RESEARCH PAPER

A Mild and Green Route for Regio-selective Amination of Oxiranes Using Nanomagnetic Supported Ferrous Ion as a Solid Lewis Acid Catalyst in Water

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ABSTRACT

A mild, green and highly efficient route for regio-selective amination of oxiranes was developed via incorporation of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) cations onto the surface of hydroxyapatite-encapsulated γ-Fe$_2$O$_3$ nanoparticles (γ-Fe$_2$O$_3$@HAp). Among six magnetically recoverable catalytic systems denoted as [γ-Fe$_2$O$_3$@HAp-M^{II}], the catalyst in which M designated as Fe(II) showed the best efficiency as well as regio-selectivity in amination of oxiranes under an ambient reaction condition. A wide variety of aromatic and aliphatic amines were reacted with epoxides using magnetically separable iron catalyst to give the corresponding amino alcohols in excellent yields and selectivities in water as solvent at room temperature. In addition, recovery of the catalyst was successfully carried out in subsequent runs without any decrease in activity even after 5 runs. High regio-selectivity toward terminal ring-opening, efficient catalyst reusability using simple magnetic separation, high yields, simplicity in operation and diversity for various substrates are of advantages of this study.

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INTRODUCTION

After decades of extensive research, it is well-known that Lewis acid catalysis is a promising approach for many organic transformations [1]. Despite acceptable results achieved in this area, major drawbacks have been left which are mainly associated with the separation of the products from the catalyst and catalyst recycling (often catalysts are destroyed after usual aqueous workup) [2-4]. These downsides commonly lead to severe environmental pollutions, limit the efficiency and widespread application of the conventional Lewis acid catalytic systems. Therefore, the development of more efficient Lewis acid catalysts that have all salient features of being green, cost-effective, mild

and reusable along with possessing the capability to improve waste-management has been long awaited.

In this context, calcium hydroxyapatite (CaHAp) has received a good deal of attention in recent years due to its physiochemical and biological properties. Besides, it has extensive applications in many fields of science such as chromatography, water purification and as absorbent of proteins, antibiotics, anticoagulants and anticancer drugs [5]. Recently, materials based on CaHAp have piqued growing interests in catalysis, because of its excellent ion-exchange ability, low water solubility, availability, low cost and high stability under oxidizing and reducing conditions [6-7]. The introduction of transition metal cations such as Sn(II), Sn(IV),

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Ru(III), Pd(II) into the apatite framework can generate stable monomeric phosphate complexes, which result in outstanding catalytic performance for different C-X and C-C bond-forming reactions [8]. Compared with the normal CaHAp particles, nano CaHAp particles are even more favorable, due to its higher surface area and binding sites as well as its higher dispersion properties [9]. However, the great difficulty when using nanocatalyst particles is related to their recovery and recycling from the reaction medium by classical methods such as filtration or centrifugation [10]. Therefore, an efficient technique for the facile separation of the nanocatalysts from the reaction mixture seems to be a milestone in this area. Recent studies have demonstrated that magnetic nanoparticles, mainly iron oxides, are excellent supports in catalysis [11-12] avoiding the loss of mass and enhancing the purity of the products using solely a simple magnetic separation technique [13].

There is much interest for ring-opening of oxirans to β-aminoalcohols because obtained products are valuable compounds that have extensive applications in medicinal chemistry, organic synthesis in general and particularly in asymmetric synthesis as chiral ligands and auxiliaries [14-15]. In recent years, different metal catalysts and reaction media such as metal-triflates [16], metal halides [17] or other metal salts [18] as well as polymer supported catalysts [19], fluorinated alcohols [20] and ionic liquids [21] have been used for the amination of oxirans. Despite lots of work dedicated to this area which has been led to significant achievements, typical shortcomings such as high temperatures or large amounts of toxic and unrecoverable/ unrecyclable metal catalysts as well as formation of side products (mainly bis-adducts) have still remained as the main challenges of this reaction. In addition, most of the transition metal catalysts used for this reaction such as Er [22], Y [23], Sb [24], Sc [25], Bi [26] and Sm [27] are very expensive rare earth metals, which their application as unrecoverable catalysts is not economical. Consequently, it seems that the design of efficient, environmentally accepted, low-cost and recoverable catalytic systems for amination of oxirans, especially in its *regio*-selective form [28-32], based on inexpensive and non-toxic transition metals is a requisite.

