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FeNi$_3$@SiO$_2$ nanoparticles: an efficient and selective heterogeneous catalyst for the epoxidation of olefins and the oxidation of sulfides in the presence of *meta*-chloroperoxybenzoic acid at room temperature

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Abstract

In this article, FeNi$_3$ nanoparticles were coated by silica and applied for green, inexpensive, selective and efficient epoxidation of alkenes as well as oxidation of sulfides to the corresponding sulfoxides. The oxidation was performed over FeNi$_3$@SiO$_2$ nanoparticles in the presence of *meta*-chloroperoxybenzoic acid as an oxygen source in dichloromethane at room temperature. High reaction conversion as well as oxidation product selectivity were obtained for both sulfoxide or epoxide compounds. The properties of the catalyst were studied by transmission electron microscopy, powder X-ray diffraction, Fourier transform infrared spectroscopy and vibrating sample magnetometer instruments. The heterogeneous nanocatalyst was magnetically recovered and could be reused in at least five consecutive runs without noticeable reactivity loss.

Introduction

The catalytic oxidation of organic materials is a substantial process in organic synthesis in order to producing practical oxidation products [1–4] including epoxides, which are useful synthetic intermediates and because of their high

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reactivity have attracted a great deal of attention for decades due to their use in a broad range of synthesis reactions [3]. They can be applied for the production of plasticizers, cosmetics, epoxy resins, surfactants, paints, perfumes, etc. [5, 6]. The epoxidation of alkenes in the presence of an oxygen source is a well-known fundamental route for the preparation of these compounds [7–10]. Sulfoxides are another class of important products in the oxidation of sulfides [11–13]. Besides their inevitable role in organic synthesis, sulfoxides have a lot of applications in biological and medicinal such as: antibacterial, antifungal, anti-hypertensive, anti-ulcer and anti-atherosclerotic [14–16].

Various heterogeneous and homogeneous catalysts have been applied for oxidation and epoxidation of organic compounds. Although homogeneous catalysts are more efficient than heterogeneous types, they suffer from some problems concerning to tedious separation and recovery of the catalyst from the reaction mixture [17, 18]. From this point of view, in order to solving this obstacle, numerous strategies have been developed for immobilization of the complexes on a suitable solid support [19] such as sepiolites [20], silica [21], zeolite [22], carbon based material [23], polymer [24], and nanomaterials [25].

The application of NPs have been manifested in various fields from chemistry, agriculture, to medicine and pharmacy [26, 27]. In chemistry, due to their high aspect ratio (surface to volume ratio) of the nanoparticles, they have become a powerful tool as supporting agent; also, their catalytic activities have been proven for decades [28, 29]. In particular, the use of magnetic NPs is a smart strategy in order to design a heterogeneous catalyst; because they not only utilize magnetically recoverability arising from super paramagnetism property, but also they are safe and biocompatible compounds that could be easily functionalized with a broad range of compounds to nailing a special application [30]. Motivated by this concept, tremendous attempts have been made for their applications as catalyst [8]. In this viewpoint, various methods have been reported for sulfide oxidation that come as follow: (1) $Fe_3O_4@SiO_2$-tris(8quinolinolato)iron [31], (2) Fe_3O_4@tryptophan-Ni(II) complex [19], (3) $Fe_3O_4@SiO_2$@DOPisatin-M(II) (M=Ni, Cu) [32], (4) Fe_3O_4@-Cu–S-(propyl)-2-aminobenzothioate [33], (5) $Fe_3O_4@SiO_2$-APTES-FeL^{GDC} [34], (6) Fe_3O_4–TBA-Br_3 [30], (7) MoO_2-CML–$Fe_3O_4@SiO_2$ [11], (8) Fe_3O_4@Gly@r-Py@VO_3 [35], (9) M/isatin@Fe_3O_4 (M=Zr(IV), Cu(II)) [36], (10) Fe_3O_4@PEI@Br [37] and (11) Fe_3O_4@CP(AEAM)/W [38]. Recently, Rayati et al., reported a Mn-Schiff base complex supported on magnetic nanoparticles for sulfide and alkene oxidation [14]. Also, different methodologies based on magnetic nanoparticles have been developed for the epoxidation of olefins. For example: MoO_3(sal-phz)/Fe_3O_4 [39], $MnFe_2O_4$@Mo(Vi) Schiff base complex [40, 41], RGO/Fe_3O_4@C-Salen-MoO_2 [42], $Fe_3O_4@SiO_2$@APTMS@Co(II) complex [43], γ-Fe_2O_3TBHP [44], Fe_3O_4/tart/Mn(TCPP)Cl [8], $Fe_3O_4@SiO_2$@APTMS@V(v) complex [28], Fe_3O_4@Cr(VI) hybrid [26] and Fe_3O_4Mn(III) porphyrin [45] were some of the recent advances nanomagnetite based catalyzed methods regarding epoxidation of alkenes.

However, most of the reported catalytic systems utilize the transition metal complexes supported on the surfaces of nanoparticles [43]. The instability of some heterogeneous complexes, metal leaching concerns, use of toxic heavy metals, metal oxidation during the process, high cost, tedious procedure, and et cetera, are

some disadvantages regarding to the complexes supported on NPs. So, finding a more sustainable, cost effective and ecofriendly methodology for efficient oxidation of organic compounds is in demand.

We previously reported the epoxidation of alkenes by $Fe_3O_4@SiO_2$ nanoparticles [46]. In this paper, we introduce $FeNi_3@SiO_2$ magnetic nanoparticles, as a heterogeneous recoverable catalyst, for efficient epoxidation of alkenes as well as oxidation of sulfides in the presence of *meta*-chloroperoxybenzoic acid (*m*-CPBA) at room temperature.

