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Aromatic amine mediated ring opening of epoxides: A reaction catalyzed by biogenic iron oxide nanoparticles



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ABSTRACT

An efficient green method was used for the synthesis of polyphenol capped iron oxide nanoparticles (ION) from an agro waste, peanut skin. The polyphenol capped ION was characterized by Fourier transformed infra-red (FTIR), Powder XRD and X-ray photoelectron spectroscopic (XPS) analysis. To evaluate the catalytic activities of ION, ring opening of epoxides by aromatic amines has been performed and the catalyst showed good activity with yields up to 90% of the major products using only 20 mg of the catalyst under solvent free neat condition at room temperature (28 °C) after 5 h. These nanoparticles can be reused for three times without significant loss in their activities.

1. Introduction

β-Amino alcohols are resourceful key intermediates for the generation of biologically potent molecules [1,2], amino acids [3,4], and also several chiral auxiliaries [5]. They can act as intermediates or precursors for manufacturing daily use products, cosmetics including photo developers, perfumes, hair dyes, etc [6]. The most well-known and straightforward strategy to synthesize β -amino alcohols is the epoxide ring opening (ERO) by amines at a suitable temperature (Scheme 1). Although, several drawbacks associated with this method, like lower product yields, high reaction temperature, excess use of amines, long reaction times, poor region selectivity and application of hazardous solvents, limit their wide range applications [7–11]. Besides, under basic or acidic conditions epoxides get polymerized giving lower product yields. To eliminate these drawbacks several strategies are currently available in literature, but most of them mainly gave attention to the reactions catalyzed by activators, promoters and several metal or non-metal-based catalysts, viz., metal halides [12], ionic liquids [13], montmorillonite clay [14], zeolites [15], solid acids [16,17] and Lewis acids [18,19]. However, most of these methodologies include the application of hazardous solvent systems, moisture sensitive catalysts and expensive reagents. Therefore, development of a stable, cheap, environment friendly recyclable heterogeneous

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catalyst system is highly sought-after. Transition metal catalyzed ERO by amines are widely reported in the literature [20-23]. However, easy availability, cheap and eco-friendly nature of iron have made this metal an ideal target for catalyzing the epoxide ring opening reaction. Plant extracts are largely familiar for reducing the metal ions since the early 1900s as these methods are readily scalable, less-expensive and eco-friendly. During metal nanoparticles (NPs) formation, plant extracts are well proficient to act as a reducing agent together with stabilizing agent. Biological components, for instance polyphenolic compounds, alkaloids, terpenoids, proteins, sugars and several phenolic acids, present in the plant extracts are known to act as both reducing as well as stabilizing agents during the synthesis of metal nanoparticles. Biological components, such as polyphenols, alkaloids, terpenoids, phenolic acids, sugars and proteins present in the plant extract are proved to be responsible for the bio-reduction of the metal ions to their nano state.

In this context, the present work demonstrates the potential of the peanut skin (agro-waste, collected from peanut) for the preparation of polyphenol coated amorphous iron oxide nanoparticles. Thereafter, the iron oxide nanoparticles (IONs) are employed to prepare the β -amino alcohols through ring opening of epoxides using aromatic amines under solvent-less conditions at ambient temperature.



Scheme 1. Epoxide ring opening reactions over IONs.

2. Experimental Section

2.1. Synthesis of polyphenol coated amorphous iron oxide nanoparticles (IONs)

Polyphenol coated amorphous iron oxide nanoparticles were prepared following our previously reported literature [24]. In a typical synthetic procedure, 1 g peanut skin, collected from the sun-dried peanuts obtained from local market, was immersed in 50 mL triple distilled water and kept overnight at 4 °C. Then after filtration the peanut skin extract (PNS) was collected and its pH was adjusted to 3. Thereafter, iron oxide nanoparticles (ION) were synthesized through the drop wise addition of 2 mL Fe(NO₃)₃ solution (5 mM) to 5 mL of this PNS and an instant color change following light brown to dark green to black indicated the formation of polyphenol capped iron oxide nanoparticles. The mixture was kept overnight at 4 °C. Finally, the IONs were separated through centrifugation at 10,000 rpm for 8 min followed by re-dispersion in triple distilled water. The mass was then dried in an oven at 75 °C for 4 h.

