



# A new magnetically recoverable nanocatalyst for epoxidation of olefins

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## ABSTRACT

In this work, a new magnetically recoverable nanocatalyst was developed by covalent binding of a Schiff base ligand, *N,N'*-bis(3-salicylideneaminopropyl)amine (salpr), on the surface of silica coated magnetite nanoparticles (SCMNPs) and followed complexation with  $\text{MoO}_2(\text{acac})_2$ . Characterization of the prepared nanocatalyst was performed with different physicochemical methods such as FT-IR and atomic absorption spectroscopies, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and vibrating sample magnetometry (VSM). Finally, catalytic activity of the prepared  $\text{MoO}_2\text{salpr}/\text{SCMNPs}$  was examined in the epoxidation of olefins with tert-butyl hydroperoxide (TBHP) and cumene hydroperoxide (CHP).

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## 1. Introduction

In recent years, nanosized materials have attracted great academic interests because of their special properties, such as relatively large surface area and surface to volume ratio [1–7]. Among them magnetic nanoparticles are widely used in the various fields such as metal ion separations, enzyme immobilization, magnetic resonance imaging (MRI), drug delivery and catalysis [8–15]. The magnetite  $\text{Fe}_3\text{O}_4$  nanoparticles have superparamagnetic property which enables them to attract to an external magnetic field, but retain no residual magnetism after removing the magnetic field. Thus, suspended magnetic nanoparticles can be adhered and then removed very quickly from the sample solutions with utilization of a magnetic field and do not agglomerate after removing the external field. As the surface of  $\text{Fe}_3\text{O}_4$  nanoparticles are relatively inert to chemical reactions, functionalization with reactive species should be made to facilitate incorporation of other molecules on the surface of the  $\text{Fe}_3\text{O}_4$  nanoparticles [16–18].

On the other hand, it has been found that dioxomolybdenum (VI) complexes of multidentate Schiff base ligands are selective homogeneous catalysts for the epoxidation of olefins. Many attempts have been done for heterogenization of molybdenum catalysts within different supports such as silicates, zeolites and other molecular sieves [19–26] to facilitate the recovery and reuse of the catalysts. But, the resulted catalysts suffer from decreased catalytic

activity due to limited diffusion of substrates through the narrow pores of the support.

Due to the high surface to volume ratio of the nanoparticles surface modification of nanoparticles is an alternative route for preparation of highly active catalysts. Moreover, diffusion limitations can be avoided, as all of the surface area of the nanoparticles is external. However, the recovery of these modified nanoparticles with filtration methods is very difficult. In this respect, immobilization of homogeneous catalysts on modified magnetic nanoparticles such as iron oxides gives heterogenized catalysts that can be quickly and easily recovered in the presence of external magnetic fields [11,27–33].

In this work, our objective is to functionalize magnetite nanoparticles with chloropropyl groups and then incorporate a molybdenum Schiff base complex with anchoring method to obtain a heterogeneous molybdenum catalyst for the epoxidation of olefins. To the best of our knowledge there is no any report about preparation of such magnetically recoverable nanocatalyst for the epoxidation of olefins. The advantage of this system is facile and fast recovery of the solid catalyst at the end of reaction as well as good activity and selectivity for epoxidation of olefins.

## 2. Experimental

### 2.1. Materials and instrumentation

Ferrous chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), chloropropyl trimethoxysilane, tetraethyl orthosilicate (TEOS), ammonia (25 wt.%) were purchased from Merck chemical company. The salpr ligand was prepared according to

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the reported method [34].  $\text{MoO}_2(\text{acac})_2$  was prepared according to literature method [35].

