

Amine grafted Fe₃O₄ immobilized graphene oxide as a recyclable and effectual nanocomposite for the regioselective ring opening reaction

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Abstract

This work describes the synthesis of magnetic graphene oxide (MGO), where iron oxide (Fe₃O₄) nanoparticles were uniformly deposited over the sheets of the graphene oxide (GO). Further, the introduction of aminopropyltrimethoxysilane (APTMS) on the surface of MGO was successfully done and results in the formation of amine-functionalized magnetic graphene oxide (MGO-NH₂). The synthesized heterogeneous magnetic nanocomposite was characterized by numerous physicochemical and morphological techniques such as powder X-ray diffraction, Fourier transform infrared, thermogravimetric analysis, transmission electron microscopy, vibrating sample magnetometer, scanning electron microscopy, CHN analyzer, and energy-dispersive X-ray analysis. The synthesized nanocomposite was proved to be an effectual catalyst in the nucleophilic ring opening reactions of styrene oxide with derivatives of amines under green solvent. The present catalyst displayed good catalytic activity, short reaction time, higher regioselectivity, excellent yields and could be reutilized up to seven catalytic rounds with no substantial loss in its activity. The excellent properties of the catalyst are due to the dual character of acidic groups (existence of carboxyl groups on the sheet edges) and basic groups (amine groups anchored on the surface of GO). On completion of the reaction, the prepared nanocomposite could be effortlessly recovered from the reaction mixture by utilizing an external magnet, owing to the ferromagnetic property of Fe_3O_4 .

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Graphical Abstract



Keywords Magnetic graphene oxide · Heterogeneous catalyst · Nanocomposites · Green solvent · Regioselective ring opening

Introduction

Recently, substantial attempts have been undertaken to develop various graphenebased materials [1]. Among them, the most popular precursor, i.e., Graphene oxide (GO), a 2-D hexagonal carbon lattice [2] has shown tremendous advantages in the field of catalysis due to its various special features like large surface area accessible for further functionalization, good chemical stability, high adsorption capacity, extraordinary electrical, thermal, mechanical and structural properties [2-4]. Due to the existence of different functionalities such as carboxyl (-COOH), hydroxyl (-OH), and epoxide $((\Delta))$ groups, GO can provide a necessary platform for the incorporation of a large number of inorganic-organic moieties such as metals, alloys, fluorescent molecules, biomolecules, drugs and inorganic nanoparticles [5]. The various functionalities present on the surface of GO are accountable for ionic and non-ionic interactions and also explain the oxidizing and acidic effects in various reactions [6]. These oxygen functionalities play a vital role as activation sites for the growth and stabilization of Fe₃O₄ nanoparticles on the surface of GO [7]. Moreover, these functionalities enhance the hydrophilic character of the GO sheet which makes them easily disperse in water [8, 9]. These oxygen-rich functional groups could be further utilized as reactive sites for required modification.

 Fe_3O_4 nanoparticles (NPs) immobilized on GO surface have a wide variety of applications in catalysis, magnetic fluids, biomedicine, and environmental remediation [3, 10]. GO@ Fe_3O_4 are the magnetic nanocomposites that could afford an

effective approach for recovering by using an external magnetic source. These nanocomposites have both the advantage of magnetic separation and the large accessible surface area of GO that makes them suitable candidate in the field of catalysis [11].

At the present time, the scientific community has a profound interest in homogeneous catalysis due to high activity and selectivity [12, 13]. However, the homogeneous catalyst suffers from the major disadvantage of arduous separability from the reaction mixture [8]. To overcome this drawback associated with homogeneous catalyst, numerous heterogeneous catalytic systems could be designed having the advantage of easily recoverable catalyst simply by means of centrifugation or filtration method. Also, it could be reutilized in different catalytic cycles. In addition, the separation of the heterogeneous catalyst from the reaction medium by using centrifugation or filtration method is not always easy and mainly depends upon the size of the nanoparticles [14, 15]. In continuation of our efforts for the development of heterogeneous nanocatalyst [16–18], Herein we report the immobilized Fe_3O_4 magnetic NPs on the surface of GO which enables the easy separation of the catalyst through a magnet without using the tedious task of centrifugation or filtration method [15]. Further, 3-aminopropyltrimethoxysilane is covalently anchored onto the graphene oxide. The amine-functionalized magnetic graphene oxide as a heterogeneous catalyst has a large surface area which increases dispersion capacity as well as catalytic activity.

