

## Si-Imidazole-HSO<sub>4</sub> functionalized magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles as an efficient and reusable catalyst for the regioselective ring opening of epoxides in water

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**ABSTRACT:** An efficient and simple method for the preparation of Si-Imidazole-HSO<sub>4</sub> functionalized magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles (Si-Im-HSO<sub>4</sub> MNPs) and used as an efficient and reusable magnetic catalysts for the regioselective ring opening of epoxides under green conditions in water. This catalyst was used for the ring opening of epoxide corresponding to the thiocyanohydrins and azidohydrines. Compared to the classical ring opening of epoxides, this new method consistently has the advantage of excellent yields, short reaction times, and methodological simplicity.

**Keywords:** Magnetic catalyst; Imidazole; Epoxide; Azidohydrins; Thiocyanohydrins

### INTRODUCTION

Magnetic nanoparticles (MNPs) have been considered as attractive and interesting materials because of their high surface area and unique magnetic properties, moreover, they have a wide range of novel applications in various fields; such as magnetic fluids [1] catalysis [2,3] biology and medical applications [4] magnetic resonance imaging (MRI) [5,6] data storage [7] and environmental remediation [8,9]. MNPs have been recently viewed as attractive materials either as catalysts or as supporters for immobilization of homogeneous and heterogeneous catalysts [10,11]. Magnetic nanocatalysts can easily be separated and recycled from the other products by an external magnet, which achieves simple separation of the catalysts without filtration [12-14]. Over the last few years, Ionic liquids (ILs), have been generally used as solvents for organic synthesis, catalysis, and also media for extraction processes [15-16]. Therefore, catalytic systems developed on MNP supports have been successfully used in catalyzing a wide range of organic reactions including Knoevenagel reaction [17,18] nucleophilic substitution reactions of benzyl halides [19],

epoxidation of alkenes [20], synthesis of  $\alpha$ -amino nitriles [21], hydrogenation of alkynes [22], esterifications [23], CO<sub>2</sub> cycloaddition reactions [24], Suzuki coupling reactions [25] and three-component condensations [26]. In this research, magnetic nanoparticles which can support ionic liquids will be tested and analyzed as a new heterogeneous catalyst for the regioselective ring opening of epoxides in water.

### EXPERIMENTAL

#### General

Products were characterized by comparison of their spectroscopic data (<sup>1</sup>H NMR, <sup>13</sup>C NMR and IR) and physical properties with those reported in the literature. NMR spectra were recorded in DMSO-d<sub>6</sub> on a Bruker advanced DPX 500 and 400 MHz instrument spectrometers using TMS as internal standard. IR spectra were recorded on a Frontier FT-IR (Perkin Elmer) spectrometer using a KBr disk. All yields refer to isolated products. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. The particle morphology was examined by SEM and TEM.