Fourier transform infrared spectra were recorded using Perkin-Elmer Spectrum RXI FT-IR spectrometer, using pellets of the materials diluted with KBr. The transmission electron micrographs (TEM) of the nanoparticles were recorded using a Philips EM 208 S instrument with an accelerating voltage of 100 kV. Samples were prepared for TEM by placing droplets of a suspension of the sample in acetone on a polymer microgrid supported on a Cu grid. Scanning electron micrographs (SEM) of the samples were taken with ZEISS-DSM 960A microscope with attached camera. Magnetic susceptibility measurements were carried out using a vibrating sample magnetometer (VSM) (BHV-55, Riken, Japan) in the magnetic field range of  $-8000$  Oe to  $8000$  Oe at room temperature. The crystalline phase of the nanoparticles were identified by means of X-ray diffraction measurements using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) on a SIEFERT XRD 3003 PTS diffractometer in the  $2\theta$  range of  $10$ – $80^\circ$ . Chemical analyses of samples were carried out with VARIAN VISTA-MPX ICP-AES atomic absorption spectrometer.

### 2.1.1. Preparation of silica coated magnetite nanoparticles (SCMNPs) and chloropropyl modified SCMNP (ClpSCMNPs)

Magnetite nanoparticles (MNPs) were prepared according to reported method [36]. Modification of the prepared MNPs was performed as followed: The magnetite nanoparticles (1 g) were dispersed in deionized water in a 250 ml round-bottom flask with sonication and then an aqueous solution of TEOS (10% (v/v), 80 ml) was added, followed by glycerol (60 ml). The pH of the suspension was adjusted to 4.6 using glacial acetic acid, and the mixture was then stirred and heated at  $90^\circ\text{C}$  for 2 h under a nitrogen atmosphere. After cooling to room temperature, the silica coated magnetite nanoparticles was separated from the reaction mixture using a permanent magnet and washed several times with distilled water and methanol. The obtained SCMNP (2 g) were suspended in ethanol (100 ml) and then chloropropyl trimethoxysilane (2 ml, Merck) was added under dry nitrogen atmosphere. The mixture was refluxed for 12 h and the resulted solid was magnetically separated, washed with ethanol to remove the unreacted residue of silylating reagent and then vacuum dried at 353 K.

### 2.1.2. Preparation of salpr/SCMNPs

ClpSCMNPs (2 g) was suspended in 100 ml of acetonitrile with sonication. To this mixture was added excess of salpr ligand (1 g, 3.2 mmol) and triethylamine (0.5 ml) and the resulted mixture was refluxed for 12 h. The resultant solid was separated magnetically and then washed with ethanol several times to remove the unreacted residue of the salpr ligand and dried under vacuum at 353 K.

### 2.1.3. Preparation of $\text{MoO}_2$ salpr modified SCMNP ( $\text{MoO}_2$ salpr/SCMNPs)

For preparation of  $\text{MoO}_2$ salpr/SCMNPs, excess of  $\text{MoO}_2(\text{acac})_2$  (500 mg, 1.5 mmol) was dissolved in ethanol (50 ml). Salpr /SCMNPs (1 g, dried in vacuum oven at 353 K) was then added to this solution and after sonication the mixture was refluxed for 12 h. After separation with an external magnet, the product was washed with methanol to remove unreacted  $\text{MoO}_2(\text{acac})_2$ . The resulted  $\text{MoO}_2$ salpr/SCMNPs material was then dried under vacuum at 353 K and characterized with FT-IR spectroscopy, X-ray diffraction, scanning and transmission electron microscopies and vibrating sample magnetometry.

## 2.2. Catalytic epoxidation of olefins in the presence of $\text{MoO}_2$ salpr/SCMNPs

Epoxidation of olefins (purchased from Merck) was carried out in a 25 ml round bottomed flask equipped with a condenser and a

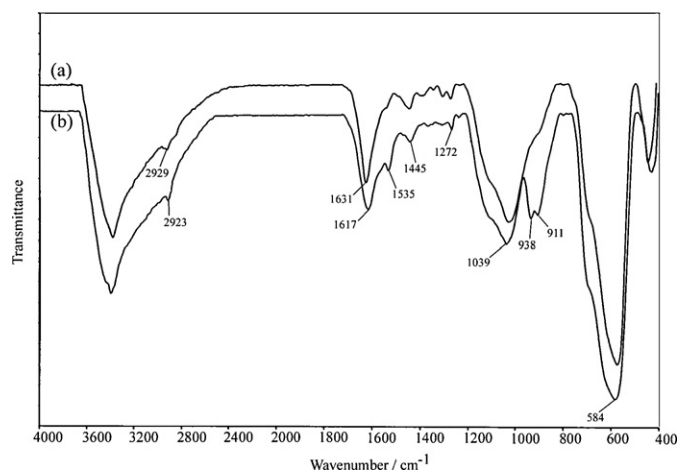


Fig. 1. FT-IR spectra of (a) salpr/SCMNPs and (b)  $\text{MoO}_2$ salpr/SCMNPs materials.

