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Molybdenum Schiff Base Complex Covalently Anchored to Silica-Coated Cobalt Ferrite Nanoparticles as a Novel Heterogeneous Catalyst for the Oxidation of Alkenes

M. Kooti · M. Afshari

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Abstract Silica-coated cobalt ferrite nanoparticles were prepared and functionalized with Schiff base groups to yield immobilized bidentate ligands. The functionalized magnetic nanoparticles were then treated with Mo $(O_2)_2(acac)_2$, resulting in the novel immobilized molybdenum Schiff base catalyst. The as-prepared catalyst was characterized by X-ray powder diffraction, transmission electron microscopy, vibrating sample magnetometry, thermogravimetric analysis, Fourier transform infrared, and inductively coupled plasma atomic emission spectroscopy. The immobilized molybdenum complex was shown to be an efficient heterogeneous catalyst for the oxidation of various alkenes using *t*-BuOOH as oxidant. This catalyst, which is easily recovered by simple magnetic decantation, could be reused several times without significant degradation in catalytic activity.

Keywords Cobalt ferrite · Alkenes oxidation · Magnetic nanoparticles · Schiff base · Surface functionalization · Molybdenum catalyst

1 Introduction

Schiff base transition metal complexes have been widely used as homogenous or heterogeneous catalysts in various organic transformations [1]. Although homogenous catalysts exhibit high catalytic activity in many organic reactions, these systems have several drawbacks such as the difficulty of catalyst recycling. Immobilization of homogeneous catalysts on a solid support, however, can provide easy recovery and recycling of the catalyst, as well as product separation which are of great importance in chemical processes [2–5]. Several insoluble solid materials have been frequently applied as support for Schiff base complexes [6–10]. Inorganic matrices show some advantages over organic supports such as high thermal, chemical, and mechanical stability.

Nanoparticles have recently attracted much attention as alternative support materials for homogeneous catalyst immobilization [11–13]. The use of nanoparticles as a support can lead to significant enhancement of catalyst activity but the problem of catalyst recovery from the reaction mixture still remains because nanoparticle materials are easily dispersed in solution and cannot be efficiently filtered out of the reaction medium. This issue can be addressed by using magnetic instead of nonmagnetic supports. Catalysts supported on magnetic nanoparticles (MNPs) can be readily isolated from the product solution merely by applying an external magnetic field. Therefore, magnetic catalytic systems developed on MNPs supports have been successfully used in catalyzing a wide range of organic reactions including C–C coupling [14–17], hydrogenation [18], oxidation [19, 20] and polymerization [21] with excellent performance. Some instructive reviews have recently reported on magnetic nanocatalysts and their applications in various fields [22–24].

The most common type of MNPs are spinel ferrites with the general formula of MFe_2O_4 (M is a divalent cation). One of the well-known ferrites is $CoFe_2O_4$, which has gained extensive attention due to its prominent chemical stability and unusual properties [25–27]. This ferrite, along with other ferrites, such as Fe_3O_4, is prone to aggregation and show poor dispersion in liquid media because of their large specific surface area and magnetization. Furthermore,

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M. Kooti (✉) · M. Afshari
Department of Chemistry, Shahid Chamran University,
Ahvaz 6135-743135, Iran
e-mail: m_kooti@scu.ac.ir

grafting the surface of these ferrite MNPs with organic molecules or metal complexes is also not an easy task. In order to overcome these disadvantages, the MNPs must be coated with a thin layer of an inert material, such as silica. Silica coating shields the magnetic dipole interaction between the MNPs and can prevent their agglomeration [28–30]. Moreover, the silica coating provides an inert barrier between the reaction solution and the MNP's core while maintaining the capacity for surface modifications [31].

There are many reports in the literature on the preparation and applications of silica-coated MNPs in various fields [32–35]. However, to the best of our knowledge, no example of using silica-coated cobalt ferrite nanoparticles as support for Schiff base complexes has been reported to date. In this study, we wish to present a novel method for the immobilization of a Schiff base molybdenum complex on silica-coated cobalt ferrite nanoparticles. The as-fabricated Schiff base molybdenum complex anchored on silica-coated MNPs was examined towards oxidation of alkenes which showed excellent catalytic efficiency.