In this respect and in pursuit of our on-going programme in devising novel "*catalytic assemblies*" based on the 'green chemistry' concepts [33-38],

we report herein a highly active and *regio*-selective method for the amination of oxirans using a magnetic nanoparticle supported Fe(II) catalyst in water. To do so, hydroxyapatite-encapsulated γ-Fe_2O_3 nanocrystallities was prepared and used for the immobilization of various transition metals. The catalytic activity and selectivity of the prepared metal catalysts were compared in a model reaction and it was revealed that the Fe(II) based catalyst is superior to all others. To the best of our knowledge, eco-friendly Fe(II) cations have not been reported as a catalyst for this reaction yet.

EXPERIMENTAL
Materials and Methods

All materials and solvents are in analytical-grade and purchased from Merck and Fluka Companies without further purifications. Water was deionized before the usage. Catalysts were characterized using XRD, SEM, EDX, VSM and FT-IR. The XRD patterns were recorded at r.t. by a Philips X'pert 1710 diffractometer using Co Kα (λ = 1.78897 Å) and Cu Kα (λ = 1.54056 Å) in Bragg-Brentano geometry (θ-2θ). Scanning electron microscopy (SEM) images were obtained *via* SEM (Philips XL 30 and S-4160) with gold coating equipped with energy dispersive X-ray spectroscopy (EDX). FT-IR spectra were obtained over the region 400-4000 cm^{-1} with NICOLET IR100 FT-IR. A home-made VSM was used for the magnetic properties of the catalysts (Meghnatis Daghigh Kavir Company, Iran). ^{1}H NMR (500 MHz) spectra were recorded in CDCl$_3$ on a Bruker Avance DRS spectrometer.

Synthesis of γ-Fe_2O_3@HAp-M^{2+} Catalysts (M^{2+}: Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+})

Preparation of HAp-encapsulated magnetite was carried out according to the previously reported methods [39]. 500 mg γ-Fe_2O_3@HAp was stirred with different aqueous solutions of M(II) salts ($MnCl_2.4H_2O$, $FeCl_2.4H_2O$, $CoCl_2$, $NiCl_2$, $Cu(NO_3)_2.4H_2O$ and $Zn(NO_3)_2.6H_2O$) (6.4 mmol in 50 ml DW) separately at r.t. for a period of 24 h. The obtained slurry was separated with an NdBFe (Neodymium-Bohr-Fe) magnet, washed with DW and methanol twice and dried overnight at 50 °C (Scheme 1).

General Procedure for Aminolysis of Epoxides

1 mmol of epoxy compound and 1.2 mmol of amine in the presence of 9 mol% of γ-Fe_2O_3@HAp-Fe^{II} were stirred in 3 ml water at room temperature.
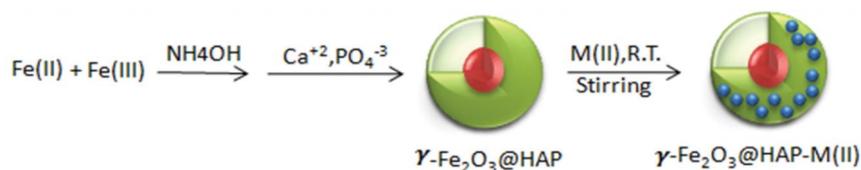
Scheme 1. Preparation of various γ-Fe$_2$O$_3$@HAp-MII catalysts
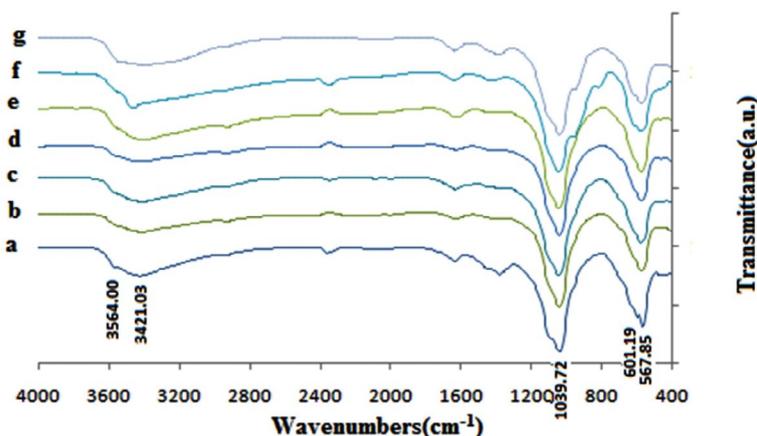
Fig. 1. FT-IR spectra of γ-Fe$_2$O$_3$@HAp (a) and M(II) doped γ-Fe$_2$O$_3$@HAp: Mn(II) (b), Fe(II) (c), Co(II) (d), Ni(II) (e), Cu(II) (f), Zn(II) (g).