Experimental

Material and instruments

Tetraethoxysilane (TEOS), $NiCl_2 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, polyethylene glycol (average $M_n = 6000$), NaOH, N_2H_4 hydrate (80 wt%), ammonia solution (25 wt%) and Na_2SO_4 were purchased from Sigma Aldrich and Merck and used without purification. All alkenes and sulfides including: styrene, α-methyl styrene, 1*H*-indene, cyclohexene, 4-chlorostyrene, cyclooctene, 1-hexen, *cis*- and *trans*-stilbene, thioanisole, 2-chlorothioanisole, 4-methoxythioanisole, 4-methylthioanisole, 4-nitrothioanisole, 4-bromothioanisole, diphenylsulfane, and dibutylsulfane were of the highest grade available (Aldrich) and were used as received. Dichloromethane (DCM, anhydrous 99.8%), ethyl acetate (EtOAC), ethanol (EtOH, absolute grade. ≥ 99.8%), CH_3CN, $CHCl_3$, THF, *m*-CPBA, $NaIO_4$, *t*-BOOH, $PhI(OAC)_2$, PhIO, H_2O_2 (30 wt%) and Oxone was purchased from Sigma Aldrich and Merck and used without further purification. Fourier transform infrared (FTIR) spectra were recorded on a JASCO FT/IR 4600 instrument in the range of 450–4000 cm^{-1}. The crystal structure of the $FeNi_3$ and $FeNi_3@SiO_2$ NPs was studied by a Bruker AXS D8-advance X-ray diffractometer using Cu-Kα radiation. Transmission electron microscopy (TEM) images were obtained on a JEOL-2010 transmission electron microscope with an accelerating voltage of 200 kV. The magnetization behavior of the NPs were investigated on a Lake Shore vibrating sample magnetometer (VSM) at room temperature. Progress of the reactions and reaction conversions were conducted on a YL 6100 gas chromatograph system (GC) with a CBP5 column (Shimadzu 30 m × 0.32 mm × 0.25 mm). Conversion and selectivity of the products were measured qualitatively by gas chromatography. Conversion of the product was obtained by comparing the area of the product and the starting material. For each experiment, the resulting mixture (0.2 μL) was injected to GC instrument then the selectivity of the oxidation product was calculated by the following Eq. (1) [6]:

$$Epoxide/sulfoxide \ selectivity = \frac{GC \ peak \ area \ of \ epoxide/\ sulfoxide}{GC \ peak \ area \ of \ all \ products} \times 100. \quad (1)$$

Preparation of FeNi$_3$ NPs

FeNi$_3$ NPs were prepared using a wet chemical approach according to the previously reported work [46, 47]. Briefly, FeCl$_2$·4H$_2$O (10 mmol) and NiCl$_2$·6H$_2$O (30 mmol) were dissolved into 200 mL distilled water. Then, 0.1 g of polyethylene glycol (average M$_n$ 6000), as a surfactant agent, was added to the mixture. NaOH (10%, w/w) was added dropwise until the pH of the solution reached to 12, followed by the addition of N$_2$H$_4$·H$_2$O 80% (N$_2$H$_4$·H$_2$O/FeNi$_3$ molar ratio was 24:1). The reaction was stirred for 24 h at room temperature under nitrogen atmosphere. During the reaction, the pH value was controlled and adjusted in the range of 12–13. After completion of the reaction, the magnetic nanoparticles FeNi$_3$ NPs were collected with an external magnetic field and washed with deionized water (5 × 10 mL) and dried at oven (50 °C) for 12 h.

Preparation of FeNi$_3$@SiO$_2$ core–shell NPs

FeNi$_3$@SiO$_2$ core–shell NPs were prepared by a modified Stöber method [25]. FeNi$_3$ NPs (0.5 g) were dispersed in a mixture of ethanol and deionized water (80:20 mL) and concentrated ammonia aqueous solution (2.0 mL, 25 wt%). Tetraethylzorthosilicate (0.20 g) was added to the above mixture and the mixture vigorously stirred at room temperature for 24 h. Then, FeNi$_3$ NPs were magnetically separated, rinsed with deionized water (5 × 10 mL), and dried at 60 °C.

General procedure for epoxidation of alkenes and oxidation of sulfides catalyzed by FeNi$_3$@SiO$_2$

The oxidation reactions were performed in the presence of 50 mg and 40 mg of the catalyst respectively, for epoxidations and sulfide oxidation. Typically, a mixture of the catalyst dispersed in dichloromethane (3.0 mL), was sonicated for 10 min at room temperature. The substrate (1.0 mmol) and *m*-CPBA (2.0 mmol) were added to the above flask containing the catalyst and oxidant. The mixture was stirred at room temperature for appropriate time. The progress of the reaction was screened using GC or TLC. Upon the reaction completion, the catalyst was separated by an external magnet, washed with EtOH (2 × 10 mL), dried at 50 °C in air atmosphere and set aside for the next run. The remaining solution was washed with NaOH (1 N, 8.0 mL) and brine (8.0 mL), then dried over Na$_2$SO$_4$. Then, the solvent was removed using rotary evaporator. Conversion and selectivity of the products were determined by GC.

Results and discussion

Characterizations of the catalyst

The FTIR spectra of FeNi$_3$ and FeNi$_3$@SiO$_2$ were shown in Fig. 1. In Fig. 1a, the absorption bands at 560–590 and 3400 cm^{-1} were assigned to stretching vibrations
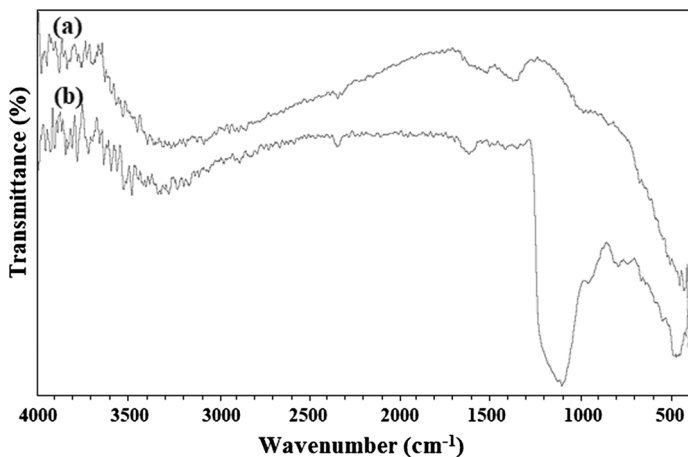
Fig. 1 FTIR spectra of *a* FeNi$_3$ and *b* FeNi$_3$@SiO$_2$

of Fe–O and O–H respectively. Three main characteristic peaks at 560–590, 954, and 3400 cm^{-1}, showing the stretching vibrations of Fe–O, Si–OH, and O–H. Also, the bands at 756 and 1105 cm^{-1} are due to symmetric and asymmetric stretching vibrations of Si–O–Si. The results were completely in agreement with the reported FTIR spectra for coating of silica shell on the surface of NPs [25, 47].