2 Experimental

2.1 General

All chemicals were purchased from Sigma-Aldrich or Merck and used as received without further purification. The used *t*-BuOOH was 70% w/w solution in water. Mo $(O_2)_2(acac)_2$ complex was synthesized according to the published procedure [36]. X-ray diffraction (XRD) patterns of the samples were taken with a Philips X-ray diffractometer (Model PW1840) over a 2θ range from 10° to 70° using Cu K_α radiation ($\lambda = 1.54056$ A°). The morphology and size of the particles were determined by transmission electron microscopy (TEM) using a Philips CM10-HT 100 kV microscope. IR spectra were recorded on a BOMEM MB-Series 1998 FT-IR spectrometer. GC analysis was performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 m. NMR spectra were recorded in $CDCl_3$ on a Bruker Advanced DPX 400 MHz spectrometer using TMS as internal standard.

2.2 Preparation of Silica-Coated Cobalt Ferrite (Si-MNPs)

Cobalt ferrite MNPs were prepared by the co-precipitation method according to the procedure reported by Maaz et al. [37]. Silica-coated magnetic nanoparticles (Si-MNPs) were synthesized by the Stober method [38] with some modification. In this procedure, 1 g of cobalt ferrite was dispersed by ultrasonic vibration in a mixture of 20 mL of water and 80 mL of ethanol. After one hour of sonification, 2.4 mL of ammonium hydroxide (25%) was added, followed by gradual addition of 2 mL of tetraethoxysilane (TEOS) to the dispersed nanoparticles and the mixture was stirred mechanically for 24 h. The resulted black precipitate of

Si-MNPs were collected by applying a permanent magnet and rinsed three times with ethanol. The product was dried in an oven at 120 °C for 2 h.

2.3 Synthesis of Molybdenum Schiff Base Complex Immobilized on Si-MNPs

The Schiff base used in this study was prepared by the addition of 1.77 g (8 mmol) of amiopropyltriethoxysilane, $NH_2\ (CH_2)_3Si\ (OEt)_3$, to a stirred methanolic (20 mL) solution of salicylaldehyde (0.98 g, 8 mmol). The resulting bright -yellow solution was stirred at room temperature for 2 h. Removal of the solvent under vacuum afforded an oily yellow liquid of silylethoxy-modified 5-boromosalicylaldimine (salenSi) product [39]. The obtained salenSi was dissolved in 15 mL of dried toluene and then added to 0.250 g of Si-MNPs dispersed in 25 mL of dried toluene. After sonication for 30 min, this mixture was refluxed for 2 days and then cooled to room temperature to yield a dark black solid material. The product, salenSi@Si-MNPs, was separated by a magnetic field, washed with toluene and ethanol and dried at room temperature in a vacuum dessicator.

Finally, the immobilized Schiff base, salenSi@Si-MNPs, was dispersed in 25 mL of DMF and added to a solution containing 0.33 g (1 mmol) of Mo $(O_2)_2(acac)_2$ dissolved in 10 mL of DMF. The mixture was then stirred vigorously at 70 °C under an N_2 atmosphere for 2 h. After that, the solid product was isolated by magnetic decantation and washed with DMF, ethanol and diethyl ether and dried under vacuum at room temperature to afford the immobilized Molybdenum catalyst (Mo-salenSi@Si-MNPs).

2.4 Catalytic Studies

The catalytic oxidation reactions of alkenes were carried out in a 25 mL flask equipped with a magnetic stirrer and a reflux condenser. In a typical run, the reaction vessel was charged with: Mo-salenSi@Si-MNPs catalyst (50 mg), 1,2-dichloroethane (5 mL), alkene (1 mmol), *t*-BuOOH (70%, 3 mmol). This mixture was heated in an oil bath at 70 °C and the progress of the reaction was monitored by GC. At the end of the reaction, the catalyst was fixed magnetically at the bottom of the flask and the solution was taken off with a pipette. The solutions were purified on a silica-gel plate to obtain the pure product. The identities of the products were confirmed by FT-IR and ^{1}H NMR spectral data.