After completion of the reaction (monitored by TLC), 5 ml CH$_2$Cl$_2$ was added to the reaction mixture and the catalyst was separated with an external magnetic device. The resulting CH$_2$Cl$_2$ phase was concentrated on a rotary evaporator to obtain crude products. Further purification was performed *via* recrystallization from n-hexane and ethyl acetate or using column chromatography eluted by AcOEt and hexane (1:10 to 1:4). All of the products were known compounds and their NMR spectra were consistent with the reported compounds.

RESULTS AND DISCUSSION

γ-Fe$_2$O$_3$@HAp nanoparticles were prepared according to the previously reported procedure [39] via the mixing of iron(II) and iron(III) salts followed by the addition of Ca(II) and phosphate sources. Afterwards, the immobilization of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) cations was successfully achieved on the surface of γ-Fe$_2$O$_3$@HAp as outlined in Scheme 1 by treatment of aqueous solutions of divalent metal salts with γ-Fe$_2$O$_3$@HAp nanoparticles at room temperature for 24 h. The presented simple route

provides nanoparticles of the catalysts in uniform morphologies, narrow size distributions and excellent magnetic properties.

The prepared catalysts (denoted as γ-Fe$_2$O$_3$@HAp-M^{II}) were characterized by various spectroscopic techniques. Fig. 1 shows the FT-IR spectra of all catalysts. The absorption bands at 3564 cm^{-1} represent the stretching vibration of the O-H groups in HAp component. Signals at 1039 cm^{-1} assigned as the stretching mode of phosphate group (PO$_4^{3-}$, P-O), while the bands at 601 cm^{-1} and 567 cm^{-1} exhibited it's bending vibration (PO$_4^{3-}$, O-P-O) which were in overlap with Fe-O stretching. As expected, there was no obvious difference between FT-IR spectrum of γ-Fe$_2$O$_3$@HAp and its M(II) supported analogues.

The crystalline phase of the prepared M(II) supported on HAp encapsulated γ-Fe$_2$O$_3$ nano structures was investigated by X-ray diffraction (XRD) analysis. All of the M(II) supported structures show the diffraction patterns similar to their parent γ-Fe$_2$O$_3$@HAp. Hydroxyapatite and maghemite constituents were obviously detected in XRD patterns. The XRD patterns of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} supported γ-Fe$_2$O$_3$@HAp
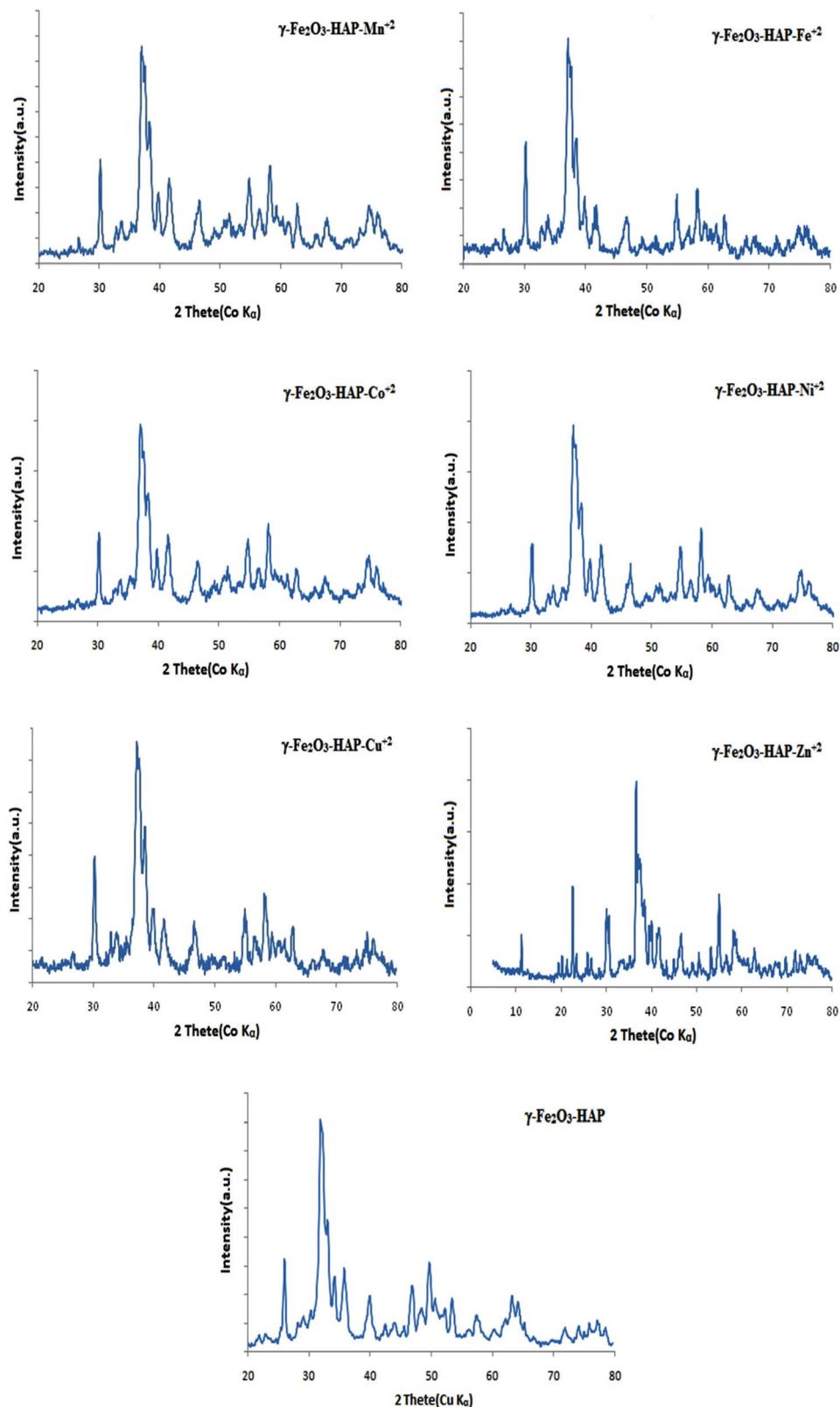
Fig. 2. The XRD patterns of γ-Fe₂O₃@HAp and the synthesized γ-Fe₂O₃@HAp-MII.

