Res Chem Intermed
DOI 10.1007/s11164-017-3176-0

Magnetic g-C_3N_4 nanocomposite-catalyzed environmentally benign aminolysis of epoxide

Tahereh Soleymani Ahooie[1] · Najmedin Azizi[1,2] · Mohammad Mahmoudi Hashemi[1] · Issa Yavari[1]

Received: 26 July 2017 / Accepted: 28 August 2017

Abstract A magnetic graphitic carbon nitride (g-C_3N_4) nanocomposite was prepared and used as a novel magnetically retrievable nanocatalyst for efficient ring opening of epoxides with aromatic amines. A variety of aryl and alkyl epoxides were examined under the mild reaction condition and the corresponding β-amino alcohols were obtained in good to excellent yields under solvent-free condition. Using the Fe_3O_4 as a low-priced magnetic support to immobilize an active material g-C_3N_4 can provide a better result than using traditional catalysts with respect to the efficiency, yield, easy work-up, short reaction time, possibility of regeneration, and ease of applicability .

Keywords Epoxide · Magnetic g-C_3N_4 · Ring opening · Aminolysis

Introduction

Carbon-based nanocomposite materials can provide a better result than using traditional catalysts with respect to applications in energy, pharmaceutical, [1, 2] magnetic resonance imaging, separation technique, optical application and especially in catalytic performances [3–5]. Over the past two decades, the rapid progress of nanomaterials- and nanostructures-based technology has enabled researchers to fabricate devices on the molecular and nanoscale to a great extent [6, 7]. Among the nanostructure materials, graphitic carbon nitride (g-C_3N_4) has

✉ Najmedin Azizi
azizi@ccerci.ac.ir

[1] Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran

[2] Chemistry and Chemical Engineering Research Center of Iran, P.O. Box 14335-186, Tehran, Iran

Published online: 25 October 2017

been recognized as an excellent and promising catalyst for a variety of applications due to several advantages such as low cost, non-toxicity, and excellent thermal and chemical stability [8–12].

Epoxides are the most fascinating targets in synthetic chemistry as useful electrophiles, due to the advantage of their predictable highly regioselective ring-opening reactions [13]. Furthermore, they are novel therapeutic agents, natural products [14] and active biologically compounds [15]. They usually undergo a variety of transformations with a broad range of nucleophiles which is due to their rich chemistry caused by a reactive moiety of the strained oxirane, and play a considerable role in the development of modern organic chemistry as well as in the total synthesis of natural products [16]. Nucleophilic ring opening of epoxides in the presence of various catalysts or promoters has been extensively studied in the literature [17–35].

Regarding our interest in the ring-opening reactions of epoxide using green media/catalytic systems [36–39], we here report a solvent-free ring opening of symmetrical and unsymmetrical epoxides with aromatic amines to prepare β-amino alcohols in the presence of new heterogeneous magnetic g-C_3N_4 nanocatalysts.

Experimental

Materials and methods

All chemicals and solvents were obtained from commercially available sources and all products were confirmed by ^{1}HNMR, FT-IR spectroscopy and mass spectrometry. ^{1}H NMR spectra were recorded on a 500- or 300-MHz ^{1}HNMR, ^{13}C NMR 125.7- and 75-MHz NMR spectrometer using DMSO-d_6 as a solvent, and chemical shifts have been expressed in (ppm) 40 downfield from TMS. Melting points were recorded on a Buchi 535 melting point apparatus and are uncorrected. FT-IR spectra were determined on a Bruker Vector-22 infrared spectrometer using KBr disks.

Preparation of magnetic g-C_3N_4 catalyst

Bulk g-C_3N_4 was prepared by directly calcining melamine in air, with 2 g melamine being placed in a muffle furnace with an alumina crucible with a loose cover. Then, the programmed temperature was set to 550 °C for 3 h with a ramp rate of 5 °C min^{-1}. After heat treatment, a light yellow powder was obtained [42]. In the next step, Fe_3O_4/g-C_3N_4 was prepared by reported methods [43]. The g-C_3N_4 (500 mg) was dispersed in 300 mL of ethanol/water (1:1) using sonication for 4 h at room temperature. Then, FeCl3·6H_2O (1.838 g, 0.0216 mol) and $FeCl_2$·4H_2O (0.703 g, 0.0108 mol) were dissolved in the solution using sonication and 10 mL of ammonia solution (NH_4OH) (28 wt%) was quickly injected into the mixed solution. Under nitrogen atmosphere, the reaction mixture was stirred for 2 h at 90 °C, and cooled to room temperature, washed with water and ethanol, separated magnetically, and dried overnight at 60 °C under vacuum.