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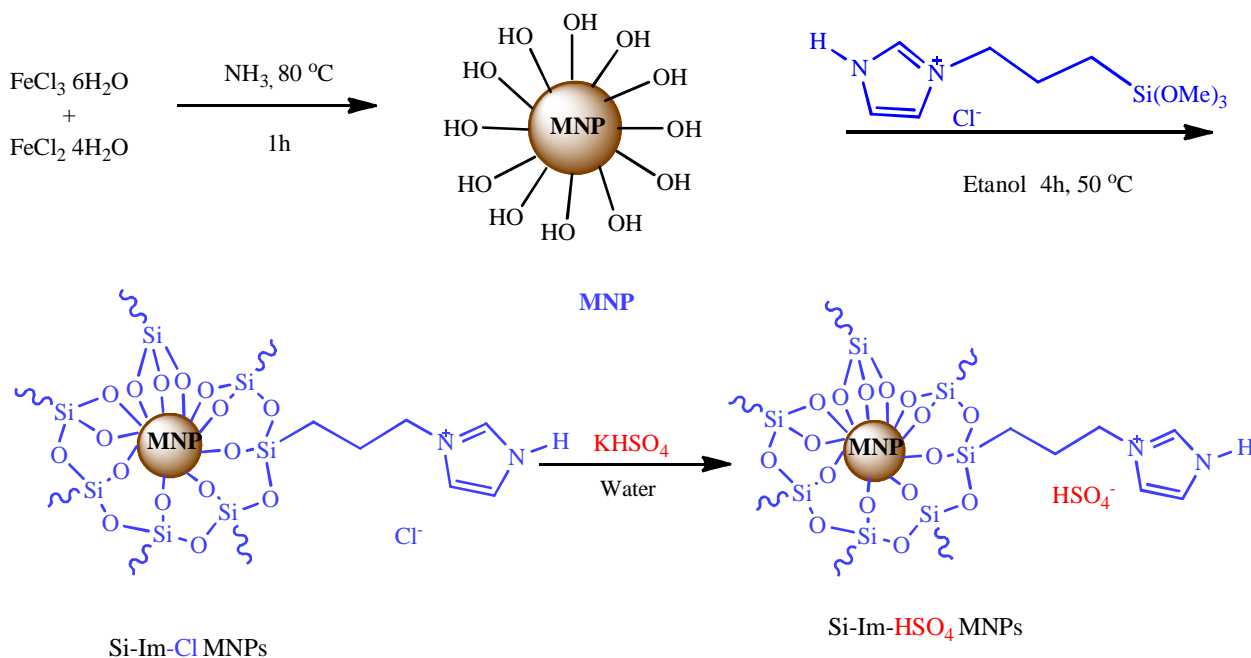
**Synthesis of Si-Imidazole- $\text{HSO}_4$  functionalized magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles (Si-Im- $\text{HSO}_4$  MNPs).** The magnetite nanoparticles were prepared by the conventional co-precipitation method [27]. A schematic representation of the synthesis of magnetic nanoparticles supporting ionic liquids is shown in Scheme 1. Then, 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride (IL), this IL was prepared from the reaction of imidazole with (3-chloropropyl)trimethoxysilane and heated at  $120\text{ }^\circ\text{C}$  for 8 h with continuous stirring under  $\text{N}_2$  atmosphere [28]. Then an excess amount of  $\text{KHSO}_4$  was added into deionized water and stirred for 24 h at room temperature.  $\text{KCl}$ , prepared during the exchange of chloride anions with  $\text{HSO}_4^-$  [29] and  $\text{MNP-IL-}\text{HSO}_4$ , was separated by magnetic decantation, washed with acetonitrile and dichloromethane, and left to dry in a desiccator.

**General procedure for the preparation of  $\beta$ -hydroxythiocyanates and 2-azidoalcohols in water.** Si-Im- $\text{HSO}_4$  MNPs (20 mg) was added to a mixture of the epoxide (1.0 mmol) and  $\text{KSCN}$  or  $\text{NaN}_3$  (3 mmol) in water

(5 ml). The reaction mixture was magnetically stirred at  $80\text{ }^\circ\text{C}$  for the appropriate time. Progress of the reaction was monitored by TLC using ethylacetate:*n*-hexane (1:4). After reaction completion, the mixture was extracted with ethyl ether (5 ml  $\times$  3), washed with brine, dried with  $\text{CaCl}_2$  and evaporated under reduced pressure. The desired thiocyanohydrins and azidoalcohols were obtained in good to excellent isolated yields (83-94%).

The spectral ( $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and IR) of some representative compounds are given below: Spectral data for 1-azido-3-phenoxy-2-propanol (Entry 1). IR  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 2103 ( $\text{N}_3$ )  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz): 3.45-3.54 (m, 2H), 3.89 (m, 1H), 3.97-4.03 (m, 2H), 4.18 (s, 1H), 6.95-7.00 (m, 2H), 7.02-7.06 (m, 1H), 7.27-7.36 (m, 2H)  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz): 53.51, 69.21, 69.30, 114.35, 121.16, 129.42, 158.36.