are shown in Fig. 2 in comparison with XRD of their γ-Fe$_2$O$_3$@HAp parent. In all materials, the observed diffraction peaks are agreed well with the cubic structure of maghemite (1999 JCPDS file No 39-1346) and the hexagonal structure of hydroxyapatite (1999 JCPDS file No. 24-0033). Only, in the case of γ-Fe$_2$O$_3$@HAp-Zn^{2+}, little amounts of a new phase, Zn$_3$(PO$_4$)$_2$.4H$_2$O, is detected at around 11.25°, 22.58° and 36.54° (1999 JCPDS file No. 37-0465) as impurity. Except for γ-Fe$_2$O$_3$@HAp-Zn^{2+}, in all of the XRD patterns, no other phase was observed. Therefore, XRD analysis proved that modification

of the surface of γ-Fe$_2$O$_3$@HAp with metal ions does not greatly change the crystalline structure and phase purity of γ-Fe$_2$O$_3$@HAp. Also, other iron oxides phases such as Fe$_3$O$_4$ and metallic Fe are not detected in XRD patterns. Importantly, no oxidized phase of metals such as metal oxides is observed in XRD patterns indicating that metal species on the surface of γ-Fe$_2$O$_3$@HAp are stable and would not be oxidized under air.

Moreover, the SEM images of the prepared nanoparticles (Fig. 3) confirmed their nano-metric sizes, spherical morphologies and uniform size
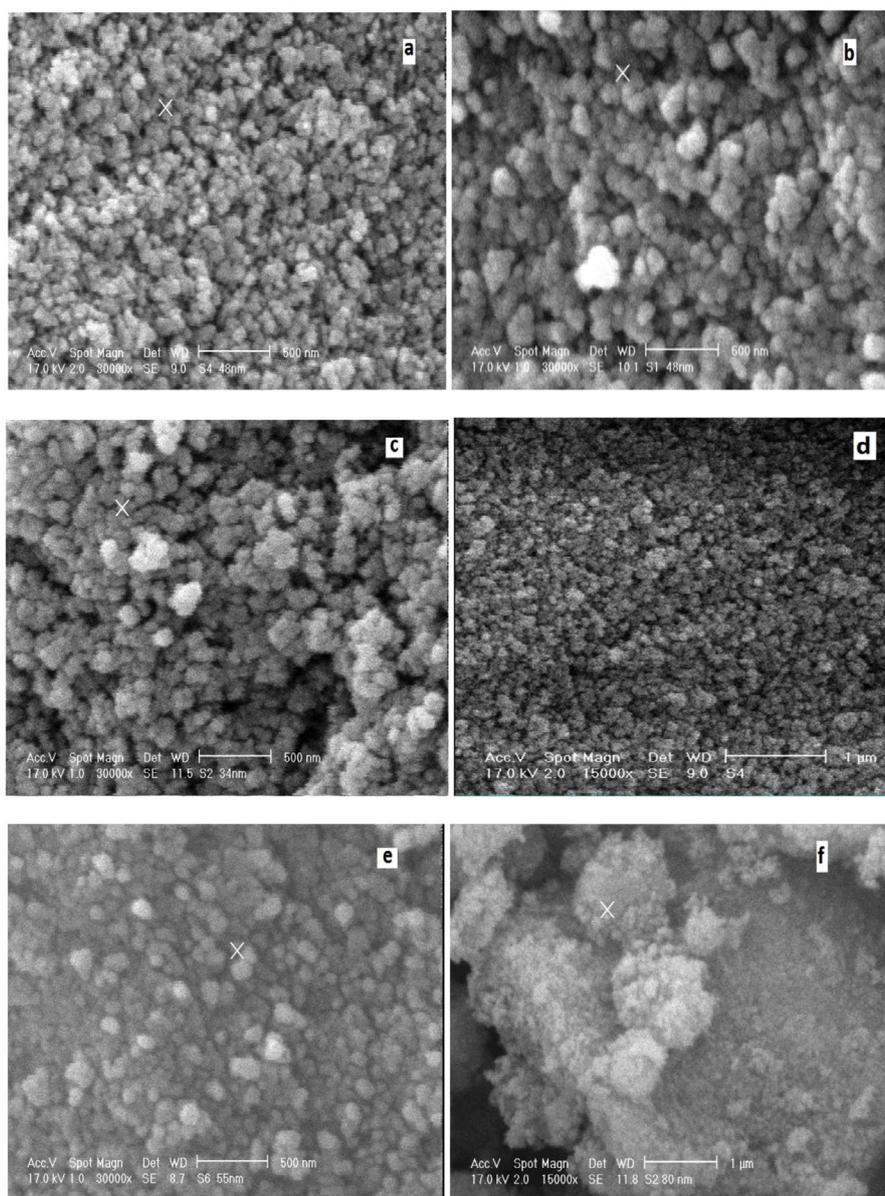