General procedure

To a dry test tube containing a magnetic bar, 75 mg magnetic g-C_3N_4, amine (1 mmol) and epoxide (1 mmol) were added and the mixture was stirred under heating at 60 °C. When the reaction was completed, as indicated by TLC, or GC, the crude reaction mixture was diluted with ethyl acetate or diethyl ether (10 mL) and magnetic g-C_3N_4 was removed with external magnet. The organic solvent was evaporated under vacuum and the crude products were purified by flash column chromatography using silica gel or recrystallization from ethanol or diethyl ether to give pure products. All products are known compounds and the characterizations of these compounds were identical to literature reports.

*2-(Phenylamino)cyclohexanol (**3a**)*

FT-IR (KBr) $\nu = 3398$, 2960, 1606,1345, 1100 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.20–7.15 (m, 2H), 6.72–6.64 (m, 3H), 3.32–3.07 (m, 2H), 2.95–3.01 (brs, 2H), 2.10–2.08 (m, 2H), 1.74–1.64 (m, 2H), 1.40–1.22 (m, 3H), 1.09–0.98 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 147.9, 128.8, 118.1,114.1, 73.9, 59.8, 33.1, 31.4, 25.1, 24.2.

*2-(4-methoxyphenylamino)cyclohexanol (**3b**)*

FT-IR (KBr) $\nu = 3380$, 2945, 1600,1158, 1068 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 6.72–6.59 (m, 4H), 3.67 (s, 3H), 3.28–2.78 (m, 2 H), 2.95–2.72 (m, 3H), 2.00–1.99 (m, 2H), 1.71–1.64 (m, 2H), 1.34–0.90 (m, 4H); ^{13}CNMR ($CDCl_3$, 125 MHz): δ 152.4, 140.9, 116.1, 113.9, 74.1, 61.3, 55.1, 33.0, 31.2, 25.4,24.1

*2-(3-chlorophenylamino)cyclohexanol (**3c**)*

^1H NMR (500 MHz, $CDCl_3$): δ 7.10–6.69 (m, 4H), 3.28–2.78 (m, 2 H), 2.95–2.72 (m, 3H), 2.00–1.99 (m, 2H), 1.71–1.64 (m, 2H), 1.34–0.90 (m, 4H).

*2-(4-i-propylphenylamino)cyclohexanol (**3d**)*

^1H NMR (500 MHz, $CDCl_3$): δ 7.05 (d, $J = 7.8$ Hz, 2H), 6.66 (d, $J = 7.8$ Hz, 2H), 3.56 (brs, NH), 3.01–2.58 (m, 3H), 2.01–1.82 (m, 2H), 1.50–1.25 (m, 7H).

*2-(2-tolylamino)cyclohexanol (**3e**)*

^1H NMR ($CDCl_3$, 500 MHz): δ 7.15–6.70 (m, 4 H), 3.42–3.40 (m, 1 H), 3.22–3.14 (m, 1 H), 2.13 (s, 3 H), 2.14–2.11 (m, 2 H), 1.80–1.71 (m, 2 H), 1.45–1.10–1.05 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.9, 130.1, 126.9, 122.8, 116.71, 110.8, 73.5, 58.2, 32.9, 30.6, 24.1, 23.2, 16.6.

*2-(4-bromophenylamino)cyclohexanol (**3f**)*

^{1}H NMR (500 MHz,$CDCl_3$): δ 7.12 (d, $J = 7.8$ Hz, 2H), 6.68 (d, $J = 7.8$ Hz, 2H), 3.36–3.10 (m, 2H), 2.64 (brs, NH), 2.10–2.02 (m, 2H), 1.70–1.64 (m, 2H), 1.35–1.01 (m, 4H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.1, 131.8, 115.2, 109.1, 73.05, 60.0, 32.9, 31.8, 24.1, 23.7.

*2-(2-tolylamino)cyclohexanol (**3g**)*

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.01 (d, 2H, $J = 7.8$ Hz), 6.55 (d, 2H, $J = 7.8$ Hz), 3.24–2.94 (m, 4H), 2.14 (s, 3H), 2.00–1.92 (m, 2H), 1.64–1.56 (m, 2H), 1.29–1.14 (m, 3H), 0.91–0.83 (m,1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.1, 129.2, 127.3, 113.4, 73.8, 60.0, 32.8, 31.2, 25.3, 24.1, 20.1.