Epoxides are organic intermediates that are extremely important in the synthesis of several pharmaceutical and medicinal compounds [19]. The synthesis of β -substituted amino alcohols involves the nucleophilic and regioselective ring opening of various epoxides with derivatives of amines which represents an important role in the broad range synthesis of various biologically and pharmaceutically active synthetic and natural products, chiral auxiliaries, and amino acids [20, 21]. This ring opening reaction of epoxides has been reported with many heterogeneous catalysts such as NaMCM-22 [19], nano SiO₂-Cl [22], Nano Fe₃O₄ [23], Zr-MOR zeolite [24], sulfated tungstate [25], silica nanoparticles [26]. The reported catalysts suffer many drawbacks such as lack of appreciable regioselectivity, high catalyst amount, low yields, high temperature, and use of toxic organic solvent. To address these issues, the synthesized amine-functionalized magnetic graphene oxide was utilized as an effectual and heterogeneous catalyst for the regioselective ring opening reaction of styrene oxide with amines which leads to the formation of β -substituted amino alcohols in the medium of water as a green solvent at 50 °C. Several reports have been published on a similar type of amine- functionalized magnetic graphene oxide nanocomposite and employed for catalyzing different type of reactions[8, 27-30]. However, the reported catalysts were never utilized for catalyzing ring opening reactions. The synthesized nanocomposite plays an imperative role in the activation of styrene oxide and increases the regioselectivity in the reaction. The synthesized catalyst could be effortlessly recovered from reaction medium and recycled for multiple cycles.

Experimental section

Materials and methods

Natural flakes of graphite, $FeSO_4 \cdot 7H_2O$, and $Fe_2(SO_4)_3$ were purchased from Sigma-Aldrich. 3-aminopropyltrimethoxysilane (APTMS) was provided by Alfa Aesar. Liquor ammonia (25%) was purchased from Fisher Scientific. H_2SO_4 , HCl, H_2O_2 , and KMnO₄ were obtained from Spectrochem (India). The rest of the chemicals were used acquired from either Alfa-Aesar, Merck, or Spectrochem (India). All the purchased chemicals and reagents were not purified by any methods, they were used directly.

Preparation of graphene oxide (GO)

GO was prepared by means of an improved Hummers' process [31]. Typically, a mixture of H_3PO_4/H_2SO_4 (10: 90 mL) was added to graphite flakes (250 mg). Then, $KMnO_4$ (2.5 g) was added slowly in the acidic solution and stirred at 50 °C for 12 h. Afterward, the reaction mixture was kept at room temperature then poured into an ice bath (50 mL) followed by the subsequent addition of H_2O_2 (0.75 mL). The resultant mixture was centrifuged and washed with H_2O , HCl, MeOH several times and then lastly with diethyl ether. The acquired solid brown color GO was dried overnight in a vacuum at 60 °C.

Preparation of Fe₃O₄ nanoparticles immobilized over graphene oxide sheets (MGO)

MGO nanoparticles were prepared through the Chemical deposition method [32]. Typically, GO (80 mg) was dispersed in distilled water (20 mL) in a 100-mL round bottom flask (solution A) and then ultra-sonicated for an hour. On another 100 ml round bottom flask, $Fe_2(SO_4)_3$ (1199.64 mg) and $FeSO_4$ ·7H₂O (834.06 mg) were dissolved in distilled water (solution B) and stirred vigorously for 15 min till the solution becomes clear. After stirring, solution B was mixed with solution A at room temperature. Then, liquor ammonia (25%) was gently added to the above reaction mixture to maintain the pH of the mixture to 10. Then, the reaction mixture was vigorously stirred at 60 °C for 2 hours. The precipitated nanoparticles were isolated via an external magnetic force and washed numerous times using distilled water and methanol till the pH reached 7. The obtained MGO nanoparticles were parched at 30 °C in a vacuum oven.