2.2. Characterization of polyphenol coated amorphous iron oxide nanoparticles (IONs)

2.2.1. TEM analysis

Transmission microscopic (TEM) images were obtained to confirm the nanodimension of the material. TEM images were obtained by a JEOL JEM 2100 HR with EELS transmission electron microscopy. To obtain the images a colloidal solution containing the IONs was drop cast on a carbon-coated Cu grid. Then the grid was dried under an IR lamp before introducing into the microscope.

2.2.2. FTIR analysis

The Fourier Transform InfraRed (FTIR) spectra of the ION samples were analysed and compared with the free ligand in the range 400–4000 cm⁻¹ on a Perkin Elmer FT-IR 783 spectrophotometer with resolution 1 cm⁻¹ using KBr pellets. FTIR analysis was done to understand the bonding present in the nanomaterials and match the functionalities with the previous experiment. For the experiment, a small fleck of the sample was thoroughly mixed with dried KBr using a mortar-pestle. A pellet of the mixture was prepared by applying 5 tons of pressure in a steel arrangement through a hydraulic pressure. This pellet was placed on a sample holder inside the FTIR instrument analyzer before obtaining the spectra.

2.2.3. Powder XRD

After synthesis the IONs were dried and then PXRD analysis was done to analyze the nature of the material.

2.2.4. XPS

X-ray photo electron spectroscopy (XPS) was applied to analyze the possible composition and the oxidation state of the elements present in the IONs. XPS was executed on a Kratos Axis HSi X-ray photoelectron spectrometer attached with a charge neutralizer and magnetic focusing lens, utilizing Al K α monochromatic radiation (1486.7 eV). Spectral fitting was achieved using Casa XPS version 2.3.14. Binding energies were corrected to the C 1s peak at 284.6 eV.

2.3. General procedure for epoxide ring opening by amines

Polyphenol capped amorphous IONs were used as a heterogeneous catalyst for the ring opening of epoxide with amines. The synthetic procedure for this ERO reaction is detailed in electronic supplementary information (ESI).

2.4. Procedure for recycling of the catalyst

After the completion of a reaction, the solution was centrifuged at 3000 rpm for 10 min to separate out the solid catalyst from the reaction mixture so as to recycle the catalyst. The catalyst was separated, washed thoroughly with distilled water and then by ethanol followed by drying at 80 °C in an oven for 2 h for reactivation. The catalyst could be recycled proficiently and reused effectively for three successive runs without an appreciable loss in the product yield.

3. Results and discussion

3.1. Characterization of biogenic IONs

Polyphenol capped amorphous iron oxide nanoparticles were prepared from peanut skin extract through a simple and eco-friendly method. The detailed estimation method and the data of total polyphenol content in the peanut skin extract before and after the synthesis of the IONs were given in supporting information. Thereafter the nanoparticles were characterized and then utilized for the ERO reaction by amines.

3.1.1. TEM

TEM image (Fig. 1) shows that iron oxide nanoparticles of 15-60 nm



Fig. 1. TEM image of the IONs.

size are formed. It was clearly seen in the image that the iron oxide nanoparticles are spherical in shape and they are distributed in the polyphenol matrix. A porous structural pattern can also be seen with amorphous morphology.

3.1.2. FTIR studies

The FTIR spectrum of the ION (Fig. 2) is well matched with our previously reported catalyst. A broad peak at 3347 cm⁻¹ and peak at 2922 cm⁻¹ were observed for stretching of –OH and aliphatic –CH. The peak at 1619 cm⁻¹ corresponds to the carbonyl bond whereas the peaks at 1519, 1438, and 1372 cm⁻¹ are due to aromatic –C=C-, -C-H- bonds of alkanes and phenolic –OH, respectively. The peaks in the range of 1281 to 773 cm⁻¹ were observed due to the in plane and out of plane bending vibrations of –CH bonds. The bands near 671 and 533 cm⁻¹ correspond to the Fe–O stretching vibrations of amorphous IONs.