magnetic stirrer. Tert-butylhydroperoxide (TBHP) (obtained from Merck as 80% in di-tertiary butyl peroxide) or cumene hydroperoxide (80% in cumene, Merck) were used as oxidants. In a typical procedure, to a mixture of catalyst (100 mg) and olefin (8 mmol) in chloroform (20 ml) was added oxidant (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.

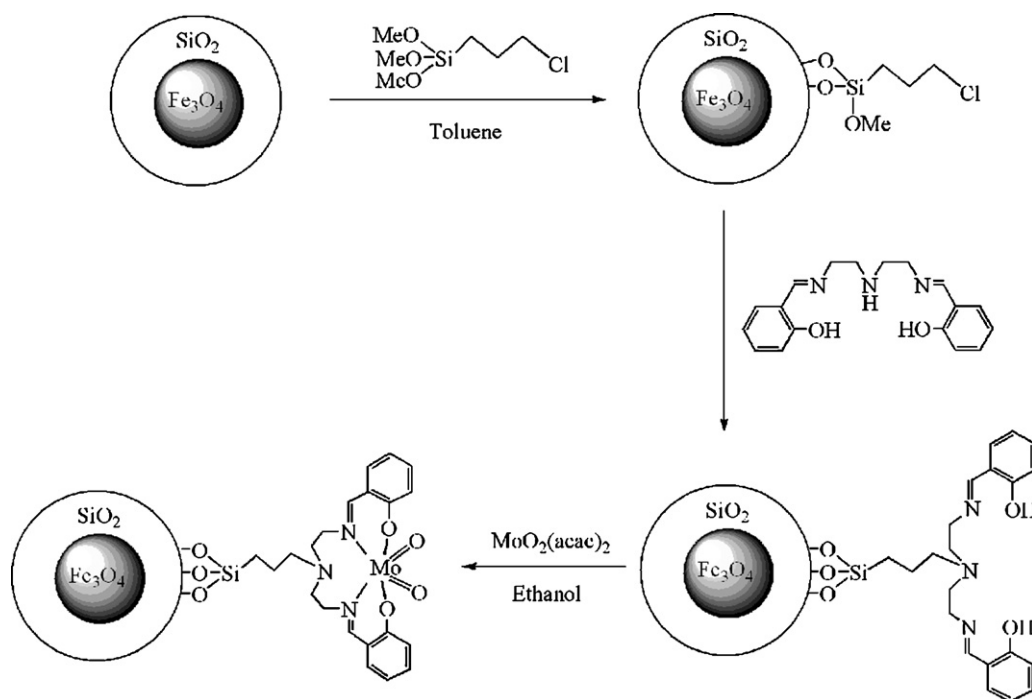
## 3. Results and discussion

### 3.1. Preparation of $\text{MoO}_2$ salpr/SCMNPs

Scheme 1 shows the sequence of events in the functionalization of MNPs with molybdenum Schiff base complex. In the first step, the external surface of MNPs was coated with a silica shell to obtain SCMNP. Then, treatment of silanol groups of SCMNP with chloropropyl trimethoxysilane affords chloropropylated magnetite nanoparticles (ClpSCMNPs). The second step involves substitution reaction of ClpSCMNPs chloro groups with secondary amine group of salpr Schiff base to yield the salpr/SCMNPs, a tetradentate Schiff base ligand supported on SCMNP. Addition of triethylamine in this step facilitates the substitution reaction. Based on the literature method [20], complexation of the salpr/SCMNPs was performed with excess of  $\text{MoO}_2(\text{acac})_2$  to afford  $\text{MoO}_2$ salpr/SCMNPs in the third step. Soxhlet extraction of the product was carried out subsequently in order to remove the unreacted  $\text{MoO}_2(\text{acac})_2$  from the resulted material.