3 Results and Discussion

3.1 Characterizations of Immobilized Molybdenum Complex (Mo-salenSi@Si-MNPs)

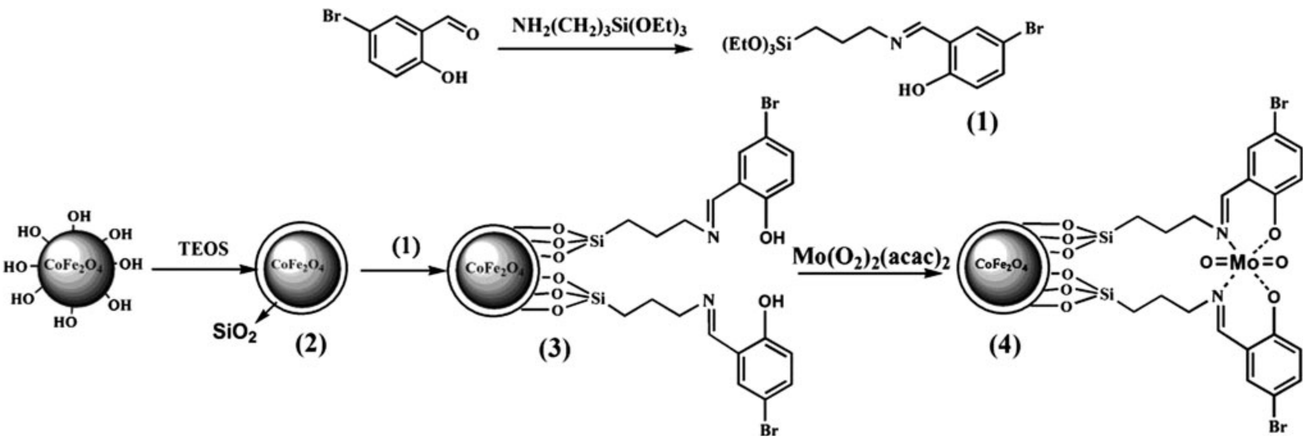
Magnetic nanoparticles can be easily coated with a layer of SiO_2 through chemical bonds to yield Si-MNPs (see Scheme 1). Further surface modification of Si-MNPs was achieved by the addition of excess salenSi (1) to yield salenSi@Si-MNPs (3). Finally, during the reaction of composite salenSi@Si-MNPs (3) with Mo $(O_2)_2(acac)_2$, the coordinated acetylacetonato (acac) ligands are replaced with two salenSi moieties to produce the immobilized molybdenum Schiff base complex, Mo-salenSi@Si-MNPs, (4).

The FT-IR spectrum of MNPs (Fig. 1) shows the expected Fe–O stretching absorption at 577 cm^{-1} and, after coating MNPs with silica, this band shifts to high wavenumbers of 588.9 cm^{-1} (see Fig. 1b). The strengthening of this bond can be attributed to the formation of Fe–O–Si bonds in the coated MNPs (Si-MNPs) where Fe–O–H groups on the surface of the $CoFe_2O_4$ nanoparticles are replaced by Fe–O–Si–O [40]. In addition, we observed a new broad and strong band at 1,088 cm^{-1} and a weak absorption peak at 802 cm^{-1}, which are characteristic peaks of the symmetrical and asymmetrical vibrations of the Si–O–Si bond [40]. The FT-IR spectrum of Schiff base anchored on silica-coated $CoFe_2O_4$ (salenSi@ Si-MNPs) shows all the expected principal bands for the free Schiff base ligand. The C–H deformation band is visible at 1,478 cm^{-1} and the sharp band at 1,634 cm^{-1} was assigned to –C=N stretching vibration of the imine group of the ligand. This last band undergoes a slight shift to higher frequencies and appears at 1,651 cm^{-1} (see Fig 1d) in the spectrum of Mo-salenSi@Si-MNPs (4), indicating the coordination of the imine moiety through nitrogen atom to molybdenum metal [41]. This finding reveals that the Mo–Schiff base complex (Mo-salenSi) has been successfully grafted onto the surface of Si-MNPs.

The XRD patterns of MNPs, Si-MNPs and Mo-salenSi@Si-MNPs are shown in Fig. 2. The position and relative intensities of all peaks are compatible with cubic CoFe2O4 crystals (JCPDS PDF #221086), indicating the retention of a crystalline cubic reverse spinel structure during functionalization of $CoFe_2O_4$. A weak broad hump appeared in the spectra of Si-MNPs and Mo-salenSi@ Si-MNPs (Fig. 2b, c) at $2\theta = 18–28°$, which could be assigned to an amorphous silica phase in the shell of $CoFe_2O_4$. Moreover, compared to the uncoated MNPs, the intensities of all peaks in the coated MNPs samples are slightly decreased. These results can be used to prove the preparation of coated MNPs, i.e. Si-MNPs and Mo-salenSi@Si-MNPs. The average crystallite size of MNPs, Si-MNPs and Mo-salenSi@Si-MNPs is calculated to be about 25.5, 34.7, and 34.8 nm, respectively, using the Debye-Scherer formula. Therefore, the mean crystallite size of the MNPs is slightly increased on coating them with silica or functionalizing with molybdenum Schiff base complex.