Fig. 3. SEM images of γ-Fe$_2$O$_3$@HAp decorated with (a) Mn(II), (b) Fe(II), (c) Co(II), (d) Ni(II), (e) Cu(II) and (f) Zn(II) (for a, b, c and e scale bar: 500 nm, for d and f scale bar: 1 μm).

distributions as well. As seen in SEM images, all of the materials are in the range of about 20-80 nm.

The presence of related M(II) ions in all of the catalysts was verified by EDX as well as ICP analysis (summarized in Table 1). These analyses showed the successful advent of metal ions into the structure of γ-Fe$_2$O$_3$@HAp nanoparticles. Notably, as can be seen in Table 1, (Ca+M)/P ratio in all of the catalysts is higher than 1.67 (Ca/P ratio in stoichiometric γ-Fe$_2$O$_3$@HAp) confirming the fact that, M(II) ions are firmly supported on the surface of γ-Fe$_2$O$_3$@HAp crystals and there is not merely a simple ion exchange with Ca(II) in the structure of HAp. Also, the existence of Cl peak in EDX spectra (see supporting information) for those catalysts at which MCl$_2$ was

used as metal source, underpinned this conclusion. If Cl was absent in the EDX spectra, M(II) would be replaced with Ca(II) [40].

After fully characterization of the prepared γ-Fe$_2$O$_3$@HAp-M^{II} catalysts, their catalytic activity and selectivity were evaluated in the ring-opening of oxiranes with amines. Firstly, the amination of 2,3-epoxypropyl phenyl ether (1a) with *p*-methyl aniline (2a) (Table 2) was selected as a model reaction to compare the catalytic performance of the present γ-Fe$_2$O$_3$@HAp-M^{II} catalysts.

As shown in Table 2 (entries 1-6), all of the prepared γ-Fe$_2$O$_3$@HAp-M^{II} catalysts successfully promoted this reaction in high isolated yields when the reactions accomplished at room temperature

Table 1. Properties of γ-Fe$_2$O$_3$@HAp-M^{2+} Catalysts Based on EDX and ICP Analyses

γ-Fe$_2$O$_3$@HAp-M^{II}	M(II) (Wt%)[a]	(Ca+M)/P[b]	Loading of M(II) (mmol g^{-1})[a]
γ-Fe$_2$O$_3$@HAp-Mn^{II}	10.34	5.85	1.88
γ-Fe$_2$O$_3$@HAp-Fe^{II}	20.20	2.35	3.63
γ-Fe$_2$O$_3$@HAp-Co^{II}	7.88	2.60	1.34
γ-Fe$_2$O$_3$@HAp-Ni^{II}	7.09	2.21	1.21
γ-Fe$_2$O$_3$@HAp-Cu^{II}	17.63	2.22	2.77
γ-Fe$_2$O$_3$@HAp-Zn^{II}	36.65	2.16	5.61

[a]Based on ICP analysis. [b]Atomic molar ratio based on EDX analysis.