Spectral data for 3-Phenoxy-2-hydroxypropyl thiocyanate (Entry 1). IR  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 2156 ( $\text{SCN}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz): 3.13-3.31 (2H, d), 3.78 (1H, s), 4.01-4.05 (2H, d), 4.29 (1H, m), 6.95 (2H, m), 7.02 (1H, m),



Scheme 1. Synthesis of Si-Imidazole- $\text{HSO}_4$  functionalized magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles (Si-Im- $\text{HSO}_4$  MNPs)

7.22-7.34 (2H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 37.39, 68.06, 69.51, 112.99, 114.64, 121.32, 129.88, 158.49.

Spectral data for 2-azido-2-phenyl-1-ethanol (Entry 2). IR  $\nu_{\max}$  (cm<sup>-1</sup>): 2102 (N<sub>3</sub>) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 3.37 (s, 1H), 3.74 (m, 2H), 4.65-4.69 (m, 1H), 7.34-7.44 (m, 5H) <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 66.37, 68.03, 127.49, 128.46, 128.61, 136.47.

Spectral data for 1-azido-3-butoxy-2-propanol (Entry 3). IR  $\nu_{\max}$  (cm<sup>-1</sup>): 2102 (N<sub>3</sub>) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 0.87 (t, 3H), 1.31-1.35 (m, 2H), 1.50-1.53 (m, 2H), 3.14 (s, 1H), 3.30-3.32 (m, 2H), 3.39-3.44 (m, 4H), 3.87 (m, 1H) <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 53.37, 69.87, 71.32, 72.07, 117.36, 134.36.

Spectral data for 3-allyloxy-2-hydroxypropyl thiocyanate (Entry 3). IR  $\nu_{\max}$  (cm<sup>-1</sup>): 2155 (SCN) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 3.04-3.24 (3H, m), 3.53 (2H, d), 4.01-4.08 (3H, m), 5.19-5.29 (2H, m), 5.87 (1H, m); (CDCl<sub>3</sub>, 100 MHz): 37.35, 69.17, 71.09, 71.59, 113.07, 117.46, 133.66.