Preparation of amine-functionalized magnetic graphene oxide (MGO-NH₂)

Typically, toluene (10 mL) was added to the solid magnetic graphene oxide nanoparticles (100 mg) and the mixture was sonicated for 10 min. Then, 3-aminopropyltrimethoxysilane (20 mmol) was added to it and the resultant mixture was refluxed at 90 °C for 12 h under an inert atmosphere. After 12 h, the final catalyst was collected magnetically, washed with toluene and methanol three times, and then dried at 80 $^{\circ}$ C for 2 h in a vacuum oven.

Ring opening of styrene Oxide using MGO–NH₂ as nanocatalyst

In a typical procedure, a mixture of an amine (1 mmol), styrene oxide (1 mmol), water (2 ml), and catalyst (7 mg) was taken in a small test tube and kept for stirring at 50 °C for a suitable time. The completion of the following reaction was tested using Thin Layer Chromatography. When the reaction was completed, then the catalyst was isolated from the mixture via an external magnetic force and used in the next reaction to check its recyclability. Then, the mixture was extracted using ethyl acetate-water and the organic layer part was passed over Na₂SO₄. The remaining solvent was evaporated under reduced pressure and concentrated in a vacuum to afford the β -substituted amino alcohol. The products were fully checked by using ¹³C NMR, ¹H NMR, and HR-MS.

Characterization techniques

Powder X-ray diffraction (PXRD) patterns were measured by using a Bruker, D8 Discover diffractometer with Cu, 3KW radiation in the 2θ region of 5–80° and a scan rate of 5° min⁻¹. Fourier transform infrared (FT-IR) spectra were recorded on Perkin Elmer Spectrum RXI-Mid IR Spectrometer in the region of 4000-400 cm⁻¹. Thermogravimetric (TG) analysis (Perkin Elmer, Pyris diamond) was used for the thermal decomposition behavior of the MGO-NH2 nanocomposites. The information about the morphology and size of the MGO-NH₂ was acquired through scanning electron microscopy (SEM) via JEOL Japan Mode: JSM 6610LV electron microscope and the transmission electron microscopy (TEM) was done through a Tachnai G²T30, U-Twin transmission electron microscope. Vibrating-sample magnetometer (VSM) was recorded to study the magnetic behavior of the prepared catalyst at room temperature. Energy-dispersive X-ray spectra (EDX) (equipped with the SEM machine) were recorded for elemental analysis. ¹H NMR and ¹³C NMR for the products acquired by the ring opening reactions of styrene oxide with amines were taken on an instrument Jeol JNM-EXCP 400 at 400 MHz and 100 MHz, respectively. During these characterizations, CDCl₃ was used as solvent, and TMS was used as an internal standard.

Results and discussion

The stepwise procedure for the production of amine-functionalized magnetic graphene oxide (MGO–NH₂) has been presented in Scheme 1. Production of graphene oxide was done via an improved Hummers' method [31]. Fe₃O₄ nanoparticles could be deposited over graphene oxide sheets through the Chemical Deposition method [32]. The resulting nanosheets of magnetic graphene oxide could be amine



Scheme 1 Preparation of amine functionalized magnetic graphene oxide (MGO-NH₂)

functionalized through the silylanization of graphene oxide sheets with 3-aminopropyltrimethoxysilane in order to obtain the required catalyst, i.e., amine-functionalized magnetic graphene oxide (MGO– NH_2).

The FT-IR spectra of synthesized GO, MGO, and MGO–NH₂ are displayed in Fig. 1. The FT-IR study of pure GO shows that it contains various functional moieties. The broad band at 3403 cm⁻¹ confirms the presence of stretching O–H vibrational modes. The band at 1740 cm⁻¹ refers to the vibrational stretching mode of C=O groups present on GO. The peaks at 1225 cm⁻¹ indicate the presence of epoxide moieties [33]. The band at 1626 cm⁻¹ is for aromatic C=C which corresponds to the unoxidized skeletal vibrations of C=C stretching vibrations. However, the FT-IR spectrum of MGO was different from that of the spectrum of GO. The typical characteristic band at 570 cm⁻¹ can be ascribed to the stretching Fe–O vibrations and this confirms the presence of Fe₃O₄. The decrease in the broadness of O–H and C=O peaks at 3364 cm⁻¹ and 1740 cm⁻¹ confirms that Fe₃O₄ nanoparticles were successfully incorporated over graphene oxide sheets through carboxylate ions.