X-ray diffraction (XRD) pattern of FeNi$_3$ and FeNi$_3$@SiO$_2$ NPs are shown in Fig. 2. FeNi$_3$ NPs exhibited good crystalline structure, which were in agreement with the standard FeNi$_3$ (JCPDS Card No. 19-0629) [46]. Three characteristic peaks
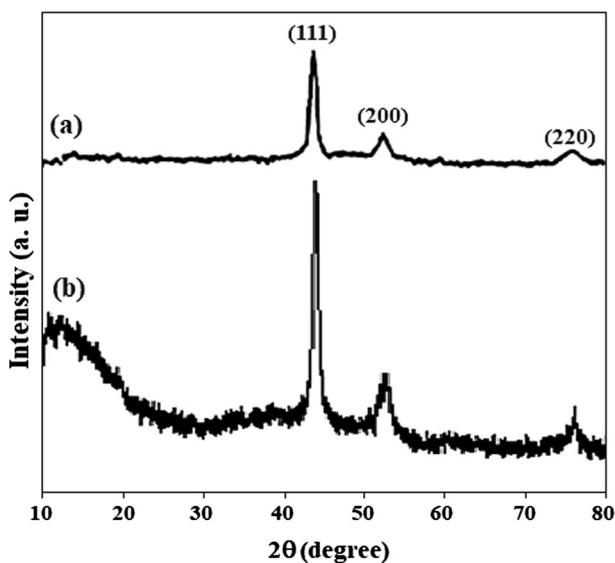

Fig. 2 XRD pattern of FeNi$_3$ (*a*) and FeNi$_3$@SiO$_2$ (*b*)

demonstrated at $2\theta = 44.3°$, $51.5°$, $75.9°$, which were marked based on their related indices (111), (200) and (220) planes, are obtained for $FeNi_3$ (Fig. 2a). The presence of these peaks in XRD spectrum of $FeNi_3@SiO_2$ proved that the surface modification of $FeNi_3$ do not lead to their phase change. An amorphous peak appeared at $2\theta = 13.2°$ was assigned to silica supported on $FeNi_3$ (Fig. 2b).

Fig. 3 shows TEM image of $FeNi_3@SiO_2$ MNPs. The nanoparticles have spherical shape with average size of 25 nm. Coated silica was discriminated by a different phase with average diameter of 2 nm, confirming the favored coating of $FeNi_3$ by silica layers (Fig. 3).

The magnetic behavior of the NPs was investigated by VSM analysis (Fig. 4). According to the Fig. 4a, $FeNi_3$ and $FeNi_3@SiO_2$ did not show hysteresis phenomenon and have zero coercivity at room temperature. This behavior belongs to superparamagnetic nanoparticles in agreement with the literature [30]. The saturation magnetization values for $FeNi_3$ and $FeNi_3@SiO_2$ NPs were found at 61.648 and 44.31 emu/g, respectively. Although the magnetization of $FeNi_3$ considerably reduced, $FeNi_3@SiO_2$ NPs can still be efficiently separated by using a simple external magnet from the solution.

Optimization of the reaction parameters

First, in order to find the best conditions for the $FeNi_3@SiO_2$-catalyzed epoxidation of alkenes and the oxidation of sulfide, styrene and methyl phenyl sulfide were used as the model substrates for epoxidation of alkene and oxidation of sulfide.
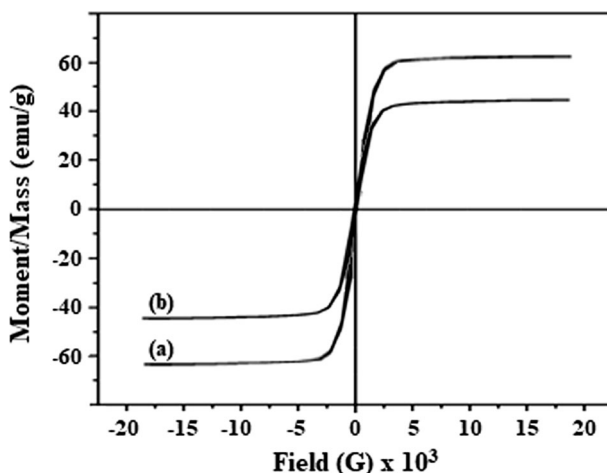

Fig. 3 TEM image of $FeNi_3@SiO_2$
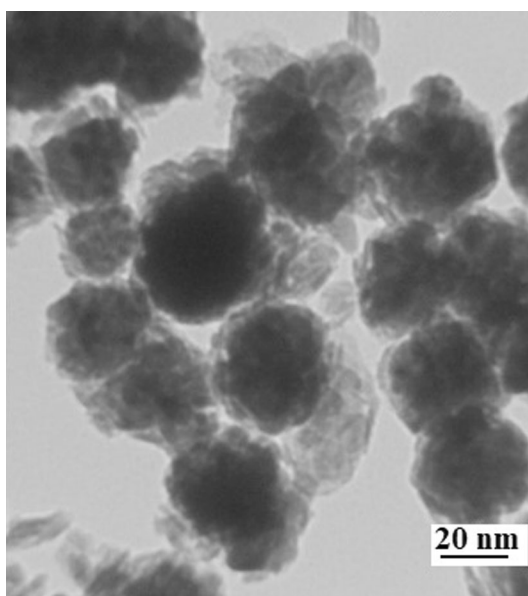
Fig. 4 VSM curves of *a* FeNi$_3$ and *b* FeNi$_3$@SiO$_2$