*2-(N-methyl-N-phenylamino)cyclohexanol (**3h**)*

^{1}H NMR (500 MHz, CDCl3): δ 7.12 (t, 2H, $J = 8.3$ Hz), 6.84 (d, 2H, $J = 8.3$ Hz), 6.76 (t, 1H, $J = 7.2$ Hz), 3.62–3.59 (m, 1H), 3.39–3.36 (m, 1H), 2.71 (s, 3H), 2.70 (s,1H), 2.17–2.14 (m, 1H), 1.73–1.65 (m, 3H), 1.40–1.20 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz):δ 151.4, 129.1, 118.5, 115.6, 70.0, 67.0, 33.4, 31.1, 26.1, 25.5, 24.4

*1-Phenoxy-3-(phenylamino)propan-2-ol (**3ia**)*

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.34 (m, 2H), 7.29–7.24 (m, 2H), 7.08–7.04 (m, 1H), 7.00–6.97 (m, 2H), 6.86–6.81 (m, 1H), 6.76–6.73 (m,2H), 4.32–4.28 (m, 1H), 4.10–4.04 (m, 2H), 3.62 (brs, 1H), 3.47 (dd, 1H, $J1 = 13.0$ Hz, $J2 = 4.3$ Hz), 3.33 (dd, 1H, $J1 = 13.0$ Hz, $J2 = 7.32$ Hz);^{13}C NMR (CDCl3, 100 MHz): δ 158.5,148.0, 129.7, 129.5, 121.4, 118.3, 114.7, 113.5, 70.1, 68.8, 46.9.

Results and discussion

Initially, in order to investigate the ring-opening reaction of epoxide using a new and greener nanocatalyst, magnetically active g-C_3N_4 has been synthesized without the generation of any hazardous product in the simplest manner, as reported in the literature [40], and the formation of the nanocomposite was confirmed by scanning electron microscopy (SEM) and Fourier transformed infrared (FT-IR).

The powder FT-IR pattern (Fig. 1) reveals that the characteristic bands in 400–3200 cm^{-1} region with peaks appearing at 11,167, 1302, 1478 and 1660, cm^{-1} are attributed to either trigonal C–N(–C)–C or bridging C–NH–C units. The broad peak around at 3135 cm^{-1} can be ascribed to the stretching mode of the amino groups (N–H, NH_2). Additionally, the characteristic sharp peak at 785 cm^{-1} is attributed to the vibrations of the striazine ring. In addition, a broad peak from 650 to 760 cm^{-1} 550 to 650 cm^{-1} corresponding to Fe–O proves the existence of Fe_3O_4 in the composite.

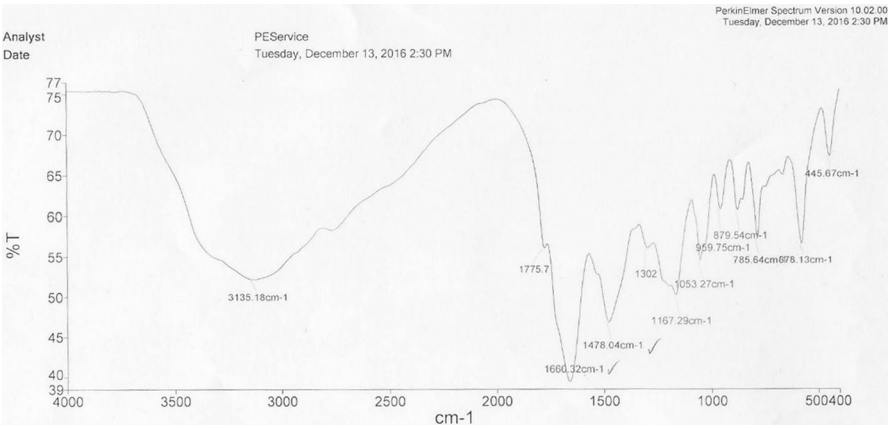


Fig. 1 FTIR spectra of the nanocomposite

The morphologies of the synthesized nanocomposite were examined by SEM and EDX images. Figure 2 shows the SEM images of the pristine Fe_3O_4/g-C_3N_4 nanocomposite. The pristine g-C_3N_4 showed an irregular sheet-like structure which is overlapped. Further, the morphology of the Fe_3O_4/g-C_3N_4 composite exhibited an irregular distribution of Fe_3O_4 NPs throughout the surface ofthe g-C_3N_4 sheets. (Figure 2). Individual EDS elemental maps clearly detected the presence of Fe, O, C, and N which indicated that the Fe_3O_4 nanoparticles are deposited on the surface of the g-C_3N_4 sheets (Fig. 3).