The FT-IR spectrum of MGO–NH₂ shows the peaks in wide range of 3363 cm⁻¹–3404 cm⁻¹ confirms the stretching vibrational mode of (–NH₂) and hydroxyl group. Two peaks at 2927 cm⁻¹ and 2859 cm⁻¹ indicate the stretching vibrations of asymmetric and symmetric C–H bands of CH₂–CH₂ moieties of the alkyl chains existing in the 3-chloropropyltrimethoxysilane. The existence of amine groups on GO could be confirmed by the characteristic band of N–H bending vibrations at 1560 cm⁻¹. Moreover, the band at 545 cm⁻¹ refers to the



Wavenumber (cm⁻¹)

Fig. 1 FT-IR spectra of GO, MGO and MGO– NH_2

Fe–O stretching vibrations. Along with, there were also two additional peaks at 1103 cm⁻¹ and 1041 cm⁻¹ which could be allotted to the Si–O–C stretching vibration and O–Si–O asymmetric stretching mode, respectively.

Hence, from the study of FT-IR spectra of MGO and MGO– NH_2 , it was concluded that the amine group could be effectively immobilized on the magnetic surface of graphene oxide sheets.

Patterns of powder X-ray diffraction (XRD) reveals the crystallinity of individual complex nanocomposite of GO and MGO-NH₂ (Fig. 2a). The analysis of XRD patterns was carried out from 5.0° (2θ) to 80.0° (2θ) in which the broad bands from 12.0° (2θ) to 29.0° (2θ) were obtained which are indicative of the amorphous state. A sharp characteristic diffraction peak at $2\theta = 9.3^{\circ}$ highly demonstrates the crystalline nature of graphene oxide which corresponds to the (001) crystal plane. The band at 43° depicts the crystalline nature of carbon present in graphene oxide. The XRD analysis of MGO–NH₂ displayed a very broad diffraction peak at $2\theta = 30^{\circ}$, 35° , 43° , 53.3° , 57° and 62.7° which indicates the crystalline nature of cubic Fe₃O₄ and these could be designated to (220), (311), (400), (422), (511) and (440) crystal planes, respectively [16]. These assigned peaks are in close agreement with the typical XRD pattern of Fe₃O₄ having spinel crystal



Fig.2 a Powder XRD patterns of a GO and b MGO–NH₂, b Magnetization curves of a MGO and b MGO–NH₂

FCC structure (indexed to JCPDS No. 19–0629). Hence, it could be concluded that the Fe_3O_4 strong peak inhibited the GO peak.

The magnetization behavior of the MGO and MGO– NH_2 at room temperature was determined by VSM with a magnetic field from -10000 Oe to +10000 Oe as presented in Fig. 2b. The saturation magnetization value of MGO was measured to be 37 emu g⁻¹ whereas there was a little drop in the magnetization values of MGO– NH_2 i.e., 30 emu g⁻¹. This inappreciable decrease in the magnetization value for MGO– NH_2 could be ascribed to the effective immobilization of the amine group over the surface of magnetic graphene oxide (MGO) sheets and it could be effortlessly isolated by means of an external magnet from the reaction mixture.

The morphology and shape of MGO–NH₂ nanomaterials were explored by SEM and TEM as shown in Fig. 3. From SEM analysis, it was found that Fe_3O_4 nanoparticles were statistically spread over the surface of (a) and (b) GO sheets. The TEM images of (c) GO show the high surface area having a sheet-like shape for the immobilization of various groups. Also, the TEM images show a black spot (d) and (e) which confirms the presence of Fe_3O_4 nanoparticles which are well dispersed over the GO sheets. Graphene oxide maintains a well-defined sheet-like structure as no considerable changes were noticed in the morphology of GO sheets. The SAED (selected area electron diffusion) patterns (f) reveals the crystalline nature of Fe_3O_4 nanoparticles and it could be attributed to its cubic spinel structure. The strong five diffraction rings in the SAED pattern were allotted to the (220), (311), (400), (511), and (440) reflections of the spinel cubic structure of Fe_3O_4 nanoparticles, respectively. These outcomes are very well in agreement with the XRD results.