The TEM images of the as-prepared MNPs, Si-MNPs and Mo-salenSi@Si-MNPs, are presented in Fig. 3, which show that most of the particles are quasi-spherical. The size of these nanoparticles can be estimated from the images of Fig. 3 to be in the range of 20–30 nm, which is in a close agreement with the sizes obtained from XRD studies. Interestingly, the magnetic core is visible as a dark spot inside the bright spherical SiO_2 thin shell in the TEM images of Si-MNPs and Mo-salenSi@Si-MNPs samples (see Fig. 3b, c).

Magnetic measurements of all the prepared MNPs were carried out at room temperature using a vibrating sample



Scheme 1 Schematic representation of the formation of Mo-salenSi@Si-MNPs catalyst

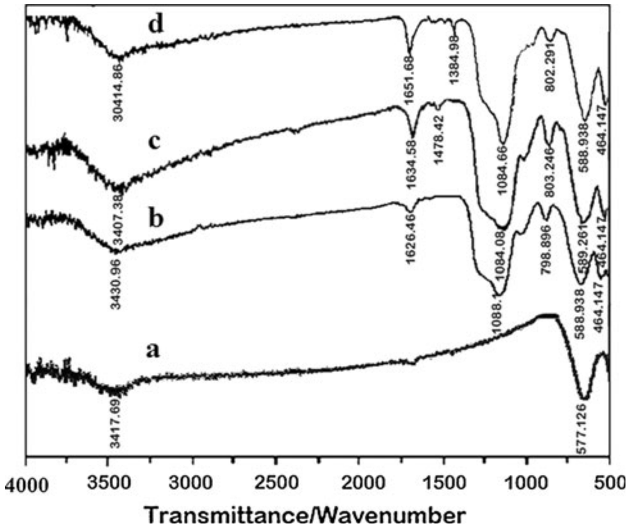


Fig. 1 FT-IR spectra of **a** MNPs, **b** Si-MNPs, **c** salenSi@Si-MNPs, and **d** Mo-salenSi@Si-MNPs

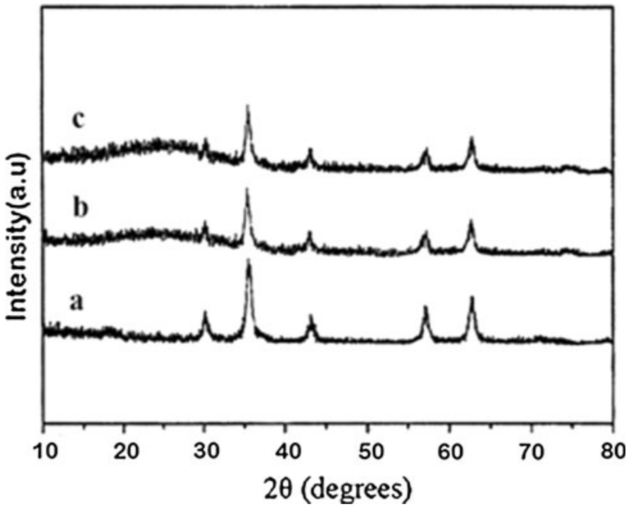


Fig. 2 XRD pattern of **a** MNPs, **b** Si-MNPs, and **c** Mo-salenSi@ Si-MNPs

magnetometer (VSM) with a peak field of 8 kOe and the hysteresis loops were obtained. As seen in Fig. 4, the hysteresis curves of Si-MNPs and Mo-salenSi@Si-MNPs are more or less the same but slightly different from that of MNPs. Figure 4 showed that all the fabricated samples had good magnetic properties at room temperature and the saturation magnetization (M_s) values of the coated samples are slightly less than that of uncoated MNPs. This is probably caused by the formation of amorphous silica on the surface of $CoFe_2O_4$ nanoparticles as well as the restriction of domain wall motion due to the magnetic dilution effect of inert silica. Even with this reduction in the saturation magnetization, the coated and functionalized samples could still be efficiently separated from solution with a permanent magnet.