Catalyst amount

In order to finding optimum amount of the catalyst, the model reactions were investigated by varying amount of the catalyst (Fig. 5). The experiments elucidated that 40 mg and 50 mg were sufficient enough for achievement of the most efficiency for the methyl phenyl sulfoxide and styrene oxide, respectively. No more efficiency was attained for the two model reactions with higher aforementioned above amount of the catalyst (Fig. 5). The reactions in the absence of the catalyst (blank experiments) gave just 10% conversion for both substrates (Fig. 5).
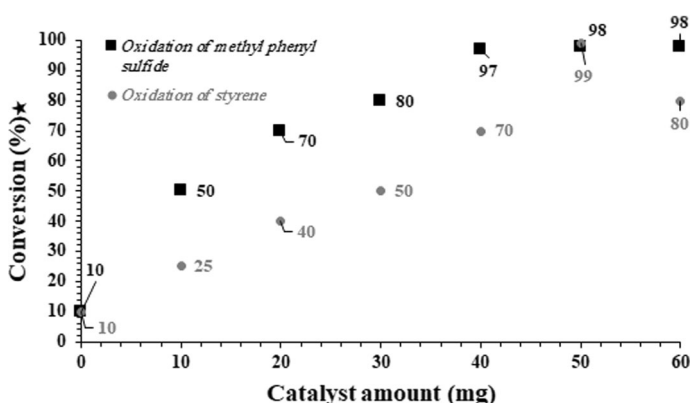

Fig. 5 Optimization of the catalyst amount for epoxidation of styrene and oxidation of methyl phenyl sulfide. Reaction conditions for the two oxidations: styrene or methyl phenyl sulfide (1.0 mmol), *m*-CPBA (2.0 mmol), DCM (3.0 mL), FeNi$_3$@SiO$_2$ (Catalyst), 1.5 and 1.0 h for oxidation of styrene and methyl phenyl sulfide oxidation respectively, r.t. * GC analysis

Effect of oxidant

Various types of oxidant were tested for the model reactions (Fig. 6). It was observed that m-CPBA gives the most possible conversion of epoxy styrene (97%) and methyl phenyl sulfoxide (99%) than other tested oxidants. Moreover, it was found that the highest conversion was obtained with 2.0 equivalent of the m-CPBA in the presence of the $FeNi_3@SiO_2$. Low conversion of the products ($\leq 35\%$) were obtained with H_2O_2, UHP, PhI(OAc) and PhIO. On the other hand, t-BuOOH and oxone gave a moderate yield (Fig. 6). In a blank experiment, the reactions were done in $FeNi_3$ and/or $FeNi_3/SiO_2$ NPs alone (Not shown in the figure). The results did not show any reaction progress and they were inactive towards the epoxidation of styrene or oxidation of methyl phenyl sulfide and demonstrated the mandatory role of oxidant as oxygen source.

Effect of solvent

The two model reactions were checked in different solvents including EtOAc, CH_3CN, H_2O, EtOH, H_2O: EtOH (1:1 v/v), $CHCl_3$, THF and DCM (Fig. 7). As shown in Fig. 7, H_2O and EtOH give the lowest reaction conversions. EtOAc (75% epoxy styrene, 79% methyl phenyl sulfoxide), CH_3CN (65% epoxy styrene, 65% methyl phenyl sulfoxide) and $CHCl_3$ (55% epoxy styrene, 64% methyl phenyl sulfoxide) provided moderate efficiency for the both oxidation systems. The highest conversion was obtained in DCM (97% epoxy styrene, 99% methyl phenyl sulfoxide) and provide the oxidation products in quantitative yield (Fig. 7).
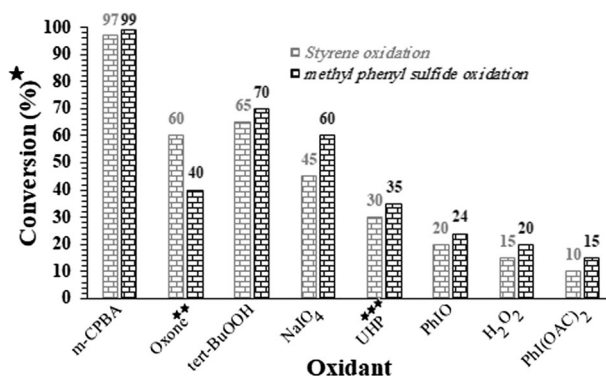

Fig. 6 Influence of oxidant type on epoxidation of styrene and oxidation of methyl phenyl sulfide. Reaction conditions for the two oxidations: styrene or methyl phenyl sulfide (1.0 mmol), oxidant (2.0 mmol), DCM (3.0 mL), $FeNi_3@SiO_2$ (Catalyst, 40 and 50 mg for oxidation of methyl phenyl sulfide and styrene, respectively), 1.5 and 1.0 h for oxidation of styrene and methyl phenyl sulfide oxidation respectively, r.t. * GC analysis. ** $KHSO_5$. *** Urea-Hydrogen peroxide
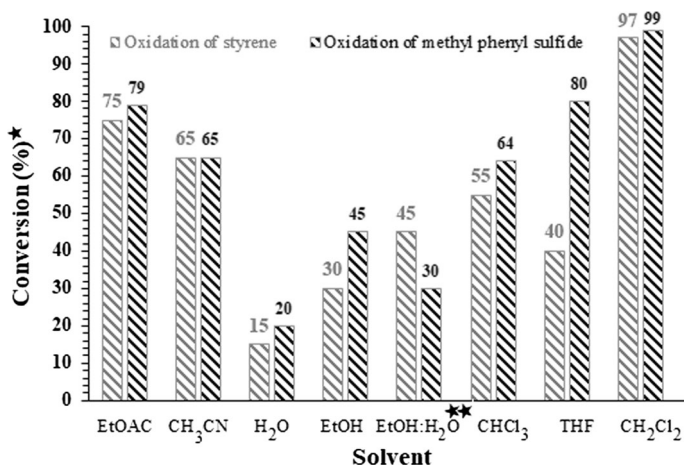
Fig. 7 Effect of solvent on epoxidation of styrene and oxidation of methyl phenyl sulfide. Reaction conditions for the two oxidations: styrene or methyl phenyl sulfide (1.0 mmol), *m*-CPBA (2.0 mmol), solvent (3.0 mL), $FeNi_3@SiO_2$ (Catalyst, 40 and 50 mg for oxidation of methyl phenyl sulfide and styrene respectively), 1.5 and 1 h for oxidation of styrene and methyl phenyl sulfide oxidation respectively, r.t. ★ GC analysis. ★★ 1:1. The conversion in solvent free conditions was 8% for the two experiments (not shown in the figure)

Effect of temperature

The effect of temperature was also investigated for the reactions. The model reactions were performed at 0 and 40 °C and under reflux conditions. The oxidation reactions exhibited the same behavior: the reaction rates increased with temperature. No change in reaction selectivity was observed at 0 °C, but the selectivities of the both systems slowly decreased with temperature (Fig. 8). Due to economical aspects, room temperature was chosen in this study with a very slightly difference from reflux conditions (Fig. 8).

