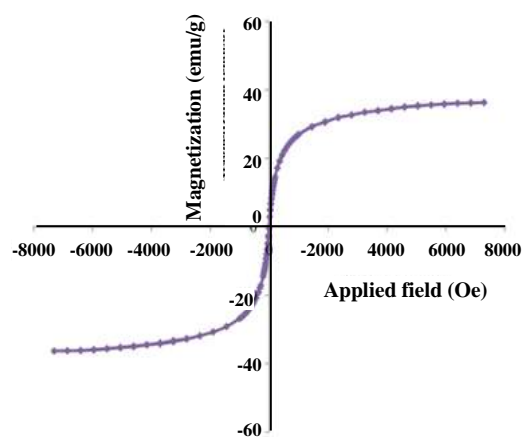


Fig. 6: Magnetization curve of Mo-Schiff base-SCMNPs catalyst after 3rd recovery.

Elemental analysis of the recovered Mo-Schiff base-SCMNPs catalyst was used to examine possible molybdenum leaching. About 0.11 mmol/g of molybdenum was detected in the recovered catalyst which is close to that in the fresh catalyst.

To illuminate the function of the active molybdenum species, a molybdenum-Schiff base free counterpart (SCMNPs) was used as a control catalyst. We noticed that this material offered a slight conversion of the cyclooctene under identical reaction conditions (Table 3). This observation clearly indicated that the molybdenum-Schiff base complex played a critical role in the epoxidation reaction.

The magnetic behavior of the Mo-Schiff base-SCMNPs catalyst after 3rd recovery test was investigated with VSM analysis. As seen in Fig. 6, the recovered Mo-Schiff base-SCMNPs catalyst shows superparamagnetic

behavior and there is no considerable change in its magnetic property. Hence, the magnetite core is stable during the epoxidation reaction due to the protective function of the silica layer.

CONCLUSIONS

In summary, we have designed novel magnetite nanoparticle-supported molybdenum-Schiff base complex as a heterogeneous catalyst for the epoxidation of olefins with high activity and selectivity. The heterogenized catalyst can be readily recycled by magnetic decantation and used for epoxidation of olefins for up to three times without loss of activity and selectivity.