TGA was performed to determine percent weight loss of the Si-MNPs and salenSi@Si-MNPs samples. The weight decrease observed in the slop of diagram (b) in Fig. 5, in the range of 300–600 °C, must be related to the loss of organic group (Schiff base ligand). Therefore, the difference between the remaine weights of Si-MNPs and salenSi@Si-MNPs at 600 °C can be hypothetically attributed to the loss of Schiff base adsorbed on the surface of Si-MNPs. Since this difference was 9.35%, the amount of Schiff base loaded on Si-MNPs is estimated to be 0.36 mmol/g.

Elemental analysis of the catalyst was carried out and its nitrogen content was 0.542%. According to the obtained nitrogen content, the amount of grafted ligand was estimated (0.38 mm/g) which is in a good agreement with the data obtained from TGA studies. The content of molybdenum in the Mo-salenSi@Si-MNPs catalyst, as determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), was 0.98 wt%. This is another proof for the fact that molybdenum complex was be immobilized onto the silica-coated MNPs.

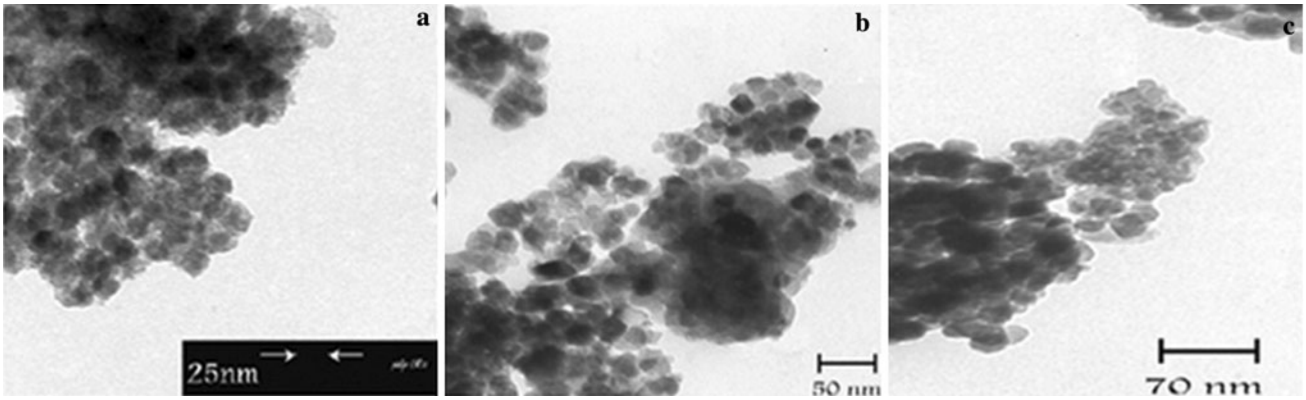


Fig. 3 TEM images of **a** MNPs, **b** Si-MNPs, and **c** Mo-salenSi@Si-MNP

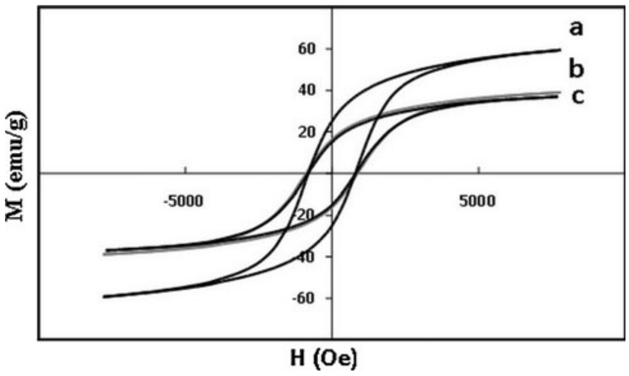


Fig. 4 Hysteresis loops of **a** MNPs, **b** Si-MNPs, and **c** Mo-salenSi@Si-MNPs