Next, using well-characterized magnetically active g-C_3N_4 (75 mg), the ring-opening reaction between aniline (1.0 mmol) and cyclohexene oxide (1.0 mmol) was selected as the probe reaction to determine the catalytic activity of magnetic g-C_3N_4 and to optimize the reaction conditions. The results are summarized in Table 1. When the model reaction proceeded at room temperature in the presence of Fe_3O_4/g-C_3N_4 and under these conditions, we observed the formation of the desired β-amino alcohols **3a** with 40% yield after 2 h (Table 1, entry 1). A repeat of this experiment using 140 mg of nanocatalyst resulted in a 58% yield under otherwise identical conditions (Table 1, entry 2). The chemical yield of **3a** jumped to 92% when the reaction temperature had been increased to 60 °C (Table 1, entry 3). To reveal this unprecedented reaction, we embarked on studying the feasibility of this novel nonocomposite. It was observed that g-C_3N_4 (Table 1, entry 4) or Fe_3O_4 (Table 1, entry 5) alone as the nanocatalyst are not effective for this nucleophilic ring-opening process and a conversion of 68% and 45% towards the target product has been realized, respectively. This impressive boost in catalytic activity is expected to be the result of a synergitic effect of g-C_3N_4 and Fe_3O_4 while preserving the high catalytic rates.

When a similar experiment was carried out in an organic solvent such as ethyl acetate, acetonitrile, dichloromethane, ethanol and isopropanol as well as water at 60 °C, (Table 1, entries 6–11) unsatisfactory formations of the product were observed. The reaction did not take place without a catalyst and only starting

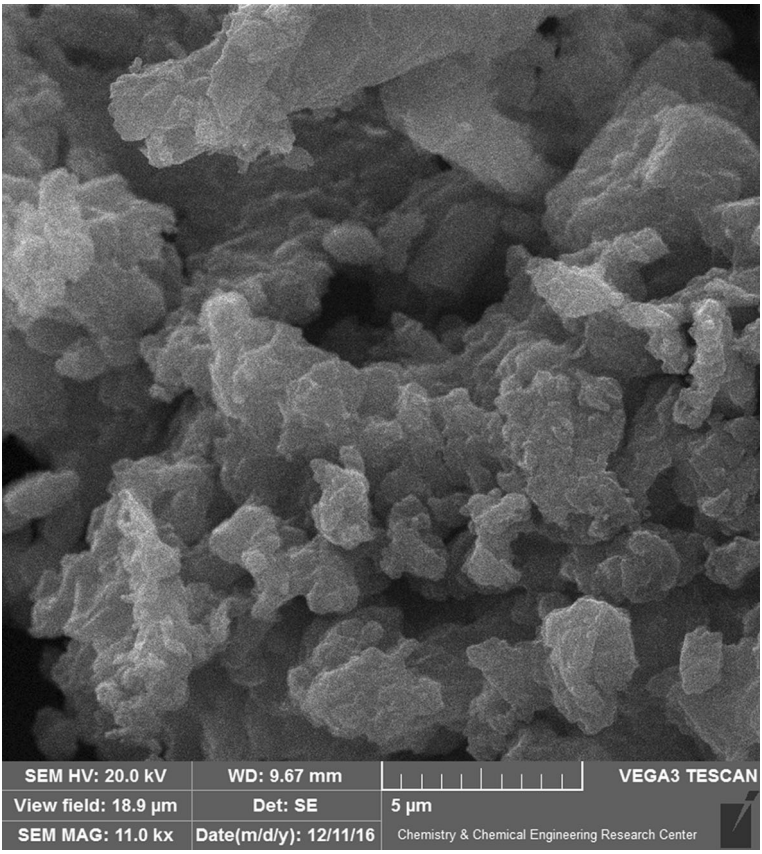


Fig. 2 SEM image of the nanocomposite

materials were obtained (Table 1, entry 12). Therefore, the optimized reaction condition was 75 mg of magnetic g-C_3N_4 under solvent-free condition at 60 °C for the subsequent experiments.

Under the optimum reaction condition, to elaborate the generality and scope of our protocol, we have also investigated the aminolysis of a variety of sterically, electronically, and functional arylamines with cyclohexene oxide. The results are summarized in Table 2. It was observed that sterically, electronically and functionally diverse arylamines reacted with cyclohexane oxide without any difference, and the corresponding products were obtained in good to excellent yields (Table 2). Furthermore, the reactions were strostereo selective and the *trans* stereochemistry of the ring products were determined from the coupling constants of the C–H protons to the heteroatoms in the ^{1}H NMR spectra.