Received : Sep. 30, 2016 ; Accepted : Nov. 20, 2017

REFERENCES

- [1] Valkenberg M.H., Holderich W.F., [Preparation and Use of Hybrid Organic–Inorganic Catalysts](#), *Catal. Rev.* **44**: 321-374 (2002).
- [2] Shylesh S., Jia M., Thiel W.R., [Recent Progress in the Heterogenization of Complexes for Single-Site Epoxidation Catalysis](#), *Eur. J. Inorg. Chem.*, **28**: 4395-4410 (2010).
- [3] Sreedhar B., Radhika P., Neelima B., Hebalkar N., [Regioselective Ring Opening of Epoxides with Amines Using Monodispersed Silica Nanoparticles in Water](#), *J. Mol. Catal. A: Chem.* **272**: 159-163 (2007).
- [4] Hoffmann F., Cornelius M., Morell J., Froba M., [Silica-Based Mesoporous Organic–Inorganic Hybrid Materials](#), *Angew. Chem. Int. Ed.*, **45**: 3216-3251 (2006).
- [5] Ge J., Huynh T., Hu Y., Yin Y., [Hierarchical Magnetite/Silica Nanoassemblies as Magnetically Recoverable Catalyst-Supports](#), *Nano Lett.*, **8**: 931-934 (2008).
- [6] Shao D., Xia A., Hu J., Wang C., Yu W., [Monodispersed Magnetite/Silica Composite Microspheres: Preparation and Application for Plasmid DNA Purification](#), *Colloids Surf. A: Physicochem. Eng. Aspects*, **322**: 61-65 (2008).
- [7] Qiao R., Yang C., Gao M., [Superparamagnetic Iron Oxide Nanoparticles: from Preparations to in Vivo MRI Applications](#), *J. Mater. Chem.*, **19**: 6274-6293 (2009).
- [8] Sun C., Lee J.S.H., Zhang M., [Magnetic Nanoparticles in MR Imaging and Drug Delivery](#), *Adv. Drug Delivery Rev.*, **60**: 1252-1265 (2008).
- [9] Ichiyanagi Y., Moritake S., Taira S., Setou M., [Functional Magnetic Nanoparticles for Medical Application](#), *J. Magn. Magn. Mater.*, **310**: 2877-2879 (2007).
- [10] Polshettiwar V., Luque R., Fihri A., Zhu H., Bouhrara M., Basset J.M., [Magnetically Recoverable Nanocatalysts](#), *Chem. Rev.*, **111**: 3036-3075 (2011).
- [11] Shylesh S., Schnemann V., Thiel W.R., [Magnetically Separable Nanocatalysts: Bridges between Homogeneous and Heterogeneous Catalysis](#), *Angew. Chem. Int. Ed.*, **49**: 3428-3459 (2010).
- [12] Gawande M.B., Branco P.S., Varma R.S., [Nano-Magnetite \(Fe₃O₄\) as a Support for Recyclable Catalysts in the Development of Sustainable Methodologies](#), *Chem. Soc. Rev.*, **42**: 3371-3393 (2013).
- [13] Hille R., [The Mononuclear Molybdenum Enzymes](#), *Chem. Rev.* **96**: 2757-2816 (1996).
- [14] Burgess B.K., Low D.J., [Mechanism of Molybdenum Nitrogenase](#), *Chem. Rev.*, **96**: 2983-3011 (1996).
- [15] Mol J.C., [Industrial Applications of Olefin Metathesis](#), *J. Mol. Catal. A: Chem.*, **213**: 39-45 (2004).
- [16] Handzlik J., Ogonowski J., Stoch J., Mikolajczyk M., [Comparison of Metathesis Activity of Catalysts Prepared by Anchoring of MoO₂\(acac\)₂ on Various Supports](#), *Catal. Lett.*, **101**: 65-69 (2005).
- [17] Jorgensen K.A., [Transition-Metal-Catalyzed Epoxidations](#), *Chem. Rev.*, **89**: 431-458 (1989).
- [18] Oyama S.T. (Ed.), [“Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis”](#), Elsevier, Amsterdam (2008).
- [19] Najafi M., Abbasi A., Masteri-Farahani M., Rodrigues V.H., [A Novel Inorganic–Organic Hybrid Compound Based on Heteropolyoxomolybdate Nanocluster as Selective Catalyst for Epoxidation of Cyclooctene](#), *Inorg. Chem. Comm.*, **46**: 251-253 (2014).
- [20] Abednatanzi S., Abbasi A., Masteri-Farahani M., [Post-synthetic Modification of Nanoporous Cu₃\(BTC\)₂ Metal-Organic Framework via Immobilization of a Molybdenum Complex for Selective Epoxidation](#), *J. Mol. Catal. A: Chem.*, **399**: 10-17 (2015).

- [21] Masteri-Farahani M., Farzaneh F., M. Ghandi, Synthesis and Characterization of Molybdenum Complexes with Bidentate Schiff Base Ligands within Nanoreactors of MCM-41 as Epoxidation Catalysts, *J. Mol. Catal. A: Chem.*, **248**: 53-60 (2006).
- [22] Masteri-Farahani M., Farzaneh F., Ghandi M., Synthesis of Tetradentate N₄ Schiff Base Dioxomolybdenum (VI) Complex within MCM-41 as Selective Catalyst for Epoxidation of Olefins, *Catal. Commun.*, **8**: 6-10 (2007).
- [23] Mohammadikish M., Masteri-Farahani, Mahdavi S., Immobilized Molybdenum-Thiosemicarbazide Schiff Base Complex on the Surface of Magnetite Nanoparticles as a New Nanocatalyst for the Epoxidation of Olefins, *J. Magn. Magn. Mater.* **354**: 317-323 (2014).
- [24] Coleman W., Taylor L., Pentadentate Ligands. I. Nickel (II) Complexes of the Linear Schiff Base Ligands Derived from Substituted Salicylaldehydes and Diethylenetriamine and 2,2'-Bis(aminopropyl)amine, *Inorg. Chem.* **10**: 2195-2199 (1971).
- [25] Chen G.J.J., Mc Donald J.W., Newton W.E., Synthesis of Mo(IV) and Mo(V) Complexes Using Oxo Abstraction by Phosphines Mechanistic Implications, *Inorg. Chem.* **15**: 2612-2615 (1976).
- [26] Topich J., Ligand Control of the Redox Properties of Dioxomolybdenum(VI) Coordination Complexes, *Inorg. Chem.* **20**: 3704-3707 (1981).