The energy-dispersive X-ray (EDX) spectroscopy (equipped with the SEM machine) was utilized for elemental analysis of the MGO– NH_2 nanocomposite (Fig. 4a). The characteristic peaks of iron, carbon, nitrogen, silicon, and oxygen present in the EDX spectrum of MGO– NH_2 confirm the successful immobilization of the amine group over the surface of magnetic graphene oxide (MGO) sheets. Moreover, CHN analysis was also performed out. The nanocomposites (MGO– NH_2) contain 1.12, 2.19, and 0.28 mol of carbon, hydrogen, and nitrogen, respectively.



Fig. 3 a–b SEM images of MGO-NH₂, c TEM images of GO, d–e MGO–NH₂ at different magnification and f SAED pattern of the Fe₃O₄ nanoparticles

The TG analysis was performed to study the thermal decomposition of the prepared nanomaterial MGO–NH₂ (Fig. 4b). The TGA graph for graphene oxide shows a 20% weight loss near the initial heating stage (up to 150 °C) which could be due to the loss of the absorbed water molecule from the sample as well as from the slow disintegration of the thermally unstable graphene oxide. At around 150–200 °C, a sharp weight loss of around 62% occurred which could be ascribed to the flexible oxygen-containing functional groups that decomposed to carbon dioxide moiety. Between the temperature range 300 °C and 700 °C, a slow and steady weight loss of 4% was observed which occurred due to the elimination of the most stable oxygen functionalities of the GO [17]. In the TGA spectra of MGO–NH₂, there is a small weight loss near 150 °C which could be due to the loss of some water molecules. Also, the small weight loss in the region of 300–800 °C could be due to the decomposition of the most thermally stable amine group over the surface of GO. Hence, the TG analysis confirms the thermal stability of the amine group over the magnetic graphene oxide (MGO) sheets.

From the FT-IR, TEM, SEM–EDX, TGA, PXRD, VSM and CHN analysis, it ultimately proved that the NH_2 group has been statistically anchored over the magnetic graphene oxide surface.

The catalytic efficiency of the prepared catalyst $MGO-NH_2$ was investigated with the ring opening reactions of styrene oxide. Initially, in order to examine the different reaction conditions, aniline and styrene oxide were employed as substrates for the model reaction (Table 1). Studies with different solvents showed that the excellent product yield (3) could be obtained at 99% when water was utilized as a solvent at 50 °C (Table 1, entry 5). On the contrary, the product yield could not found satisfactory when EtOH and CH_3CN were chosen as solvents (Table 1, entries 1 and 2). Therefore, water was chosen as the appropriate green solvent for catalyzing the ring opening reactions. At room temperature, the yield



Lsec: 100.0 0 Cnts 0.000 keV Det: Octane Plus Det



Fig. 4 a EDX spectra of MGO–NH₂, b TGA curves of a GO and b MGO–NH₂

of the product was found to be 72%. However, a good amount of product could be obtained at elevated temperatures (50 °C) (Table 1, entries 5–7). The amount of catalyst used also affected the yield of the reaction (Table 1, entries 5 and 8). On optimizing the amount of the catalyst, it could be concluded that the maximum yield (99%) of the reaction was found with 7 mg of the catalyst (Table 1, entry 5). Although, it also seen that the good yield (90%) of the product (Table 1, entry 8) was found with 5 mg of the catalyst. Also, we observed that the product yield is comparatively less when GO and MGO were used as catalysts even when the reaction was continued for a prolonged time (Table 1, entry 10–11). Moreover, in absence of catalyst, a very low yield was obtained even when the reaction persisted for a longer period of time (Table 1, entry 12). Thus, it could be concluded that the MGO–NH₂ nanocomposites exhibit excellent catalytic activity in terms of catalyst amount and reaction time. These observations confirm that the amine