Fig. 8 Influence of temperature on styrene epoxidation (grey columns and markers) and oxidation of methyl phenyl sulfide (black columns and markers)
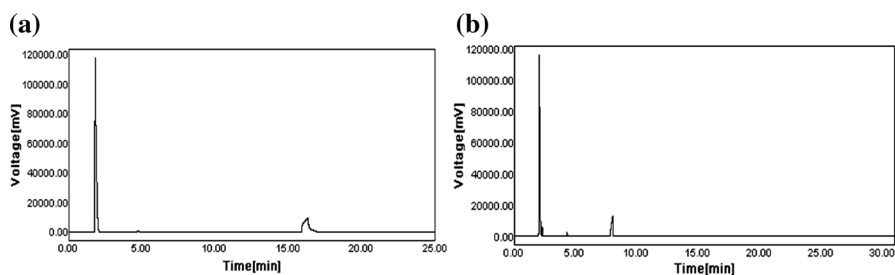
(a)

(b)
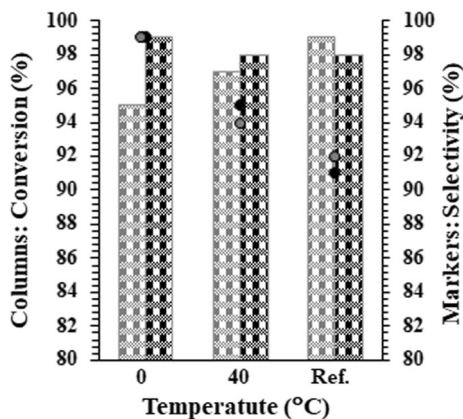
Fig. 9 GC diagrams for **a** epoxidation of styrene and **b** oxidation of methyl phenyl sulfide catalyzed by FeNi$_3$ in the presence of *m*-CPBA at room temperature

The selectivity of the reactions were investigated by GC. Fig. 9 shows the results for the model reactions. As shown in the figure, epoxy styrene and methyl phenyl sulfoxide were obtained with excellent selectivity without observation of any other oxidation product demonstrating the selective performance of the catalyst. No sulfone was seen in the case of sulfide oxidation resulting further oxidation of sulfoxide (Fig. 9). This excellent selectivity was also obtained for all of substrates under the present study.
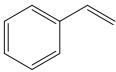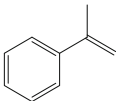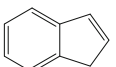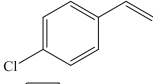
Catalytic activity

With the optimum conditions in hand, i.e. substrate (1.0 mmol), DCM (3.0 mL), *m*-CPBA (2.0 mmol) and catalyst (40 mg for sulfide oxidation and 50 mg for epoxidation), room temperature, we applied the catalyst toward epoxidation of a variety of alkenes as well as oxidation of various sulfides to sulfoxides. A series of alkenes investigated are reported in Table 1. Terminal benzylic alkenes show the highest efficiency [Table 1, entry 1 (97%), entry 2 (97%), entry 5 (95)]. As expected [40], Cl as deactivation group for benzene ring, delayed the epoxidation and reduced the conversion (Table 1, entry 5). Lower efficiencies were achieved for internal alkenes, *cis*-stilbene, cyclohexene and cyclooctene, with 90% yield. Excellent selectivity was obtained for the all of substrates (GC analysis, 98–99%).

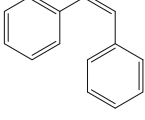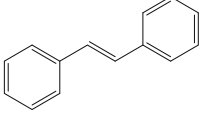Also, the catalyst shows good activity toward sulfide oxidation. A series of sulfides were oxidized to sulfoxide by magnetic FeNi$_3$@SiO$_2$ NPs at room temperature. The results were tabulated in Table 2. The catalyst demonstrated high to excellent selectivity and reaction conversion as same as epoxidation reaction with average conversion of 97%.

In order to validate th recyclability of the catalyst, the epoxidation of styrene was chosen as model reaction. The catalyst was magnetically separated, washed with ethanol and deionized water, dried, and re-used directly for the next reaction run without any further purification. The residue mixture was analyzed by GC on every run. The results, as shown in Fig. 10, indicated insignificant reactivity loss after five runs, in which only 2% reduction in efficiency was seen on average per cycle. It is worth nothing that this method is superior to other methods containing transition metal complexes with metal leaching concern. Moreover, the resulting TEM image from the recovered catalyst after the 5th run showed that the NPs retained their

Table 1 Epoxidation of different alkenes catalyzed by FeNi$_3$/SiO$_2$ NPs[a]

Entry	Alkene	Time (h)	Selectivity %	T (°C)	Conversion[a] (%)
1		1.5	99	25	97
2		1.5	99	25	97
3		3	98	25	95
4		3	99	25	90
5		3	99	25	95
6		3	98	25	90
7		3	99	25	85
8		3	99	25	90
9		3	99	25	90

Reaction conditions: alkene (1.0 mmol), DCM (3.0 mL), m-CPBA (2.0 mmol), FeNi$_3$@SiO$_2$ (50 mg), room temperature

[a]Determined by GC

spherical shape, although a slight agglomeration occurred. Also, the size of the NPs increased after 5th cycle and that could be responsible for decreasing in the conversion. This behavior is expected due to their high aspect ratio of the nanoparticles [25].