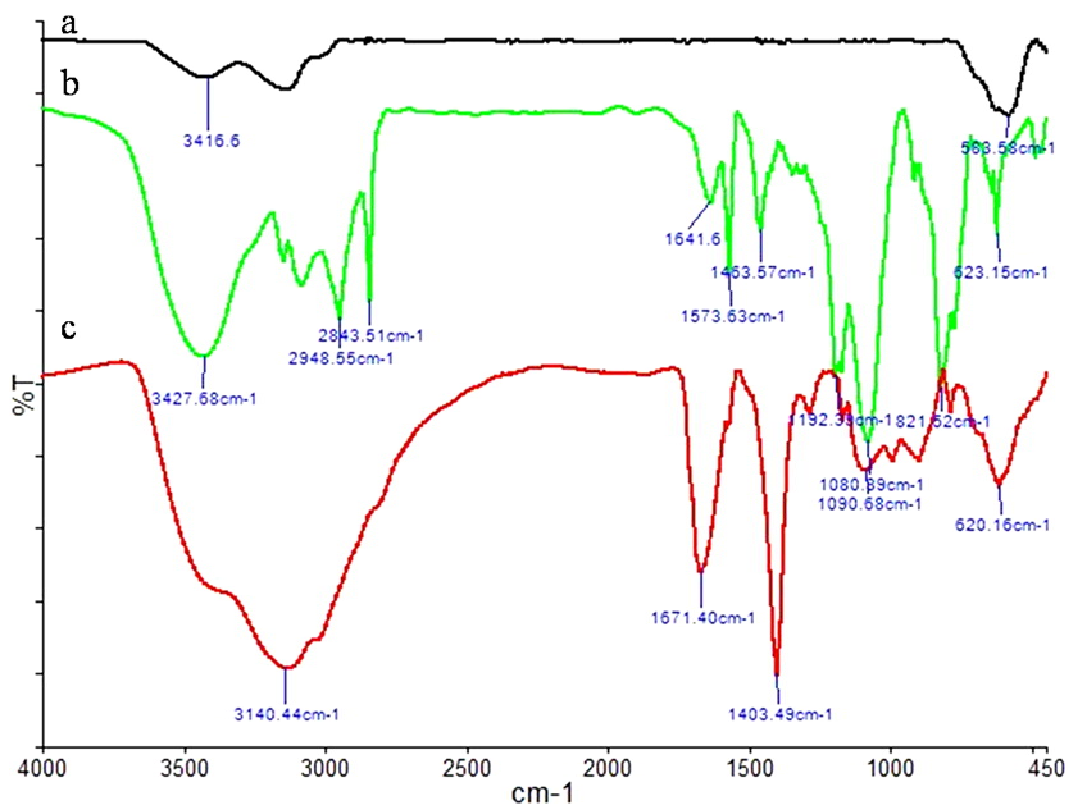
## RESULTS AND DISCUSSION

### Characterization of Si-Im-HSO<sub>4</sub> Ionic Liquid Supported on MNP; Preparation, Structural and Morphological Analysis

Immobilization of Si-Im-HSO<sub>4</sub> functionalized MNPs combines the advantages of ionic liquids with those of heterogeneous catalysts. The Si-Im-HSO<sub>4</sub> MNPs catalyst was synthesized by a multi-step procedure, as shown in Scheme 1, and characterized by various techniques.

An infrared spectrum was obtained in the 400-4000 cm<sup>-1</sup> range, by a Perkin-Elmer FTIR spectrometer. KBr pellets were used for solid samples. The infrared spectroscopy presents a useful tool to initially detect the success of the immobilization process.

Figure 1 presents the FTIR spectra of MNPs, IL and Si-Im-HSO<sub>4</sub> MNPs. Comparing with the spectra of MNPs without modifiers (curve a), spectrum of Si-Im-HSO<sub>4</sub> MNPs



**Fig. 1.** FT-IR spectra of (a) MNP, (b) IL, (c) Si-Im-HSO<sub>4</sub> MNPs.

curve c) presented a new peak at  $1090\text{ cm}^{-1}$  indicative of the Si-O band on  $\text{Fe}_3\text{O}_4$ . The bands at  $2948$  and  $2843\text{ cm}^{-1}$  wave numbers was assigned to the stretching vibrations of  $\text{CH}_3$  and  $\text{CH}_2$  in IL, while new peaks at  $1403$  and  $1287\text{ cm}^{-1}$  are their bending vibrations. Accordingly, one can be sure that IL has been immobilized successfully on the surface of MNPs.

The positions and relative intensities of all the peaks in the XRD pattern of Si-Im- $\text{HSO}_4$  MNPs conform well with the standard XRD pattern of MNPs (Fig. 2). Peaks of Si-Im- $\text{HSO}_4$  MNPs ( $2\theta = 30, 36, 37, 38, 39, 46, 55, 58$ ) and iron oxide phase ( $2\theta = 33, 41, 63, 68$ ) indicate the structure of the catalyst. It is implied that the resultant nanoparticles are pure MNPs with a spinel structure and that the grafting process did not induce any phase change of the MNPs nanoparticles.