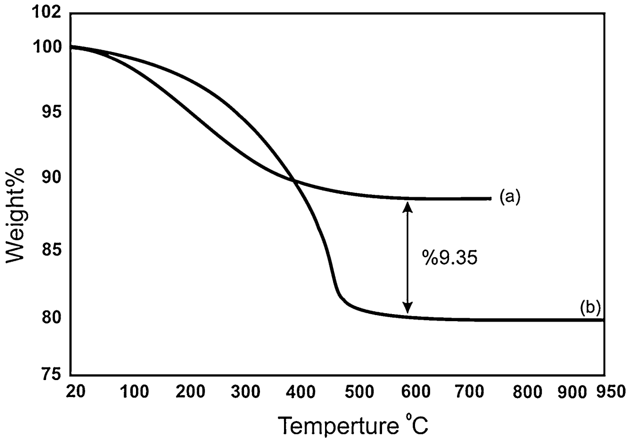
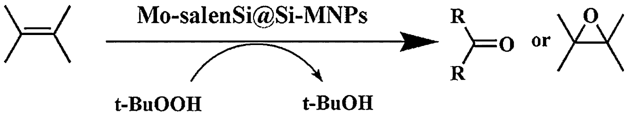


Fig. 5 TGA of **a** Si-MNPs and **b** salenSi@Si-MNPs

3.2 Oxidation of Alkenes

In order to find the optimized reaction conditions, styrene was examined as model substrate using *t*-BuOOH as oxidant in the presence of catalytic amount of Mo-salenSi@Si-MNPs. The optimum conditions used for oxidation of styrene by this catalytic system are: catalyst 50 mg, oxidant and substrate in a molar ratio of 150:50, respectively. In this reaction, benzaldehyde was produced in 95% conversion. Different solvents, such as acetone, chloroform, acetonitrile and 1,2-dichloroethane were also examined for the oxidation of styrene by *t*-BuOOH and 1,2-dichloroethane gave the highest conversion of styrene. Beside *t*-BuOOH, other oxidants, such as H_2O_2 and H_2O_2/Urea (UHP), were also investigated for the oxidation of styrene and the results showed that *t*-BuOOH is the best source of oxygen. The reaction temperature was set at 70 °C, since the observed conversion of styrene was very low at room temperature and reaches 95% at 70 °C. It is worth mentioning that only trace styrene conversion was observed when the reaction was carried out in the absence of catalyst or oxidant, keeping the rest of the reaction conditions constant.



Scheme 2 Oxidation of alekenes using Mo-salenSi@Si-MNPs catalyst

The as-prepared Mo-salenSi@Si-MNPs catalyst was used towards oxidation of various alkenes, under the optimized conditions obtained for oxidation of styrene (see Scheme 2).

Under the optimized conditions which obtained for oxidation of styrene, various alkenes such as cyclohexene, α-methylstyrene, 4-methoxystyrene, 4-nitrostyrene, and 1-heptene were oxidized. The results are shown in Table 1. Oxidation of cyclohexene gave an allylic oxidation product, 2-cyclohexene-1-one with 95% yield. With styrene and its derivatives, however, the major products were the corresponding carbonyl compounds with high yield and selectivity. The explanation given by Moghadam et al. (Scheme 3) might be applicable for our catalysis system [42]. It was proposed that epoxide is formed in the first step of the reaction. The epoxide is subsequently attacked by *t*-BuOOH to give aldehyde or keteone products. Apparently, in these cases the conjugation of aromatic ring with the carbonyl group can stabilize the products. The great feature of the catalytic oxidation with Mo-salenSi@Si-MNPs is that non-activated terminal olefin, 1-octene, could be proficiently transformed to the corresponding epoxide in high yield.

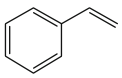
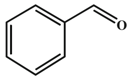
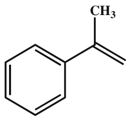
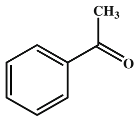
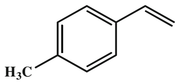
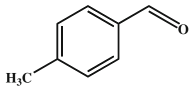
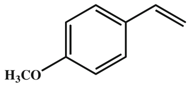
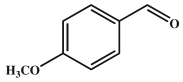
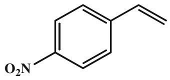
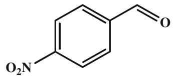
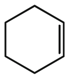
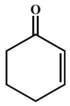
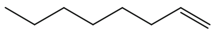
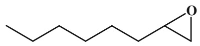
Compared with the homogeneous and heterogeneous MoO_2-salen catalysts, used by Moghadam et al. [42], our novel catalyst (Mo-salenSi@Si-MNPs) has shown much more superiority.The observed high activity of the catalyst can be attributed to the nanosized character of the support which increases surface area for more interaction with substrates This new catalytic system has some remarkable features including that the catalyst, Mo-salenSi@Si-MNPs, is stable at used conditions and can be readily isolated from the reaction mixture by means of an external magnet. Neither obvious loss of activity nor leaching of the catalyst was observed when the catalyst had been reused in five consecutive runs.