Entry	Catalyst	Catalyst amount (in mg)	Solvent	Temp (°C)	Time (min)	Yield ^a (%)
1	MGO-NH ₂	7	EtOH	50	60	50
2	MGO-NH ₂	7	CH ₃ CN	50	60	30
3	$MGO-NH_2$	7	CH_2Cl_2	50	60	30
4	MGO-NH ₂	7	Toluene	80	60	45
5	MGO-NH ₂	7	H_2O	50	30	99
6	$MGO-NH_2$	7	H_2O	80	30	99
7	MGO-NH ₂	7	H_2O	rt	30	72
8	MGO-NH ₂	5	H_2O	50	30	90
9	MGO-NH ₂	7	Neat	50	60	80
10	GO	7	H ₂ O	50	120	60
11	MGO	7	H ₂ O	50	120	60
12	Blank	-	H_2O	50	120	20

Table 1 Optimization study for MGO– $\rm NH_2$ catalyzed ring opening of styrene oxide by derivatives of amines

Reaction conditions: Aniline (1 mmol), styrene oxide (1 mmol), solvent (2 mL). aIsolated yield

groups which are immobilized on the MGO sheets play a key role in the development of catalysts. Amine groups help in activating the epoxide ring for the ring opening procedure and also increases the regioselectivity of the reaction. Therefore, the presence of amine functionalities in the MGO– NH_2 could efficiently enhance the rate of the reaction.

In order to probe the scope of the MGO–NH₂ catalyst, a variety of amines were used with styrene oxide under the optimized conditions so as to synthesize various β -subsituted amino alcohols. All the reactions proceeded smoothly to give β -substituted amino alcohols in excellent yield with high regioselectivity under extremely shorter reaction times (Table 2). The reaction of various aryl amines with styrene oxide predominantly gave the corresponding regioselective β -substituted amino alcohols (3) with a preferably nucleophilic attack at the phenyl position of the styrene oxide following SN¹ mechanism. On the other side, aliphatic amines reacted with styrene oxide with a nucleophilic attack at a non-benzylic site of the styrene oxide following an SN² mechanism [20, 26]. When compared with aniline, benzylamine or cyclohexylamine (Table 2, entries 1, 8–9) gave the major product (4) in longer reaction intervals. It was also noticed that aromatic amines with electronwithdrawing groups reacted with longer reaction time and produced lower yields when compared to those with electron releasing groups.

MGO–NH₂ not only showed the advantage of recyclability when related with other specified homogeneous catalysts employed for the production of β -substituted amino alcohols but also displayed higher activity and produced higher yields in lesser reaction time (Table 3). We have also done the comparison for the recyclability of the recovered catalyst with the various reported heterogeneous nanocatalyst for a similar reaction. The results showed that the MGO–NH₂ was active till the seventh catalytic run with a 91% yield of the reaction.

$1 \qquad \qquad$	Entry	Amines	Epoxide	Product	Time (min)	Yield ^a (%)
$2 \qquad \qquad$	1	NH ₂	C ^A	HN-OH	30	99
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	H ₃ CO			30	99
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3	H ₃ C			30	98
$ \begin{array}{c} 5 \\ & & & & & \\ \mathbf{Br} \left(\begin{array}{c} \mathbf{H} \\ \mathbf{H} \\$	4	NH ₂ NO ₂			45	95
$ \begin{cases} & (f) = (f) + (f) +$	5	Br NH ₂	C ^Å	HN Br OH	50	96
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	6	F NH2	C ^A	HN - F	50	95
8 $()$ $($	7	CI NH ₂			60	95
9 10 I_{O} $I_{$	8		€ A		40	90
$10 \qquad \qquad$	9	NH ₂			50	90
$R-NH_2 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + $	10	CI CI			45	95
1 2 3 4 If R= Aryl, 99% traces	R-NH;	2 +	Catalyst (mg) temp, solvent	HN ^{-R} OH +	OH H.	R
		2 If R= Aryl,	evulamine Port	3 99%	4 traces	