Table 2. Amination of 2,3-Epoxypropyl Phenyl Ether (1a) with p-Methyl Aniline (2a) in the Presence of Prepared Catalysts
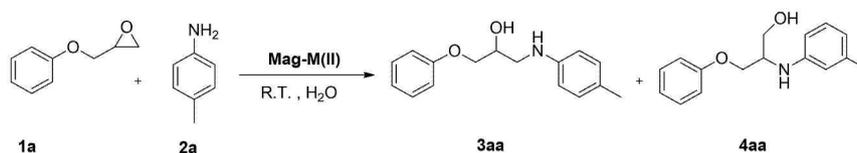
| Entry	Catalyst (M(II))	Time (h)	Yield (%)[a]	Selectivity (3:4)[b]
1	Mag-Mn^{II}	15	80	62:38
2	Mag-Fe^{II}	15	86	100:0
3	Mag-Co^{II}	15	80	57:43
4	Mag-Ni^{II}	15	79	60:40
5	Mag-Cu^{II}	15	75	73:27
6	Mag-Zn^{II}	15	73	68:32
7	No Catalyst	4 day	Trace	-
8	γ-Fe$_2$O$_3$@HAp[c]	15	20	-
9	Mag-Fe^{II}[d]	10	94	100:0
10	Mag-Fe^{II}[e]	4	96	100:0
11	Mag-Fe^{II}[f]	4	96	100:0

[a]Reaction conditions: 1 mmol epoxide, 1.2 mmol amine, 2.5 mol% *cat.* (based on M(II)), 3 ml H$_2$O, room temperature.
[b]Based on ^{1}H NMR. [c]2.5 mol% based on Ca(II). [d]5 mol% *cat.* was used. [e]9 mol% cat. was used. [f]11 mol% *cat.* was used.

in water. Interestingly, in all cases 1-phenoxy-3-(*p*-tolylamino)propan-2-ol (3a) was the main product. It is important to note that in the absence of any catalyst or using unmodified γ-Fe$_2$O$_3$@HAp, the reaction did not progressed effectively (Table 2, entries 7, 8) indicating the crucial role of the decorated transition metals on the surface of γ-Fe$_2$O$_3$@HAp for catalysis. Since the ferrous ion containing catalyst (γ-Fe$_2$O$_3$@HAp-Fe^{II}) showed the best catalytic activity *and more*

importantly excellent selectivity in the model reaction (Table 2, entry 2), and since the iron is inexpensive and one of the most abundant and environmentally friendly transition metals, our next investigations focused on the γ-Fe$_2$O$_3$@HAp-Fe^{II}. In the next stage, the amount of γ-Fe$_2$O$_3$@HAp-Fe^{II} catalyst was screened (Table 2, entries 9-11) and it was found that the best result is obtained using 9 mol% of the catalyst in which the reaction is completed during 4

Table 3. Ring-opening of Epoxides with Various Amines Catalysed by γ-Fe$_2$O$_3$@HAp-FeII
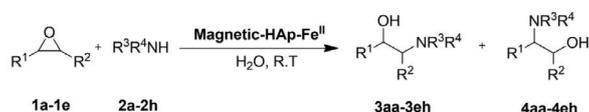
Entry	R^1/R^2	X	Time (h)	Yield (%)[a] (3:4)[b]	Ref. for NMR
1	PhOCH$_2$/H 1a	2a	4	96 (100:0)	[41]
2	PhOCH$_2$/H 1a	2b	5	96 (75:25)	[42]
3	PhOCH$_2$/H 1a	2c	3	90 (77:23)	[43]
4	PhOCH$_2$/H 1a	2d	6	93 (77:23)	[41]
5	PhOCH$_2$/H 1a	2e	15	85 (100:0)	[44]
6	PhOCH$_2$/H 1a	2f	20	87 (100:0)	[44]
7	PhOCH$_2$/H 1a	2g	24	84 (100:0)	[44]
8	PhOCH$_2$/H 1a	2h	20	85 (100:0)	[45]
9	Ph/H 1b	2b	4	94 (0:100)	[46]
10	(CH3)$_2$CHOCH$_2$/H 1c	2b	5	95 (55:45)	[47]
11	CH$_2$=CHCH$_2$OCH$_2$/H 1d	2b	5	94 (50:50)	[48]
12	-(CH$_2$)$_4$- 1e	2b	5	96	[20]