### 3.2. Characterization of the prepared nanomaterial

In order to confirm the modification of the magnetite surface the FT-IR spectra of the prepared salpr/SCMNPs and  $\text{MoO}_2$ salpr/SCMNPs materials were obtained and have been shown in Fig. 1. The observation of two broad bands at around  $430$ – $584 \text{ cm}^{-1}$  indicates the presence of magnetite core in the prepared nanoparticles. The silica coating of magnetite nanoparticles was confirmed by observation of a broad band about  $1000$ – $1100 \text{ cm}^{-1}$  assigned to Si–O–Si and Si–OH stretching

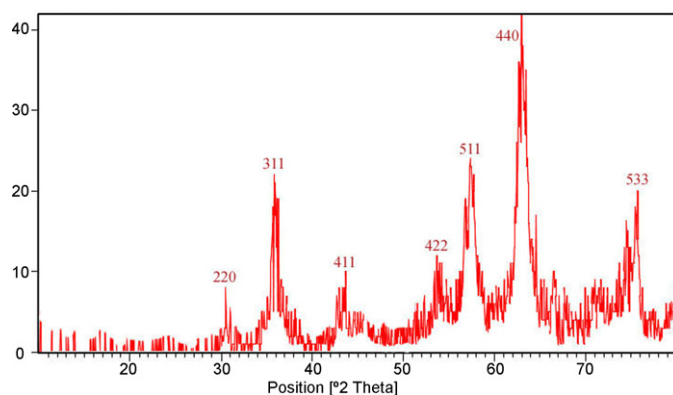


**Scheme 1.** The sequence of events in the preparation of MoO<sub>2</sub>salpr/SCMNPs.

vibrations. The presence of anchored propyl groups were confirmed by stretching vibrations appeared at about 2923 cm<sup>-1</sup> in the FT-IR spectrum of ClpSCMNPs (not shown here). In the FT-IR spectrum of salpr /SCMNPs (Fig. 1a) a band at 1631 cm<sup>-1</sup>, assigned to C=N stretching vibration of salpr ligand [20,35], and some weak bands at 1400–1500 cm<sup>-1</sup> assigned to stretching vibrations of aromatic rings of salpr ligand were observed that were not present in parent SCMNPs. The band at 1631 cm<sup>-1</sup> upon reaction of slapr ligand with MoO<sub>2</sub>(acac)<sub>2</sub> shifted to lower frequency (1617 cm<sup>-1</sup>) (Fig. 1b) indicating complexation of C=N group of supported ligand with molybdenum. Also, appearance of two adjacent bands at 911 and 938 cm<sup>-1</sup> in the FT-IR spectrum of complexed material is characteristic of presence of cis-MoO<sub>2</sub> group [37] and formation of MoO<sub>2</sub>salpr/SCMNPs nanomaterial.

Molybdenum content of the prepared nanomaterial was found to be 0.71 wt.% on the basis of ICP-AES chemical analysis.

Fig. 2 depicts the XRD pattern of prepared nanomaterial. The diffraction peaks can be assigned to the planes of inverse cubic spinel structured Fe<sub>3</sub>O<sub>4</sub> (JCPDS no. 19-0629). The



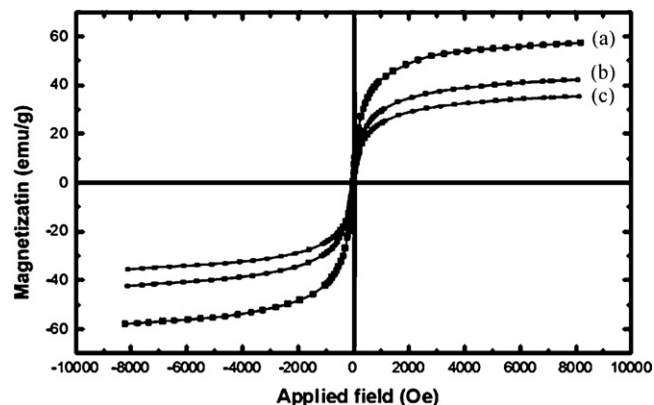
**Fig. 2.** XRD pattern of prepared MoO<sub>2</sub>salpr/SCMNPs.

broad peaks indicate the nanocrystalline nature of the prepared MoO<sub>2</sub>salpr/SCMNPs.