Further investigations were carried out using various alkyl/aryl-epoxides such as phenyl-2,3-epoxypropyl ether, isopropyl-2,3-epoxypropyl ether, 1,2-epoxy butane, allyl-2,3-epoxypropyl ether and styrene oxide, with aryl amines (Table 3). Aryl amines with different substituents (e.g., 4-MeO, 4-Cl, 4-Br and 4-Me) at the phenyl

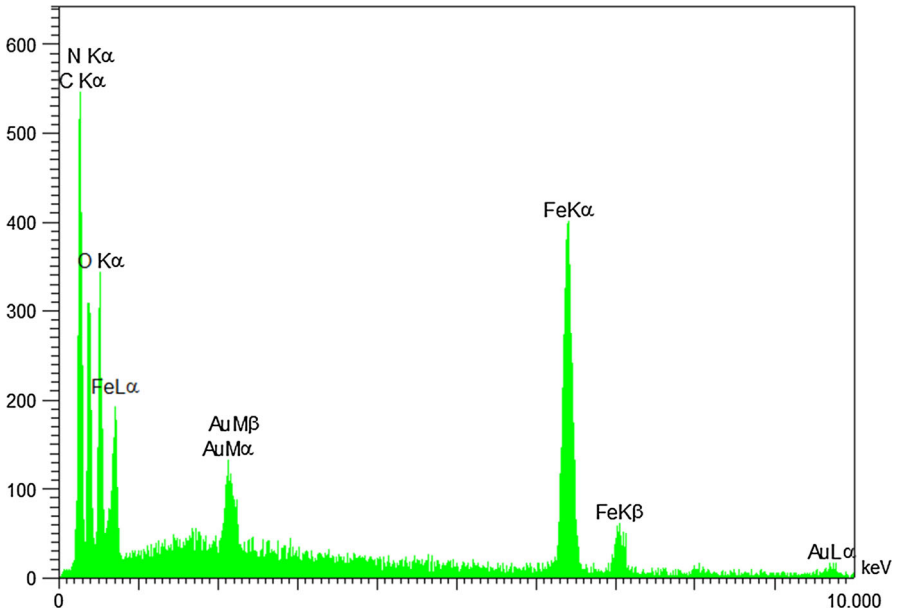


Fig. 3 The EDX image of the nanocomposite

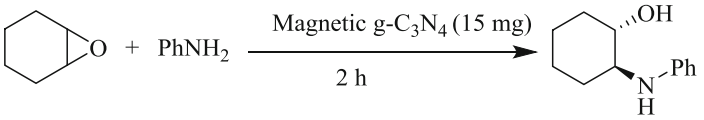
ring proceed smoothly in the presence of magnetic g-C_3N_4 to afford the corresponding 2-amino alcohols in good to excellent yield with good regioselectivity (Table 3). The regioselectivity in the reaction for unsymmetrical epoxides is governed by both steric and electronic effects. Aliphatic oxiranes underwent cleavage by aromatic amines with the preferential attack at the less substituted carbon atom. These results suggest that the steric hindrance effect should still be the predominant factor affecting the regioselectivity. In the cases of the styrene oxide, an α-attack was preferred as the major product due to the formation of a carbocation intermediate (Table 3).

The combination ease of preparation and reuse of magnetic g-C_3N_4 as novel reaction media and catalyst are expected to contribute to the development of a novel protocol for the simple and rapid preparation of 2-amino alcohol derivatives. The recycling of magnetic g-C_3N_4 was examined using the reaction of aniline and cyclohexene oxide under optimized conditions. After the reaction was completed, ethyl acetate (10 mL) was added to the reaction mixture, shaken vigorously and the magnetic g-C_3N_4 be isolated by an external magnet from the products, followed by the usual work-up and chromatography. The magnetic g-C_3N_4 was dried under vacuum and reused for the next batch and recycled again (Fig. 4).

Although there are no mechanistic insights into the precise role of Fe_3O_4/C_3N_4 in this process, based on the experimental results, synchronous reaction mechanism has been suggested (Fig. 5).