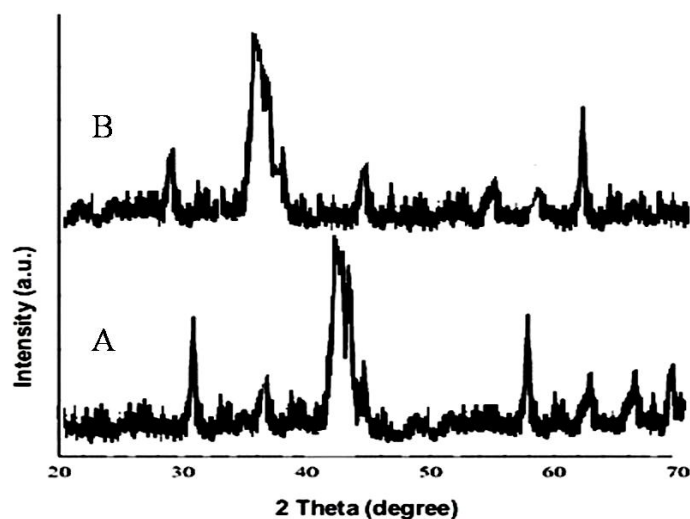
The structural and morphological characterization of  $\text{Fe}_3\text{O}_4$  and Si-Im- $\text{HSO}_4$  MNPs nanostructure were performed by measuring SEM using a Philips XL30 scanning electron microscope. The surface morphologies of the  $\text{Fe}_3\text{O}_4$  nanoparticles without modifiers and Si-Im- $\text{HSO}_4$  MNPs are shown in Figs. 3A and 3B.

The TEM images of MNPs and Si-Im- $\text{HSO}_4$  MNPs are presented in Fig. 4, showing almost homogeneous and uniform distribution of these particles in the powder samples. Figure 5 shows the magnetization curves of the

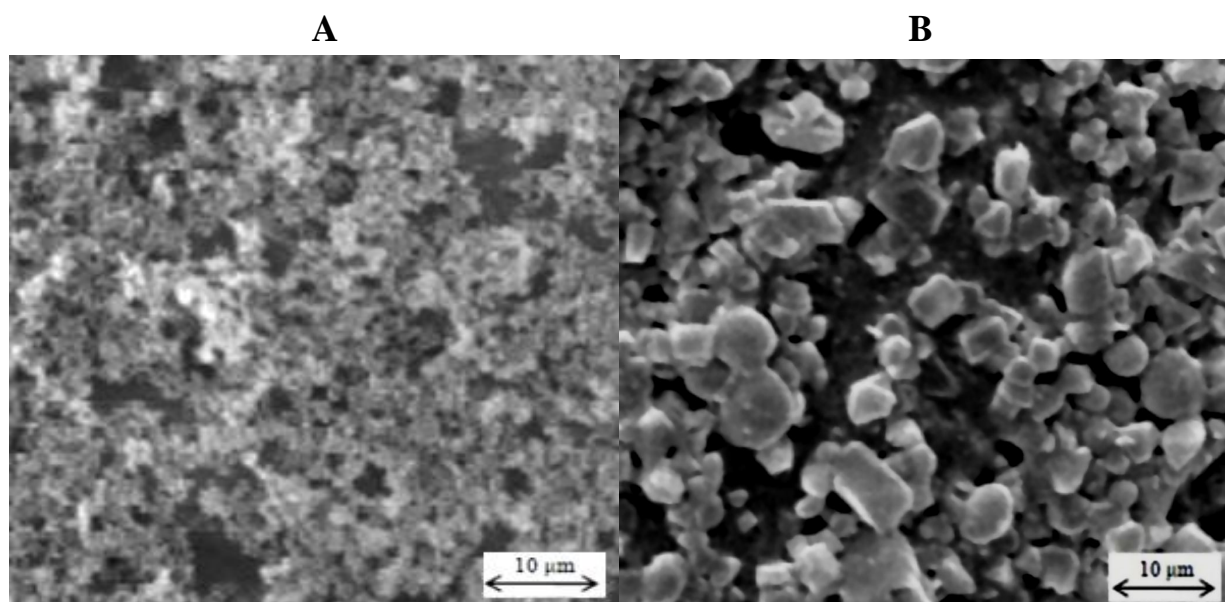
prepared MNPs, and Si-Im- $\text{HSO}_4$  MNPs. The magnetization curve of MNPs exhibited no eminence effect (indicating the superparamagnetic property) with saturation magnetization of about  $60\text{ (emu g}^{-1}\text{)}$ . As seen in Fig. 5, similar to magnetite particles, MNPs, and Si-Im- $\text{HSO}_4$  MNPs nanocomposites also indicate a zero remanence  $M_s$  and coercivity, suggesting that the superparamagnetic behavior is still retained with the nanocomposite materials.