To study the magnetic properties of magnetite nanoparticles before and after silica coating we investigated the hysteresis loops of magnetite and functionalized magnetite nanoparticles at room temperature using vibrating sample magnetometry (VSM).

Magnetization curves of prepared materials were shown in Fig. 3. The magnetization curve of MNPs exhibited no remanence effect (superparamagnetic property) with saturation magnetization of about 60 emu/g. Also, the silica coated magnetite nanoparticles showed superparamagnetic behavior with decreased saturation magnetization about 42 emu/g. The MoO<sub>2</sub>salpr/SCMNPs nanomaterial exhibited superparamagnetic properties with saturation magnetization about 37 emu/g. The superparamagnetic properties of the prepared MoO<sub>2</sub>salpr/SCMNPs are critical for their application, which prevents aggregation and enables them to redisperse rapidly when the magnetic field is removed.

Transmission electron micrographs of the magnetic nanomaterial are shown in Fig. 4a. As can be seen, most of the nanoparticles



**Fig. 3.** Magnetization curves of (a) MNPs, (b) SCMNPs, (c) MoO<sub>2</sub>salpr/SCMNPs.

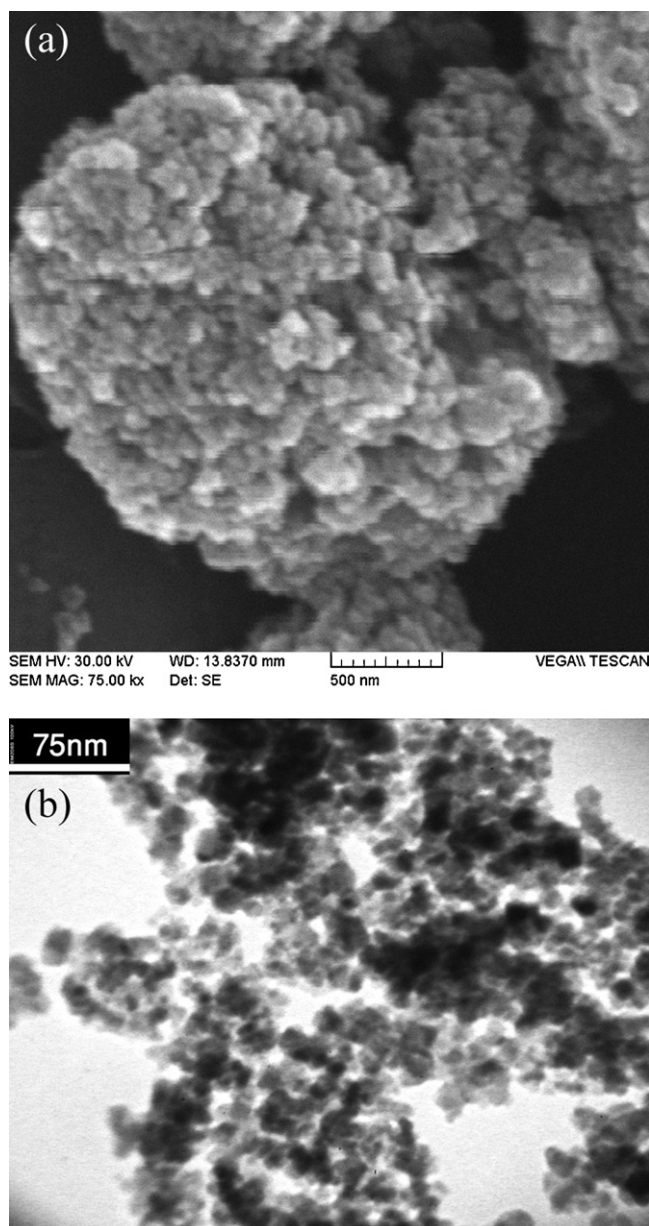


Fig. 4. (a) SEM and (b) TEM images of prepared MoO<sub>2</sub>salpr/SCMNPs.

are almost spherical in shape. The particle size is about 10 nm and relatively monodispersed.