The literature review shows that hydroxyl groups on nano silicate are well able to form hydrogen bonds with carboxylic groups [48, 49] (ESI, Figs. 1, 2, 3). Thus, an H-bonding can be found between the surface of nanoparticles containing Si–OH groups and the hydroxyl/carbonyl groups of m-CPBA. The proposed mechanism for this system was shown in Fig. 11, for an epoxidation reaction catalyzed by FeNi$_3$@SiO$_2$ in the presence of m-CPBA. In this proposed mechanism, given the presence of silica supported on the FeNi$_3$ nanoparticles (Fig. 11), m-CPBA was adsorbed on the catalyst surface by hydrogen bonding. Then, the alkene epoxidation

Table 2 Preparation of sulfoxide derivatives using FeNi$_3$/SiO$_2$ catalyst

Entry	Sulfide	Product	Time (min)	Conversion[a,b] (%)
1			60	99
2			60	95
3			40	99
4			60	98
5			75	95
6			60	98
7			60	97
8			60	95

Reaction conditions: substrate (1.0 mmol), DCM (2.0 mL), m-CPBA (2.0 mmol) and catalyst (40 mg), r.t

[a]Determined by GC

[b]The selectivities were ≥ 99% for all of substrates

with m-CPBA [50] can be carried out in the presence of FeNi$_3$ NPs. Because of the high surface to volume ratio of the nanoparticles, a high surface area is provided for the oxidation reaction. So the reaction could be proceeded with high efficiency and selectivity on such huge surface. The same explanation could be introduced for sulfide oxidation to sulfoxide. However, the mechanism of such systems still requires future investigations.
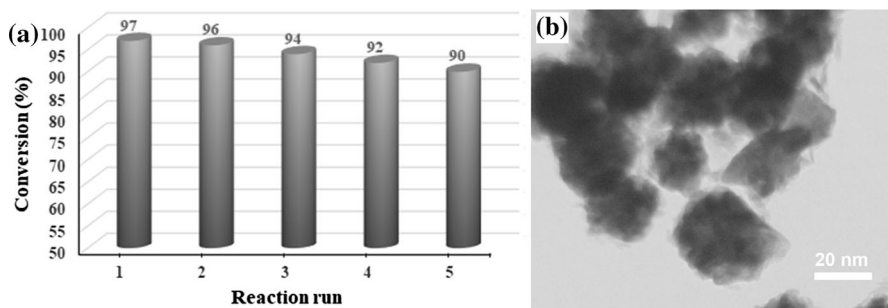
Fig. 10 a Recyclability study of the catalyst on epoxidation of styrene. Reaction conditions: styrene (1.0 mmol), *m*-CPBA (2.0 mmol), DCM (3.0 mL), the catalyst (50 mg), 1.5 h, room temperature. **b** TEM image of the recovered $FeNi_3@SiO_2$ after the 5th run
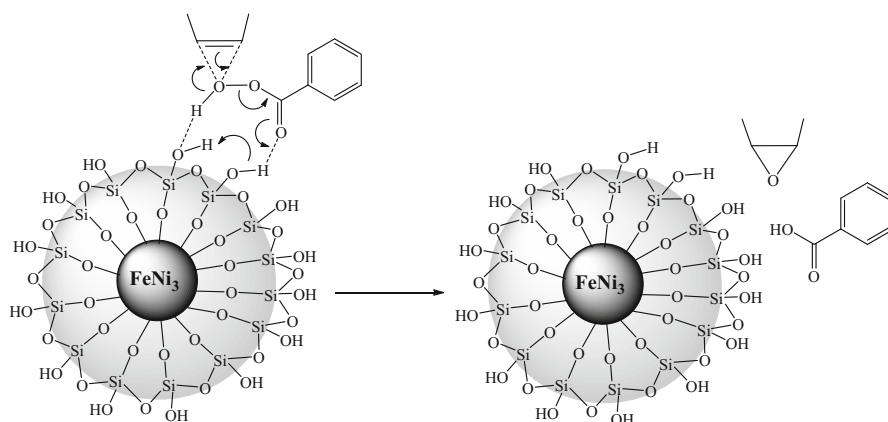

Fig. 11 A plausible reaction mechanism for catalytic epoxidation of alkene by $FeNi_3@SiO_2$ in the presence of *m*-CPBA

Conclusions

In conclusion, a facile, general, cost effective and environmentally benign method have been developed for oxidation of sulfides and epoxidation of alkenes by fabrication of heterogeneous magnetically recoverable $FeNi_3@SiO_2$ nanoparticles as an efficient catalyst in the presence of *m*-CPBA at room temperature. The catalyst shows high selectivity toward sulfoxide and epoxide products, which no sulfone or other by-products were found in the mixture. The catalyst was characterized by FTIR, TEM, VSM and XRD analyses. Oxidation was take place on the surface of the $FeNi_3@SiO_2$ nanoparticles with a high accessible surface. The catalyst showed good versatility toward a broad spectrum of alkenes and sulfide for oxidation, where high to excellent reaction conversions were obtained for all of substrates studied in this paper. High stability, easy preparation, magnetically recoverable, simple handling, good catalytic activity are some highlighted properties of the catalyst that make this methodology as a promising tool for a broad scope of oxidation goals.

Finally, the magnetic catalyst was simply recovered and reused for five consecutive runs without remarkable reactivity loss.