[a]Reaction conditions: 1 mmol epoxy, 1.2 mmol amine, 9 mol% *cat.*, 3 ml H$_2$O, room temperature, isolated yield. [b]Determined by ^{1}H NMR.
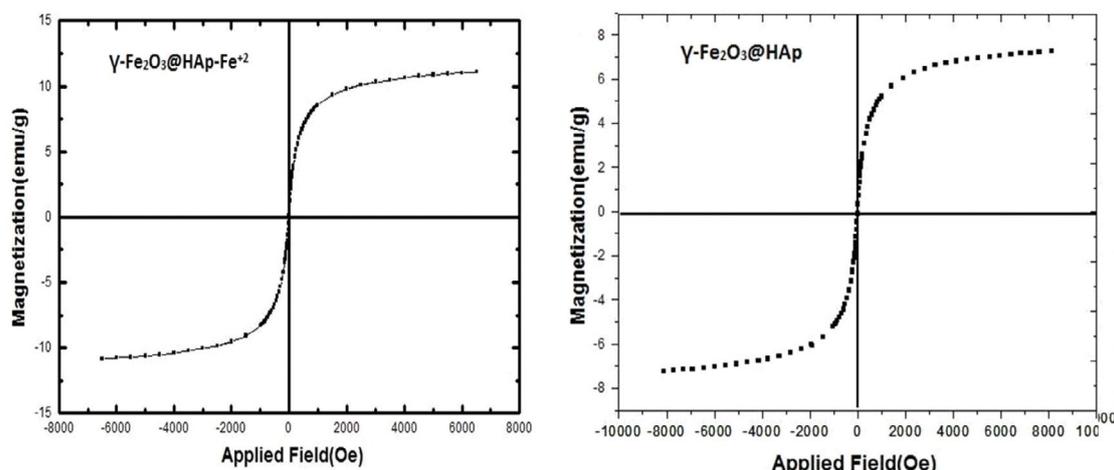
Fig. 4. VSM curves of γ-Fe₂O₃@HAp-FeII and γ-Fe₂O₃@HAp nanoparticles.

h while keeping its selectivity to 100% (Table 2, entry 10). Thus, 9 mol% of the γ-Fe₂O₃@HAp-Fe^{II} catalyst, water as solvent and room temperature were selected as a mild and green condition to explore the substrate scope of the reaction.

Having the optimized reaction conditions in hand, in the next step the substrate scope and limitations of epoxy ring opening reaction in the presence of developed Fe based catalyst were studied. As exemplified in Table 3 entries 1-4, various aromatic amines such as aniline and its *para*-substituted derivatives bearing either electron-withdrawing or electron-donating groups successfully reacted with 2,3-epoxypropyl phenyl ether (1a) during 3-6 h at room temperature with high yields and selectivities. Importantly, less reactive aliphatic, benzylic and heteroaromatic amines provided the corresponding *β*-aminoalcohols in some longer reaction times but still at room temperature with *100% selectivity* (Table 3, entries 5-8). To expand the substrate scope of the reaction, various epoxides were reacted with aniline and again it was observed that the corresponding products are obtained with high efficiencies at ambient conditions (Table 3, entries 9-12). Notably, except for 2-phenyloxirane, which was opened by internal *regio*-selectivity and 2-((allyloxy)methyl)oxirane, in all cases the terminal attack was predominant.

One of the important subjects which should be considered in the case of core/shell magnetic materials is their sufficient magnetic properties prerequisite for the practical separation from the reaction mixture [13]. Magnetic features of γ-Fe₂O₃@HAp and γ-Fe₂O₃@HAp-Fe^{II} nanoparticles were analysed using a homemade vibrating
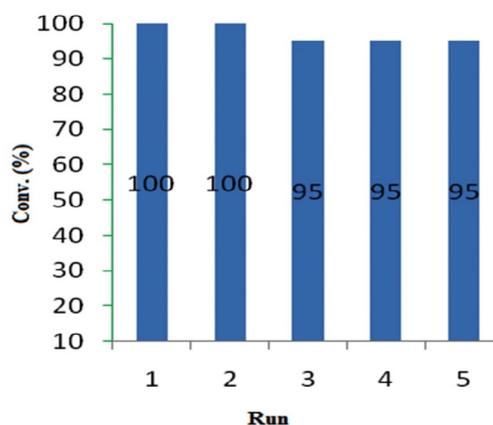
Fig. 5. Recycling of γ-Fe₂O₃@HAp-FeII in amination of 2,3-epoxypropyl phenyl ether (1a) with aniline (2a)