Fig. 4b shows the SEM image of the prepared nanomaterial. The SEM image indicates that the obtained product is composed of spherical nanoparticles. Aggregation gives rise to increasing the size of observed nanoparticles as seen in the SEM image.

### 3.3. Catalytic epoxidation of olefins in the presence of MoO<sub>2</sub>salpr/SCMNPs

Catalytic activity of the prepared nanomaterial was examined in the epoxidation of some olefins with TBHP and CHP. The oxidation results as well as turnover frequencies (TOF's), i.e. mmol of product formed per mmol of molybdenum in the catalyst are given in Tables 1–3. We have included the results of epoxidation of cyclooctene in the presence of parent SCMNP and blank (no catalyst) in Table 1 in order to clear up the catalytic effect of the prepared MoO<sub>2</sub>salpr/SCMNPs.

Table 1

Results of catalytic epoxidation of some olefins with TBHP in presence of MoO<sub>2</sub>salpr/SCMNPs.

Olefin	Time (h)	Conversion (%)	Selectivity (%) <sup>a</sup>	TOF (h <sup>-1</sup> ) <sup>b</sup>
Cyclooctene	6	99.9	99	180
Cyclooctene <sup>c</sup>	6	80	99	59
Cyclohexene	6	61	98	110
Cyclohexene <sup>c</sup>	6	72	99	53
1-hexene	6	56	99	101
1-hexene <sup>c</sup>	6	22	99	16
Cyclooctene <sup>d</sup>	3	85	99	–
	20	89	95	–
Cyclooctene (1st) <sup>e</sup>	6	99	98	178
Cyclooctene (2nd) <sup>e</sup>	6	98	99	177
Cyclooctene <sup>f</sup>	12	14	41	–
Cyclooctene <sup>g</sup>	12	9	45	–

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> Values from Ref. [20].

<sup>d</sup> Catalytic test after filtration of the catalyst.

<sup>e</sup> Catalytic test with first and second recovered catalyst.

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

<sup>g</sup> Reaction was carried out in the presence of SCMNP.

Table 2

Results of catalytic epoxidation of olefins with CHP in presence of MoO<sub>2</sub>salpr/SCMNPs.

Olefin	Time (h)	Conversion (%)	Selectivity (%)	TOF (h <sup>-1</sup> )
Cyclooctene	6	95	99	171
Cyclohexene	6	62	99	112
1-Hexene	6	45	98	81

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

As seen in Tables 1 and 2, catalytic activities and TOFs increase in the order of cyclooctene > cyclohexene > 1-hexene as internal double bond olefins with higher electron density show higher reactivities than terminal olefins.

Comparison of the obtained results with our earlier work on the similar catalyst derived from mesoporous material (MCM-41), i.e. MoO<sub>2</sub>salpr@MCM-41 [20], is interesting and instructive. Compared to MoO<sub>2</sub>salpr@MCM-41 with 1.75 wt% molybdenum, the MoO<sub>2</sub>salpr/SCMNPs with 0.71 wt% molybdenum shows more catalytic activity, e.g. TOF = 180 for the last vs. TOF = 59 in the former in cyclooctene epoxidation or TOF = 110 vs. TOF = 53 in cyclohexene epoxidation in the same reaction conditions (results showed in Table 1). This can be interpreted by considering the fact that compared to the MoO<sub>2</sub>salpr@MCM-41 catalyst with higher surface area but narrow pore size, the MoO<sub>2</sub>salpr/SCMNPs has not diffusion limitations, as all of the surface area of the nanoparticles is external. On the other hand, the MoO<sub>2</sub>salpr/SCMNPs nanocatalyst can be recovered easily with application of a permanent magnet

Table 3

Results of catalytic epoxidation of allyl alcohols with CHP in presence of MoO<sub>2</sub>salpr/SCMNPs.