In general, the ring opening of epoxides can occur more frequently under acidic conditions, and the addition of the nucleophile is considerably accelerated due to the reversible formation of the more reactive epoxide in the presence of metal catalysts,

Table 1 Optimization of model reaction



1 **2a** **3a**

Entry	Solvent	Temp. (°C)	Yield (%)[a]
1	Neat (no solvent)	r.t.	40
2[b]	Neat (no solvent)	r.t.	58
3	Neat (no solvent)	60	92
4[c]	Neat (no solvent)	60	68
5[d]	Neat (no solvent)	60	45
6	H_2O	60	40
7	$CH_3CO_2C_2H_5$	60	64
8	C_2H_5OH	60	62
9	CH_2Cl_2	40	74
10	$CH_3CH_2OHCH_3$	60	65
11	CH_3CN	60	72

[a]Isolated yields

[b]140 mg of nanocatalyst

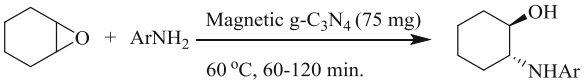
[c]Yield in the presence of g-C_3N_4

[d]Yields in the presence of Fe_3O_4

Lewis or Bronsted–Lowry acids [40]. However, the general acid- or base-catalyzed proposed mechanisms to activate the epoxide ring-opening reaction for the Fe_3O_4/C_3N_4 were certainly unexpected. This result can possibly be rationalized by *p*-stacking interactions and hydrogen bonding between the epoxide and the C_3N_4 surface. The mode of action is believed to be through the hydrogen bonding interaction between N–H and the epoxide already suggested for graphene-catalyzed ring-opening reactions [27] and organocatalyzed ring opening of epoxides [41]. However, the introduction of Fe_3O_4 on the surface of the g-C_3N_4 increases the acidity of N–H (Fig. 5), which forms strong hydrogen bonds with hydrogen bonding donor motifs such as epoxide. Thus, we propose that the mode of activation of the epoxide ring can be attributed to the synergistic contribution of Fe_3O_4 and g-C_3N_4 on the basis of the hydrogen bonding between the N–H bond and epoxide (Fig. 5).

Finally, the comparison between the catalytic activity of the aminolysis of styrene oxide with aniline (in terms of turnover number) over our nanocomposite and those reported in the literature can be found in Table 4. Turnover number for the nanocomposite was calculated per mole of C_3N_4, considering the fact that the actual catalyst was the C_3N_4.

Table 2 Ring opening reaction of cyclohexene oxide with various arylamines



1 2 3a

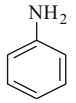
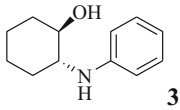
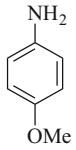
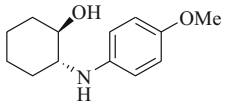
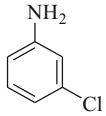
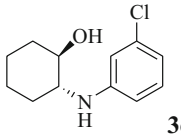
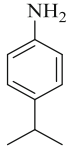
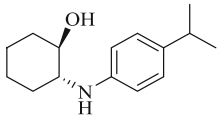
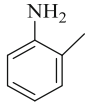
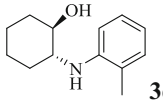
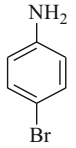
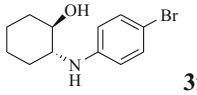
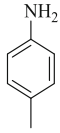
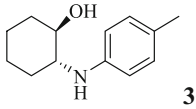
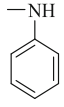
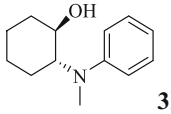
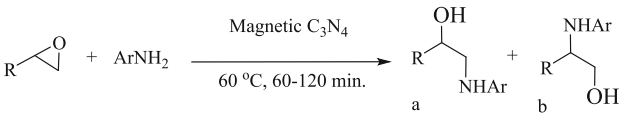
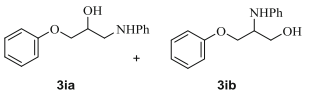
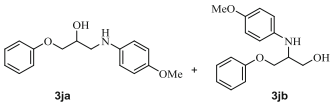
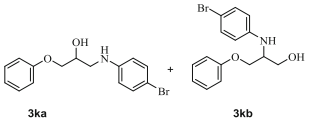
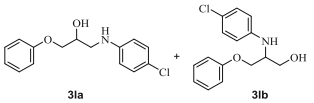
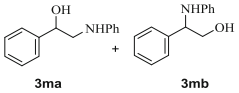
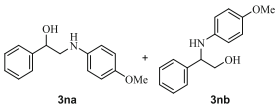
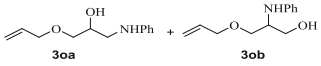
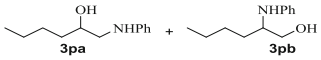
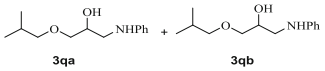
Entry	$ArNH_2$	Product (**3a-g**)	Yield (%)[a]	Time (min.)	Reported Ref.
1		 **3a**	92	60	34
2		 **3b**	94	60	36
3		 **3c**	80	120	30
4		 **3d**	74	120	32
5		 **3e**	76	120	24
6		 **3f**	84	60	28
7		 **3g**	90	60	28
8		 **3h**	82	60	27