References

1. Kamal MS, Razzak SA, Hossain MM (2016) Catalytic oxidation of volatile organic compounds (VOCs)—a review. Atmos Environ 140:117–134
2. Lee H, Lee HJ, Jeong J, Lee J, Park NB, Lee C (2015) Activation of persulfates by carbon nanotubes: oxidation of organic compounds by nonradical mechanism. Chem Eng J 266:28–33
3. Chen CY, Tang C, Wang HF, Chen CM, Zhang X, Huang X, Zhang Q (2016) Oxygen reduction reaction on graphene in an electro-fenton system: In situ generation of H_2O_2 for the oxidation of organic compounds. Chemsuschem 9:1194–1199
4. Huang H, Xu Y, Feng Q, Leung DY (2015) Low temperature catalytic oxidation of volatile organic compounds: a review. Catal Sci Technol 5:2649–2669
5. Kazemnejadi M, Shakeri A, Nikookar M, Shademani R, Mohammadi M (2018) Selective and metal-free epoxidation of terminal alkenes by heterogeneous polydioxirane in mild conditions. R Soc Open Sci 5:171541–171554
6. Kazemnejadi M, Shakeri A, Nikookar M, Mohammadi M, Esmaeilpour M (2017) Co(II) Schiff base complex decorated on polysalicylaldehyde as an efficient, selective, heterogeneous and reusable catalyst for epoxidation of olefins in mild and self-coreductant conditions. Res Chem Intermed 43:6889–6910
7. Taguchi M, Nagasawa Y, Yamaguchi E, Tada N, Miura T, Itoh A (2016) One-pot epoxidation of alkenes using aerobic photoperoxidation of toluenes. Tetrahedron Lett 57:230–232
8. Farokhi A, Hosseini-Monfared H (2016) A recyclable Mn–porphyrin catalyst for enantioselective epoxidation of unfunctionalized olefins using molecular dioxygen. New J Chem 40:5032–5043
9. Brown JW, Nguyen QT, Otto T, Jarenwattananon NN, Glöggler S, Bouchard LS (2015) Epoxidation of alkenes with molecular oxygen catalyzed by a manganese porphyrin-based metal–organic framework. Catal Commun 59:50–54
10. Huang Y, Liu Z, Gao G, Xiao G, Du A, Bottle S, Sarina S, Zhu H (2017) Stable copper nanoparticle photocatalysts for selective epoxidation of alkenes with visible light. ACS Catal 7:4975–4985
11. Aghajani M, Monadi N (2017) Schiff base complex of Mo supported on iron oxide magnetic nanoparticles (Fe_3O_4) as recoverable nanocatalyst for the selective oxidation of sulfides. J Iran Chem Soc 14:963–975
12. Carrasco CJ, Montilla F, Bobadilla L, Ivanova S, Odriozola JA, Galindo A (2015) Oxodiperoxo-molybdenum complex immobilized onto ionic liquid modified SBA-15 as an effective catalysis for sulfide oxidation to sulfoxides using hydrogen peroxide. Catal Today 255:102–108
13. Li G, Qian H, Jin R (2012) Gold nanocluster-catalyzed selective oxidation of sulfide to sulfoxide. Nanoscale 4:6714–6717
14. Rayati S, Khodaei E, Jafarian M, Wojtczak A (2017) Mn-Schiff base complex supported on magnetic nanoparticles: synthesis, crystal structure, electrochemical properties and catalytic activities for oxidation of olefins and sulfides. Polyhedron 133:327–335
15. Wang PY, Zhou L, Zhou J, Wu ZB, Xue W, Song BA, Yang S (2016) Synthesis and antibacterial activity of pyridinium-tailored 2, 5-substituted-1, 3, 4-oxadiazole thioether/sulfoxide/sulfone derivatives. Bioorg Med Chem Lett 26:1214–1217
16. Pitchen P, France CJ, McFarlane IM, Newton CG, Thompson DM (1994) Large scale asymmetric synthesis of a biologically active sulfoxide. Tetrahedron Lett 35:485–488
17. Kazemnejadi M, Sardarian AR (2016) Ecofriendly synthesis of a heterogeneous polyvinyl alcohol immobilized copper (ii) Schiff base complex as an efficient, reusable catalyst for the one-pot three-component green preparation of 5-substituted $1H$-tetrazoles under mild conditions. RSC Adv 6:91999–92006
18. Kazemnejadi M, Nikookar M, Mohammadi M, Shakeri A, Esmaeilpour M (2018) Melamine-Schiff base/manganese complex with denritic structure: an efficient catalyst for oxidation of alcohols and one-pot synthesis of nitriles. J Colloid Interface Sci 527:298–314

19. Moeini N, Tamoradi T, Ghadermazi M, Ghorbani-Choghamarani A (2018) Anchoring Ni(II) on Fe$_3$O$_4$@tryptophan: a recyclable, green and extremely efficient magnetic nanocatalyst for one-pot synthesis of 5-substituted 1H-tetrazoles and chemoselective oxidation of sulfides and thiols. Appl Organomet Chem 32:e4445

20. Bautista FM, Campelo JM, Luna D, Luque J, Marinas JM (2007) Vanadium oxides supported on TiO$_2$-sepiolite and sepiolite: preparation, structural and acid characterization and catalytic behaviour in selective oxidation of toluene. Appl Catal A 325:336–344

21. Jarupatrakorn J, Tilley TD (2002) Silica-supported, single-site titanium catalysts for olefin epoxidation. A molecular precursor strategy for control of catalyst structure. J Am Chem Soc 124:8380–8388

22. Kang J, Cheng K, Zhang L, Zhang Q, Ding J, Hua W, Lou Y, Zhai Q, Wang Y (2011) Mesoporous zeolite-supported ruthenium nanoparticles as highly selective Fischer-Tropsch catalysts for the production of C5–C11 isoparaffins. Angew Chem Int Edit 50:5200–5203

23. Rodriguez NM, Kim MS, Baker RTK (1994) Carbon nanofibers: a unique catalyst support medium. J Phys Chem 98:13108–13111

24. Kazemnejadi M, Shakeri A, Mohammadi M, Tabefam M (2017) Direct preparation of oximes and Schiff bases by oxidation of primary benzylic or allylic alcohols in the presence of primary amines using Mn(III) complex of polysalicylaldehyde as an efficient and selective heterogeneous catalyst by molecular oxygen. J Iran Chem Soc 14:1917–1933

25. Esmaeilpour M, Sardarian AR, Javidi J (2012) Schiff base complex of metal ions supported on superparamagnetic Fe$_3$O$_4$@ SiO$_2$ nanoparticles: an efficient, selective and recyclable catalyst for synthesis of 1, 1-diacetates from aldehydes under solvent-free conditions. Appl Catal A 445:359–367

26. Maleki A, Rahimi R, Maleki S (2016) Efficient oxidation and epoxidation using a chromium (VI)-based magnetic nanocomposite. Environ Chem Lett 14:195–199

27. Niederberger M, Garnweitner G, Buha J, Polleux J, Ba J, Pinna N (2006) Nonaqueous synthesis of metal oxide nanoparticles: review and indium oxide as case study for the dependence of particle morphology on precursors and solvents. J Sol-Gel Sci Technol 40:259–266

28. Azarkamanzad Z, Farzaneh F, Maghami M, Simpson J, Azarkish M (2018) Synthesis, characterization and immobilization of a novel mononuclear vanadium (V) complex on modified magnetic nanoparticles as catalyst for epoxidation of allyl alcohols. Appl Organomet Chem 32:e4168