Olefin	Time (h)	Conversion (%)	Selectivity (%)	TOF (h <sup>-1</sup> )
3-Methyl-2-butene-1-ol	6	83	99	150
1-Octene-3-ol	6	15	99	27
3-Butene-2-ol	6	73	98	132
Trans-2-hexene-1-ol	6	54	98	97

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



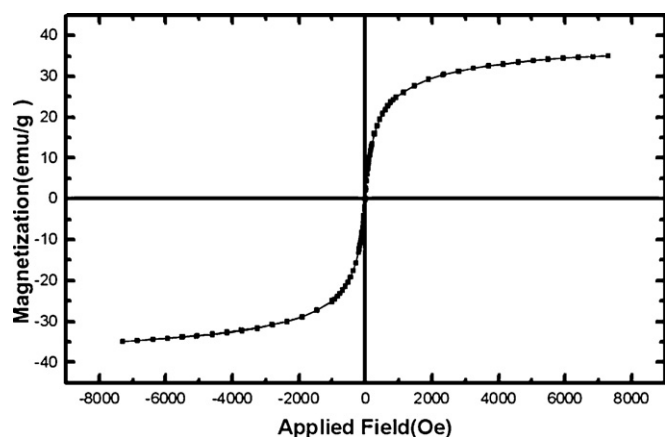


Fig. 5. Magnetization curve of nanocatalyst after second recovery.

compared to  $\text{MoO}_2\text{salpr@MCM-41}$  which needs a time consuming filtration of reaction mixture.

Table 3 exhibits the results of catalytic epoxidation of allylic alcohols with CHP in the presence of prepared  $\text{MoO}_2\text{salpr/SCMNPs}$ . As can be seen, the prepared nanocatalyst is active in the epoxidation of allylic alcohols with excellent selectivities.

Recovery test was performed on the prepared nanocatalyst to evaluate whether the catalysis was occurring via surface bound nanocatalyst. In a separate test epoxidation of cyclooctene was allowed to proceed 3 h (ca. 85% cyclooctene conversion, Table 1). The  $\text{MoO}_2\text{salpr/SCMNPs}$  was then recovered magnetically at the reaction temperature to avoid re-adsorption of the solubilized species and the solution was decanted into a clean 25 ml flask. The solution was refluxed for 20 h to elucidate whether conversion resulted from homogeneous catalyst leached from the support or surface bound molybdenum catalyst. The conversions and selectivities were determined after 3 and 20 h and it was found that the conversion only slightly increased to 89% and then remains constant (Table 1).

After using  $\text{MoO}_2\text{salpr/SCMNPs}$  as catalyst, no molybdenum was detected in the solution by ICP-AAS. On the other hand, the recovered nanocatalyst was reused for the epoxidation of cyclooctene and the reaction results are presented in Table 1. The results show that the activity and selectivity do not decrease significantly for at least two uses of the catalyst. So, from these results it can be concluded that molybdenum species is strongly bonded to the surface of SCMNPs and the prepared nanocatalyst is stable in the reaction conditions and that the epoxidation reaction is truly heterogeneous.

Also, the magnetic property of the recovered nanocatalyst was controlled after second recovery test with investigation of VSM analysis. As observed in Fig. 5, the saturation magnetization of the recovered nanocatalyst is about 35 emu/g with superparamagnetic behavior and so there is no considerable change in its magnetic

property. Thus, the magnetite core is stable during the course of epoxidation reaction as a result of protective function of the silica shell against TBHP.

#### 4. Conclusion

In this work, we have shown that functionalization of silica coated magnetite nanoparticles with a tetradentate salpr Schiff base ligand and subsequent complexation with molybdenum affords an easily recoverable truly heterogenized molybdenum nanocatalyst which is active and selective in catalytic epoxidation of olefins and allylic alcohols.

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