#### Application of Si-Im- $\text{HSO}_4$ Ionic Liquid Supported on MNP as Magnetic Catalyst for the Regioselective Ring Opening of Epoxides in Water

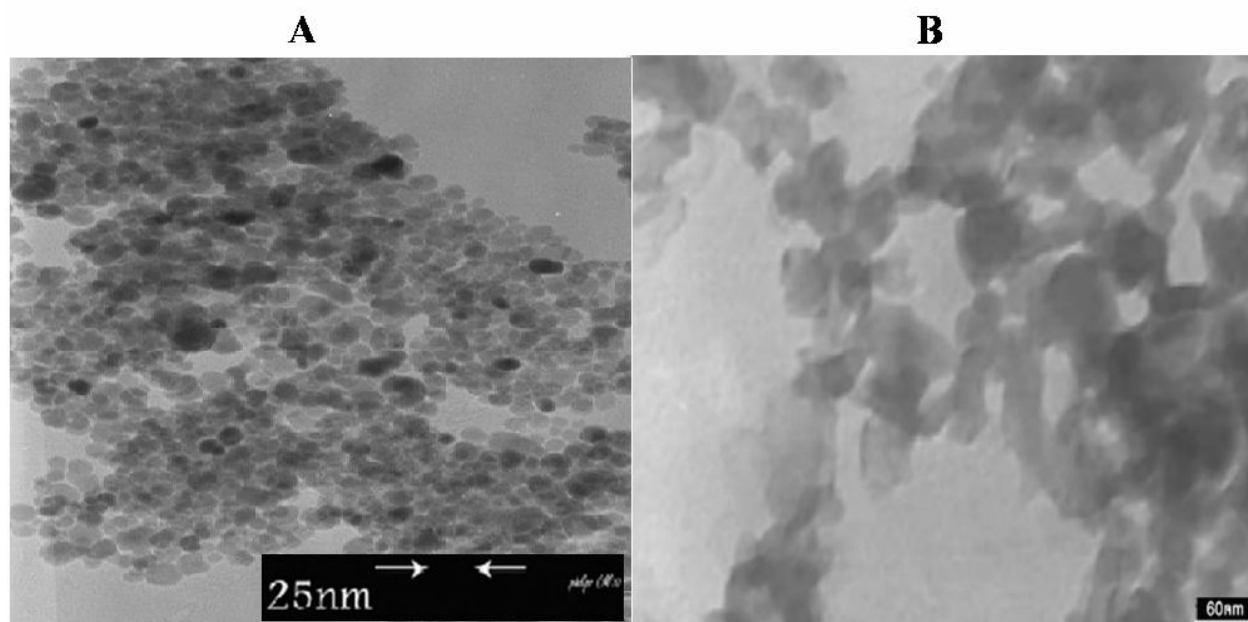
The catalyst concentration varied over a range of 5-25 mg Si-Im- $\text{HSO}_4$  MNPs on the basis of the total volume of the reaction mixture. As mentioned before, we have carried out the reaction of 2,3-epoxypropyl phenyl ether with potassium thiocyanate. Different reaction conditions have been studied for optimization (Table 1). Entry 6 in Table 1 shows optimization of reaction conditions. After optimizing the conditions, we examined the generality of these conditions to other substrates using several epoxides. The reaction proceeds efficiently in all cases. Different epoxides underwent ring opening easily in the presence of Si-Im- $\text{HSO}_4$  ionic liquid supported on MNP at  $80\text{ }^\circ\text{C}$  condition in water (Table 2). The products were formed in excellent