 Table 2 Ring opening reactions of styrene oxide catalyzed by MGO–NH2



Entry	Reactants	Catalyst	Reaction conditions	Yield (%)	Ref
1	NH ₂ + O	ZrCl ₄ (5 mol %)	Neat, rt, 15 min	100	[20]
2	NH ₂ + O	nano SiO ₂ –Cl (30 mg)	CH ₂ Cl ₂ , rt	100	[22]
3	0 + NH2	Nano Fe ₃ O ₄ (10 mol %)	rt to 80 °C, neat, open atmosphere, 20 h	99	[23]
4	R + C	Sulfated tungstate (10 wt %)	25 °C, 15 min	92	[25]
5	R +	Zr-MOR zeolite (25 mg)	313 K, 4 h, solvent free	93	[24]
6	$R + O_X$	NaMCM-22 (100 mg)	35 °C, 6 h	89	[19]
7	0 + NH ₂	BiX ₃ (10%)	25 °C, 7–9 h,	83	[34]
8	NH2 +	MGO–NH ₂ (7 mg)	30 min, 50 °C	98	Present work

Table 3 Comparison of the catalytic efficiency of MGO–NH₂ with other reported catalysts for the synthesis of β -amino alcohols

Finally, the recyclability for the synthesized catalyst was also considered and the effects are shown in Fig. 5. In all the steps, the catalyst could be isolated via an external magnetic force. Subsequently, the recovered catalyst could be washed two





to three times with hot ethanol and kept under vacuum for drying at 50 °C. The recovered magnetic nanocatalyst could be recycled for at least seven runs without much considerable loss in their catalytic activity. The ease of recovery of the recycled catalyst through an external magnetic force, suggests that there is not much metal leaching of Fe_3O_4 nanoparticles even after seven catalytic runs in the recovered catalyst.

To check the stability and recyclability of the catalyst, the FT-IR spectra of the reused catalyst after seven catalytic runs were also tested and matched with the FT-IR spectra of the fresh catalyst. After recycled up to the seventh usage, there are not much noteworthy changes in the FT-IR of the reused catalyst (Fig. 6). This shows that the prepared catalyst could be recycled and stable for up to seven runs without much major loss in its activity.

Plausible reaction mechanism

An acceptable mechanism for the ring opening reaction of styrene oxide using derivatives of amines is described in Fig. 7. The H of amine groups present at the surface of GO activates the epoxide ring through an oxygen atom. Starting of the reaction by the assistance of bronsted acidity of the intrinsic carboxylic acids present on the edges of GO and Lewis acidity of Fe^{3+} due to which the attack is preferentially through the benzylic position of the styrene oxide through SN¹ mechanism for aromatic amines and attack at the non-benzylic position for aliphatic amines proceeding through an SN² mechanism. This gives the regio-isomer of amino alcohols. After activation of styrene oxide, epoxide subjected for nucleophilic attack by aromatic amines through the path (a) and by aliphatic amines through the path (b) leading to the formation of intermediate (I) through intramolecular proton transfer or intermediate (II) through intermolecular proton transfer followed by protonolysis resulting to the product formation and regeneration of the nanocatalyst.



Fig. 6 FT-IR spectra of fresh catalyst MGO-NH₂ and the resused catalyst after seventh usages



Fig. 7 Plausible reaction mechanism for the ring opening reactions of styrene oxide with various amines using the $MGO-NH_2$ as the nanocatalyst

Conclusion

Herein, we have synthesized highly stable and bifunctional amine-functionalized magnetic graphene oxide (MGO–NH₂) as a heterogeneous hybrid nanocomposite. This was further utilized as an effective and recyclable catalyst for the regioselective ring opening of styrene oxide with amines. The prepared catalyst showed remarkable catalytic activity in water with low catalyst loading to afford the desirable β -substituted amino alcohols of synthetic and biological importance with good to excellent yield in a shorter reaction time. The amine group increases the efficiency of the reaction and also the catalytic activity of the synthesized material. This prepared material could be recovered easily through an external magnet and reused for up to seven runs with no extensive loss in its catalytic activity. The presence of carboxylic acid groups and amine groups (acid–base) played a major role in the activation of the starting material. The catalyst has a large surface area which increases dispersion capacity as well as catalytic action.

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Declarations

Conflict of interest The authors declare that they do not have any conflict of interest.

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