3.3 Catalyst Recycling

Catalyst reusability is of major concern in heterogeneous catalysis. The recovery and reusability of the catalyst was investigated using styrene as model substrate.

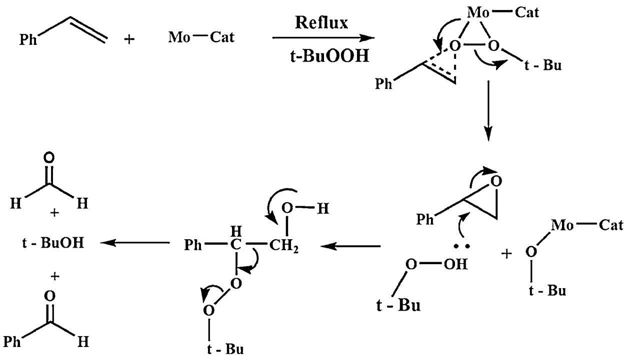
Catalyst recycling experiments were achieved by fixing the catalyst magnetically at the bottom of the flask, after which the solution was taken off with a pipette, the solid washed with 1,2-dichloroethane twice, and the fresh substrate dissolved in the same solvent was introduced into the flask, allowing the system to proceed for next run. The

Table 1 Oxidation of some alkenes by *t*-BuOOH catalyzed by Mo-salenSi@Si-MNPs

Entry	Alkenes	Product[a]	Conversion %[b]	Selectivity	Time (h)
1			95	85	8
2			100	90	8
3			100	85	8
4			100	90	8
5			70	65	8
6			100	95	6
7			68	100	6

[a] Reaction conditions: alkene(1mmol), *t*-BuOOH(3mmol), catalyst (40mg), 1,2-dichloroethane(5ml), $T = 70$ °C

[b] GC yields based on starting alkenes



Scheme 3 Proposed mechanism for oxidation of styrene and its derivatives

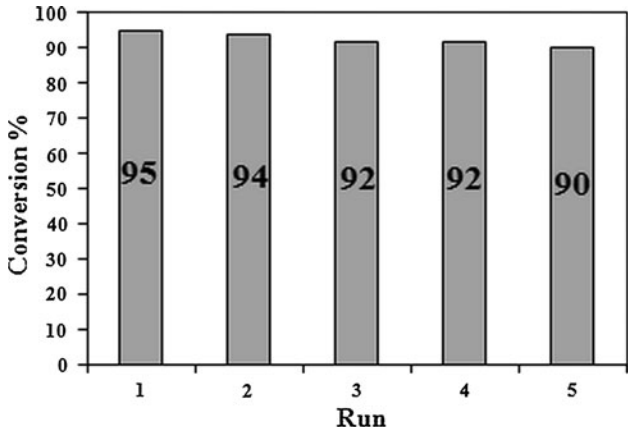


Fig. 6 Catalyst recycling experiments for styrene oxidation

catalyst was consecutively reused five times without any noticeable loss of its catalytic activity (see Fig. 6). Our catalyst is highly magnetic and its saturation magnetization value (36.88 emu/g) is much higher than other reported magnetic catalysts [43, 44]. Therefore, it could be easily and almost completely separated by an external magnet which is of a great advantage for a heterogeneous catalyst.

4 Conclusions

In summary, covalent functionalization of Schiff base molybdenum complex onto silica-coated $CoFe_2O_4$ MNPs was successfully achieved by a multiple synthetic procedure and the product was confirmed by XRD, FT-IR, TGA, TEM, ICP-AES, and VSM. This novel immobilized molybdenum Schiff base complex was examined as an efficient catalyst for the oxidation of various olefins in the presence of *t*-BuOOH. The catalyst has showed high catalytic activity in these reactions, including with non-reactive terminal olefins. Moreover, immobilized molybdenum Schiff base catalyst could be easily recovered by simple magnetic decantation and reused five times without significant loss of activity. The excellent catalytic efficiency, as well as the recyclability of this catalyst, can make it as an attractive alternative to the large number of heterogeneous molybdenum Schiff base catalysts reported to date.

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