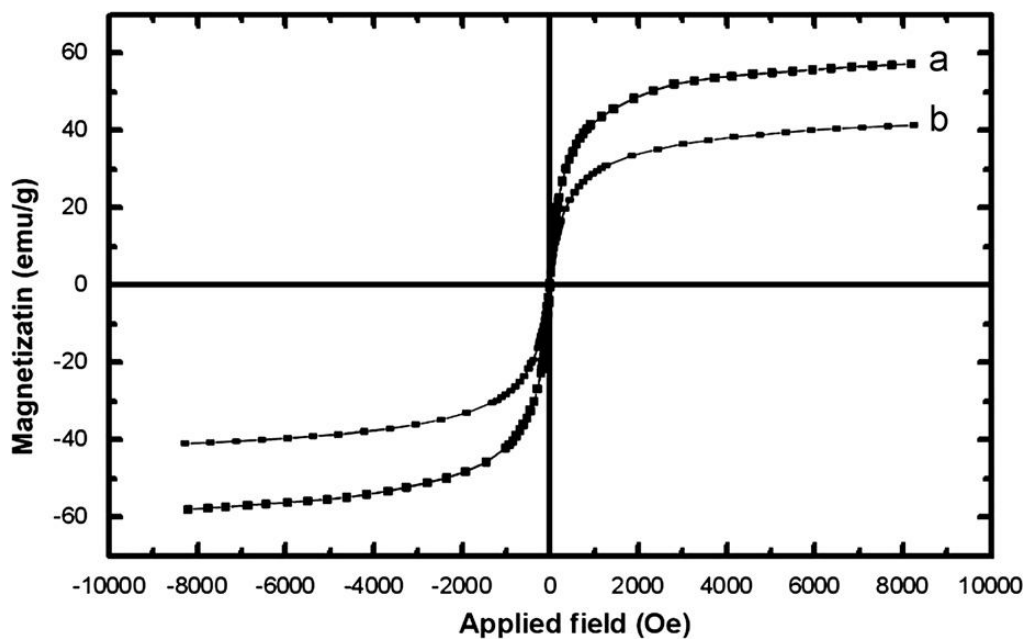
**Fig. 2.** XRD pattern of (A) MNPs, (B) Si-Im- $\text{HSO}_4$  MNPs.



**Fig. 3.** SEM images of (A) MNPs, (B) Si-Im-HSO<sub>4</sub> MNPs.

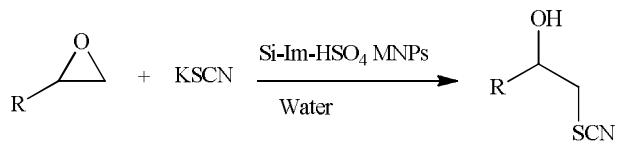


**Fig. 4.** TEM images of (A) MNPs, (B) Si-Im-HSO<sub>4</sub> MNPs.

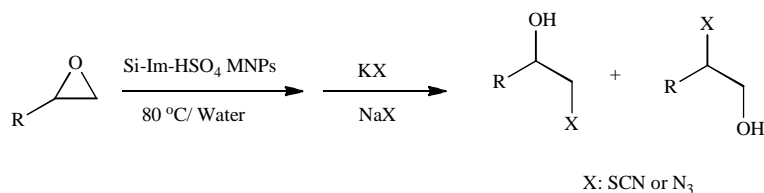


**Fig. 5.** Magnetization curves of (a) MNPs and (b) Si-Im-HSO<sub>4</sub> MNPs.

**Table 1.** Optimization of Experimental Conditions for Ring Opening of Epoxides



Entry	Catalyst (mg)	Temperature (°C)	Time (min)	Yield (%)
1	-	80	90	Trace
2	10	r.t.	90	Trace
3	10	60	90	38
4	10	80	90	52
5	15	80	45	67
6	20	80	10	93
7	25	80	10	86
8	20	100	15	90