Table 3 The ring opening of various aryl and alkyl epoxides with amines using magnetic g-C_3N_4



Entry	Product	Time (min)	Yield (%)[a]	Ratio a:b	Reported Ref.
1	 3ia 3ib	60	94	80:20	28
2	 3ja 3jb	120	90	84:16	19
3	 3ka 3kb	120	78	88:12	19
4	 3la 3lb	120	80	93:07	24
5	 3ma 3mb	60	95	20:80	23
6	 3na 3nb	60	76	19:81	17
7	 3oa 3ob	120	92	90:10	17
8	 3pa 3pb	120	85	85:15	18
9	 3qa 3qb	60	92	82:18	19

[a] ^{1}H NMR yield

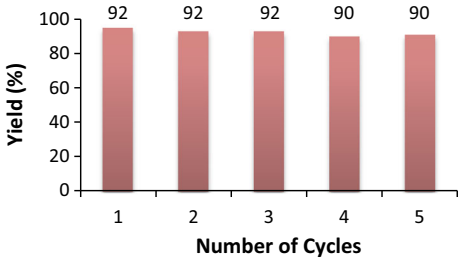


Fig. 4 Recyclability study of the magnetic C_3N_4

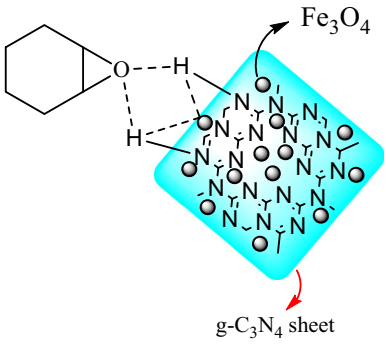
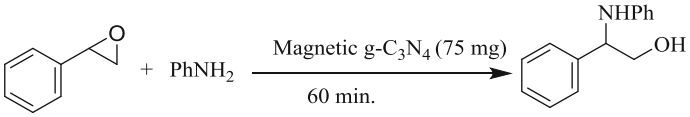


Fig. 5 Proposed reaction mechanism

Table 4 Comparison between the catalytic activity of the nanocomposite with the reported catalysts



Entry	Catalyst	Yield (%)	Turnover no.	Ref.
1	Meso-Zr-beta	95	810	40
2	Zr-Nano ZSM-5	96	566	44
3	Ti-SBA-16	86	936	45
4	$Zn(BF_4)_2$	95	4750	30
5	Graphene oxide	92	–	27
6	Fe_3O_4@C_3N_4	95	1165	This work

Conclusion

In summary, we have described a green, novel and reusable magnetic g-C_3N_4 catalyst for the aminolysis of epoxides with aromatic amines under solvent-free conditions. The notable features of this procedure are the mild reaction conditions, high conversions, short reaction times, economic viability of the reagents, simple experimental procedure and product isolation.

Acknowledgements Financial support of this work by Chemistry and Chemical Engineering Research Center of Iran is gratefully appreciated.

References

1. G.R. Navale, C.S. Rout, K.N. Gohil, M.S. Dharne, D.J. Late, S.S. Shinde, RSC Adv. **5**, 74726 (2015)
2. G.R. Navale, M. Thripuranthaka, D.J. Late, S.S. Shinde, JSM Nanotechnol. Nanomed. **3**, 1033 (2015)
3. W. Wu, Q. He, R. Hu, J. Huang, H. Chen, Rare. Metal Mater. Eng. **34**, 228 (2007)
4. C.T. Black, C.B. Murray, R.L. Sandstrom, S. Sun, Science **290**, 1131 (2000)