sample magnetometer (Meghnatis Daghigh Kavir Company, Iran) at room temperature. As depicted in Fig. 4, the hysteresis loops for the samples were completely reversible. The magnetic saturation (Ms) values for γ-Fe₂O₃@HAp and γ-Fe₂O₃@HAp-Fe^{II} are 7.24 and 11.10 emu g^{-1}, respectively. High permeability in magnetizations and reversibility in the hysteresis loops ensure that no aggregation has been imposed on the nanoparticles in the magnetic fields [31]. The superparamagnetic feature of γ-Fe₂O₃@HAp-Fe^{II} can provide the easy and complete separation of the catalyst nanoparticles from the reaction mixture using an external magnet device. Using this separation technique, the recyclability of the catalyst was examined in the reaction of 2,3-epoxypropyl phenyl ether and aniline. No significant decrease in
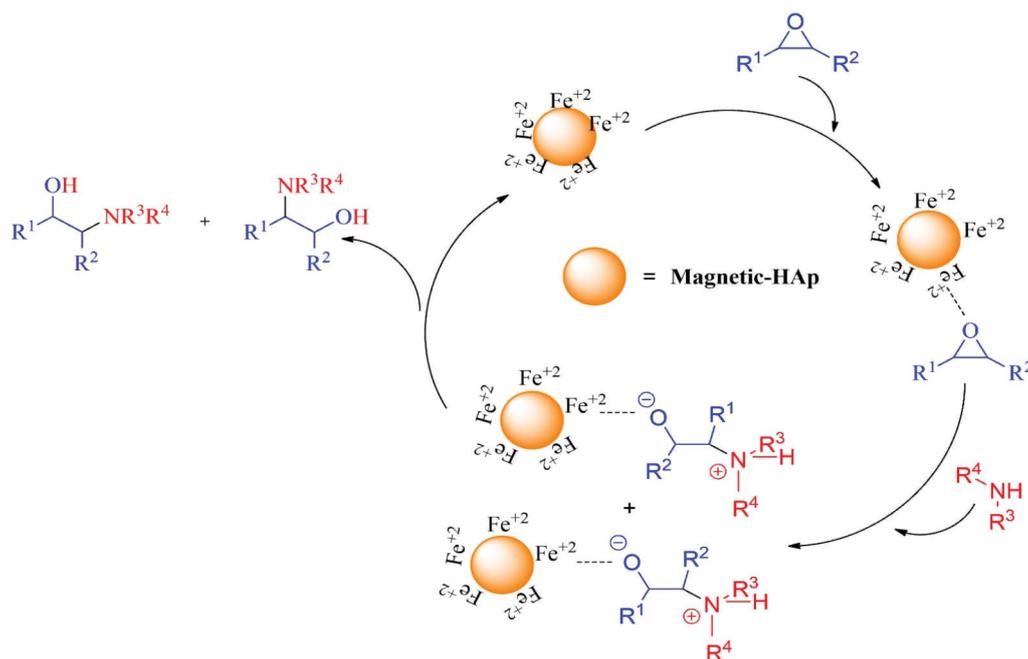
Scheme 2. Proposed mechanism for epoxy ring opening reaction using magnetically separable iron based catalyst

yields and selectivity was observed after 5 repeated reactions (Fig. 5). It is worth mentioning that no iron leaching was observed in the aqueous solution of the reaction after each recovery of the catalyst based on ICP analysis.

Furthermore, the content of iron in the recycled catalyst after 5 runs was similar to the fresh catalyst (3.63 mmol g^{-1}) indicative of the negligible leaching of iron during the reaction. Finally, to check the heterogeneity of the catalyst, in the reaction of 2,3-epoxypropyl phenyl ether (1a) and aniline (2a), the catalyst was decanted by an external magnet after 1 h from initiation and the supernatant was tested for activity during 24 h. At first 1 h period (in the presence of catalyst) the reaction progressed about 40% but in the second 24 h period (without catalyst) no promotion was observed in the reaction. This issue is consistent with the heterogeneous nature of the prepared catalyst.

It seems that the catalytic process should pass through coordination of the supported Fe^{II} ions to epoxide to generate a metal-organic activated electrophile, and subsequent nucleophilic attack by amine provides the desired product (Scheme 2).

CONCLUSIONS

In summary, six transition metals were supported on hydroxyapatite-encapsulated γ-Fe$_2$O$_3$

nanoparticles. Among all prepared catalysts, the γ-Fe$_2$O$_3$@HAp-Fe^{II} was chosen as the best catalyst, demonstrating the best *regio*-selectivity as well as the highest yield in amination of oxiranes. Studies in terms of catalytic activity and *regio*-selectivity in the ring-opening of oxiranes by amines showed that except for 2-phenyloxirane, which completely was opened by internal *regio*-selectivity, and 2-((allyloxy)methyl)oxirane, in all cases the terminal attack was predominant pathway for the reaction. The present method requires small amounts of non-toxic and inexpensive γ-Fe$_2$O$_3$@ HAp-Fe^{II} as catalyst. Also, the reactions were accomplished in water and at ambient temperature as a mild and green condition. In addition, recovery of the catalyst was successfully carried out in subsequent runs without any decrease in activity even after 5 runs. High *regio*-selectivity toward terminal ring-opening, efficient catalyst reusability using simple magnetic separation, high yields, simplicity in operation and diversity for various substrates are of advantages of this study.

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