29. Neamtu M, Nadejde C, Hodoroaba VD, Schneider RJ, Verestiuc L, Panne U (2018) Functionalized magnetic nanoparticles: synthesis, characterization, catalytic application and assessment of toxicity. Sci Rep 8:6278

30. Shiri L, Ghorbani-Choghamarani A, Kazemi M (2017) Synthesis and characterization of tribenzyl ammonium-tribromide supported on magnetic Fe$_3$O$_4$ nanoparticles: a robust magnetically recoverable catalyst for the oxidative coupling of thiols and oxidation of sulfides. Res Chem Intermed 43:2707–2724

31. Rostamnia S, Gholipour B, Liu X, Wang Y, Arandiyan H (2018) NH$_2$-coordinately immobilized tris(8-quinolinolato) iron onto the silica coated magnetite nanoparticle: Fe$_3$O$_4$@ SiO$_2$-FeQ$_3$ as a selective Fenton-like catalyst for clean oxidation of sulfides. J Colloid Interface Sci 511:447–455

32. Hajjami M, Sharifirad F, Gholamian F (2017) Synthesis of Fe$_3$O$_4$@ SiO2@ DOPisatin-Ni(II) and Cu(II) nanoparticles: highly efficient catalyst for the synthesis of sulfoxides and disulfides. Appl Organomet Chem 31:e3844

33. Ghorbani-Choghamarani A, Tahmasbi B, Moradi P, Havasi N (2016) Cu–S-(propyl)-2-aminobenzothioate on magnetic nanoparticles: highly efficient and reusable catalyst for synthesis of polyhydroquinoline derivatives and oxidation of sulfides. Appl Organomet Chem 30:619–625

34. Karimpour T, Safaei E, Karimi B, Lee YI (2018) Iron(III) amine bis(phenolate) complex immobilized on silica-coated magnetic nanoparticles: a highly efficient catalyst for the oxidation of alcohols and sulfides. ChemCatChem 10:1889–1899

35. Eftekhari-Sis B, Akbari M, Akbari A, Amini M (2017) Vanadium(V) and Tungsten(VI) oxoperoxo-complexes anchored on Fe$_3$O$_4$ magnetic nanoparticles: versatile and efficient catalysts for the oxidation of alcohols and sulfides. Catal Lett 147:2106–2115

36. Hajjami M, Kolivand S (2016) New metal complexes supported on Fe$_3$O$_4$ magnetic nanoparticles as recoverable catalysts for selective oxidation of sulfides to sulfoxides. Appl Organomet Chem 30:282–288

37. Hu Y, Ma W, Tao M, Zhang X, Wang X, Wang X, Chen L (2018) Decorated-magnetic-nanoparticle-supported bromine as a recyclable catalyst for the oxidation of sulfides. J Appl Polym Sci 135:46036

38. Zohreh N, Hosseini SH, Pourjavadi A, Soleyman R, Bennett C (2016) Immobilized tungstate on magnetic poly (2-ammonium ethyl acrylamide): a high loaded heterogeneous catalyst for selective oxidation of sulfides using H_2O_2. J Ind Eng Chem 44:73–81

39. Moradi-Shoeili Z, Zare M, Akbayrak S, Özkar S (2017) Enhanced reactivity in a heterogeneous oxido-peroxido molybdenum(VI) complex of salicylidene 2-picoloyl hydrazone in catalytic epoxidation of olefins. Transit Met Chem 42:357–363

40. Babaei B, Bezaatpour A, Amiri M, Szunerits S, Boukherroub R (2018) Magnetically reusable $MnFe_2O_4$ nanoparticles modified with oxo-peroxo Mo(VI) Schiff-base complexes: a high efficiency catalyst for olefin epoxidation under solvent-free conditions. ChemistrySelect 3:2877–2881

41. Bezaatpour A, Khatami S, Amiri M (2016) Development of the catalytic reactivity of an oxo–peroxo Mo(VI) Schiff base complex supported on supermagnetic nanoparticles as a reusable green nanocatalyst for selective epoxidation of olefins. RSC Adv 6:27452–27459

42. Li Z, Yang C, Ma Y, Li P, Guan J, Kan Q (2017) Facile fabrication of magnetic MoO_2–Salen-modified graphene-based catalyst for epoxidation of alkenes. Appl Organomet Chem 31:e3742

43. Asgharpour Z, Farzaneh F, Abbasi A (2016) Synthesis, characterization and immobilization of a new cobalt(II) complex on modified magnetic nanoparticles as catalyst for epoxidation of alkenes and oxidation of activated alkanes. RSC Adv 6:95729–95739

44. Bepari RA, Bharali P, Das BK (2017) Controlled synthesis of α-and γ-Fe_2O_3 nanoparticles via thermolysis of PVA gels and studies on α-Fe_2O_3 catalyzed styrene epoxidation. J Saudi Chem Soc 21:S170–S178

45. Dias LD, Carrilho RM, Henriques CA, Piccirillo G, Fernandes A, Rossi LM, Filipa Ribeiro M, Calvete MJ, Pereira MM (2018) A recyclable hybrid manganese(III) porphyrin magnetic catalyst for selective olefin epoxidation using molecular oxygen. J Porphyr Phthalocyanines 22:331–341

46. Nasseri MA, Allahresani A, Raissi H (2014) Mild oxidation of alkenes catalyzed by Fe_3O_4/SiO_2 nanoparticles. Reac Kinet Mech Cat 112:397–408

47. Liao Q, Tannenbaum R, Wang ZL (2006) Synthesis of $FeNi_3$ alloyed nanoparticles by hydrothermal reduction. J Phys Chem B 110:14262–14265

48. Bayat A, Shakourian-Fard M, Ehyaei N, Hashemi MM (2015) Silver nanoparticles supported on silica-coated ferrite as magnetic and reusable catalysts for oxidant-free alcohol dehydrogenation. RSC Adv 5:22503–22509

49. Tang C, Li X, Li Z, Hao J (2017) Interfacial hydrogen bonds and their influence mechanism on increasing the thermal stability of nano-SiO_2-modified meta-aramid fibres. Polymers 9:504–522

50. Bartlett PD (1950) Recent work on the mechanisms of peroxide reactions. Rec Chem Prog 11:47–51