5. T. Ramanathan, A.A. Abdala, S. Stankovich, R.K. Prud Homme, L.C. Brinson, Nat. Nanotechnol. **3**, 327 (2008)
6. H. Kim, A.A. Abdala, C.W. Macosko, Macromolecules **43**, 6515 (2010)
7. Q. Wu, Y. Xu, Z. Yao, A. Liu, G. Shi, ACS Nano **4**, 1963 (2010)
8. Y. Zheng, Y. Jiao, Y. Zhu, Q. Cai, A. Vasileff, L.H. Li, Y. Han, Y. Chen, S.Z. Qiao, J. Am. Chem. Soc. **139**, 3336 (2017)
9. W.J. Ong, L.L. Tan, Y.H. Ng, S.T. Yong, S.P. Chai, Chem. Rev. **116**, 7159 (2016)
10. Y. Wang, X. Wang, M. Antonietti, Angew. Chem. Int. Ed. **51**, 68 (2010)
11. S. Chi, J. Chunnuan, S. Sun, H. Jiang, R. Qu, C. Sun, Ind. Eng. Chem. Res. **55**, 12060 (2016)
12. P. Niu, L. Zhang, G. Liu, H.M. Cheng, Adv. Funct. Mater. **22**, 4763 (2012)
13. D.M. Hodgson, P.G. Humphreys, S.P. Hughes, Pure Appl. Chem. **79**, 269 (2007)
14. A. Minami, M. Shimaya, G. Suzuki, A. Migita, S.S. Shinde, K. Sato, K. Watanabe, T. Tamura, H. Oguri, H. Oikawa, J. Am. Chem. Soc. **134**, 7246 (2012)
15. D.M. Hodgson, Cd Bray, in *Aziridines and Epoxides in Organic Synthesis*, ed. by A.K. Yudin (Wiley-VCH, Weinheim, 2006), pp. 145–184
16. L. Fan, C.P. Davie, ChemBioChem **18**, 843 (2017)
17. M.S. Said, L. Khandare, S.S. Shinde, Tetrahedron Lett. **58**, 59 (2017)
18. D. Patel, G.R. Kurrey, S.S. Shinde, P. Kumar, G.J. Kim, S.S. Thakur, RSC Adv. **5**, 82699 (2015)
19. P.S. Shinde, S.S. Shinde, S.A. Dake, V.S. Sonekar, S.U. Deshmukh, V.V. Thorat, N.M. Andurkar, R.P. Pawar, Arab. J. Chem. **7**, 1013 (2014)
20. N. Azizi, M.R. Saidi, Org. Let. **7**, 3649 (2005)
21. H. Gaspard-Iloughmane, C. Le Roux Eur. J. Org. Chem., 2517 (2004)
22. S.S. Shinde, M.S. Said, T.B. Surwase, P. Kumar, Tetrahedron Lett. **56**, 5916 (2015)
23. M. Chini, P. Crotti, F. Macchia. Tetrahedron Lett. **31**, 4661 (1990)
24. C. Schneider, A.R. Sreekanth, E. Mai, Angew. Chem. Int. Ed. **43**, 5691 (2004)
25. A. Sarkar, S.R. Roy, N. Parikh, A.K. Chakraborti, J. Org. Chem. **76**, 7132 (2011)
26. L.E. Overman, L.A. Flippin, Tetrahedron Lett. **22**, 195 (1981)
27. M.R. Acocella, L. Urso, M. Maggio, G. Guerra, ChemCatChem **8**, 1915 (2016)
28. F.A. Saddique, A.F. Zahoor, S. Faiz, M. Usman, M. Ahmad, Synth. Commun. **46**, 831 (2016)
29. K. Seth, S.R. Roy, B.V. Pipaliya, A.K. Chakraborti, Chem. Commun. **49**, 5886 (2013)
30. A.K.Chakraborti Shivani, J. Mol. Catal. A: Chem. **263**, 137 (2007)
31. Z.H. Zhang, Synlett, 711 (2005)
32. L.P. Mo, Z.H. Zhang, Cur. Org. Chem. **15**, 3800 (2011)
33. B.H. Rotstein, S. Zaretsky, V. Rai, A.K. Yudin, Chem. Rev. **114**, 8323 (2014)
34. B. Pujala, S. Rana, A.K. Chakraborti, J. Org. Chem. **76**, 8768 (2011)
35. A. Kumar, R. Parella, S.A. Babu, Synlett **25**, 835 (2014)
36. N. Azizi, S. Dezfooli, M.M. Hashemi, J. Mol. Liq. **194**, 62 (2014)
37. N. Azizi, S. Dezfooli, M. Khajeh, M.M. Hashemi, J. Mol. Liq. **86**, 76 (2013)
38. N. Azizi, M.R. Saidi, Phosphorus, Sulfur Silicon Relat. Elem. **178**, 1255 (2003)
39. N. Azizi, M.R. Saidi, Catal. Commun. **7**, 224 (2006)
40. W. Tang, X. Dai, G. Sun, N. Wu, M. Guan, L.Li Hunger, Green Chem. **17**, 1744 (2015)
41. R. Chawla, A.K. Singh, L.D.S. Yadav, RSC Adv. **3**, 11385 (2013)
42. P. Xia, B. Zhu, J. Yu, S. Cao, M. Jaroniec, J. Mater. Chem. A **5**, 3230 (2017)
43. X. Jia, R. Dai, Y. Sun, H. Song, X. Wu, J. Mater. Sci.: Mater. Electron. **27**, 3791 (2016)