**Table 2.** Ring Opening of Various Epoxides in the Presence of Si-Im-HSO<sub>4</sub> MNPs in Water

Entry	Substrate	Products <sup>a, b</sup>	SCN <sup>-</sup>		N <sub>3</sub> <sup>-</sup>	
			Time (min)	Yield (%) <sup>c</sup>	Time (min)	Yield (%) <sup>c</sup>
1			10	93	10	89
2			15	91 (95:5)	15	87 (95:5)
3			25	88	20	89
4			35	86	30	90
5			30	85	30	87
6			20	92	25	94
7			30	90	30	92
8			40	82	35	85
9			30	86	30	89
10			40	89	40	85

<sup>a</sup>Products were identified by comparing their physical and spectral data with those of authentic samples. <sup>b</sup>X in all products is SCN<sup>-</sup> or N<sub>3</sub><sup>-</sup>. <sup>c</sup>Isolated yields.

yields. The conversion was completed in 10-40 min.

In view of the emerging importance of Si-Im-HSO<sub>4</sub> MNPs as novel reaction media, we wish to report the use of Si-Im-HSO<sub>4</sub> MNPs as efficient promoters for the ring opening of various epoxides. In this reaction, thiocyanohydrins and azidohydrines as products were obtained in good yields, short reaction times and avoid use of organic solvents (handling, cost, safety, pollution). Water is a desirable solvent for chemical reactions for reasons of cost, safety and environmental concerns, use of water in this reaction gave only greater regioselectivity ring opening of epoxide.

As seen in Table 3, Si-Im-HSO<sub>4</sub> MNPs as a catalyst afforded good results in comparison to the other catalysts. In

order to evaluate the efficiency of our introduced method, more recently developed methods were compared with our present method on the basis of the yields and reaction time parameters, the results are given in Table 3. Catalyst reusability is of major importance in heterogeneous catalysis. The recovery and reusability of the catalyst was studied using 2,3-epoxypropyl phenyl ether with potassium thiocyanate as a model reaction. Since the catalyst can be separated from the reaction mixture using an external magnetic field, it was recovered with a simple magnet after the dilution of the reaction mixture with water. The catalyst was consecutively reused seven times without any noticeable loss of its catalytic activity (Table 4).

**Table 3.** Comparison of Catalytic Ability of Catalysts

Entry	Catalyst/solvent/temperature/nucleophile	Reaction time (h)	Yield (%)	Ref.
1	Network polymer/water/80 °C/N <sub>3</sub>	1.5	89	[30]
2	[Hmim]N <sub>3</sub> /reflux/N <sub>3</sub>	55 min	94	[31]
3	[bmim]PF <sub>6</sub> ([bmim]BF <sub>4</sub> )/water/65 °C/N <sub>3</sub>	3(5)	95(89)	[32]
4	γ-Fe <sub>2</sub> O <sub>3</sub> @HAp-Ni <sup>2+</sup> /water/80 °C/N <sub>3</sub>	20 min	90	[33]
5	Al(HSO <sub>4</sub> ) <sub>3</sub> /solvent-free/r.t./SCN	5min	91	[34]
6	Selectfluor/CH <sub>3</sub> CN/r.t./SCN	2.5	95	[35]
7	PTC/CH <sub>3</sub> CN/r.t./SCN	1.5	90	[36]
8	Si-Im-HSO <sub>4</sub> MNPs/Water/80 °C/SCN(N <sub>3</sub> )	10 (10) min	93(89)	This work

**Table 4.** The Catalytic Activity of Si-Im-HSO<sub>4</sub>MNPs in 7 Cycles

Run	1	2	3	4	5	6	7
Yield (%)	93	91	90	87	85	85	81



## CONCLUSIONS

In this research, Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles were readily synthesized and functionalized with Si-Im-HSO<sub>4</sub> ionic liquid. We describe a simple and highly efficient protocol for the regioselective ring opening of epoxides using Si-Im-HSO<sub>4</sub> MNPs as catalyst. The advantages of the present procedure are its simplicity of operation, very short reaction times in comparison to the other procedures, and the high yields of products. In this way, the catalyst can be easily recovered by simple magnetic decantation and reused several times with no loss of activity.

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