3.1.3. Powder XRD

Powder XRD pattern of the as synthesized IONs is shown in Fig. 3. The PXRD pattern shows the absence of any sharp peak that indicates the amorphous nature of the IONs.

3.1.4. XPS analysis

The XPS analysis was further studied to determine the chemical compositions of IONs. XPS survey spectrum (Fig. 4a) shows the existence of three elements (C, O and Fe) in the sample. The fine XPS spectra of Fe 2p is given in Fig. 4b. As shown in Fig. 4b, along with two satellite peaks at ~719.5 and 734.8 eV, two major peaks at around 710.2 eV for Fe $2p_{3/2}$ and 724.1 eV for Fe $2p_{1/2}$ were observed which is in good agreement with the reported value of Fe³⁺ in α -Fe₂O₃ [25–27].

3.2. Biogenic ION catalyzed epoxide ring opening (ERO) by amines

The catalytic activity of IONs was investigated through ERO reactions with aromatic amines. The reaction conditions were optimized using a series of reactions between styrene oxide and aniline by varying reaction parameters, like catalyst amount, solvent, reaction temperature, and time. The results are presented in Table 1. The indispensable role of the catalyst was investigated by performing an ERO reaction without any catalyst which furnished a trace amount of the product after 8 h at room temperature. (Table 1, Entry 1). A moderate yield of the product was obtained when dichloromethane, water, tetrahydrofuran and toluene



Fig. 3. PXRD data of IONs.

were used as solvent. On the contrary, superior result has been observed under solvent-free neat condition (Table 1, Entries 2–6). It is found that the reaction temperature has a great influence on the ERO reaction as yield of the product significantly decreased with increase of reaction temperature (Table 1, Entries 6–8). The amount of catalyst and the duration of reaction were also varied (Table 1, Entries 9–12). Finally, it is found that the best yield of the product (90%) was obtained using only 20 mg of the catalyst under solvent free neat condition at room temperature (28 °C) after 5 h.

Next, following the above optimized reaction conditions, a number of ERO reactions were performed using styrene oxide, epichlorohydrin and glycidyl isopropyl ether as the epoxide partner and aniline, *m*-chloro aniline as the associated amine. The results are summed up in Table 2. The ERO of styrene oxide by aniline takes place through the preferential attack at the more hindered benzylic carbon. This is because of the presence of the phenyl group that renders the benzylic carbon become more electrophilic in nature [28] (Table 2, Entry 1). In contrast, epichlorohydrin and glycidyl isopropyl ether were efficiently converted to their corresponding products with good yields (Table 2, Entries 2–3). Here the attack of the nucleophilic amines takes place at the less hindered carbon atom of the epoxide ring.



Fig. 2. IR spectrum of the IONs.



Fig. 4. XPS spectrum of ION (a) full range XPS survey, (b) high resolution fine spectra of Fe 2p.

Table 3

 Table 1

 Optimization of different conditions for the ERO reaction using IONs.^a

Entry	Catalyst amount (mg)	Solvent	Temp. (°C)	Time (h)	Yield ^b (%)
1	-	_	rt	12	trace
2	20	DCM	rt	5	82
3	20	H ₂ O	rt	5	59
4	20	THF	rt	5	45
5	20	Toluene	rt	5	71
6	20	-	rt	5	90
7	20	-	40	5	87
8	20	-	50	5	85
9	10	-	rt	5	80
10	30	-	rt	5	87
11	20	-	rt	3	79
12	20	-	rt	6	91

 $^{\rm a}$ Condition: Aniline (1.0 mmol), Styrene oxide (1.0 mmol), solvent (1.5 mL). $^{\rm b}$ Isolated yield.

Finally, we have compared the activity of our present nano-catalyst with existing state-of-the-art catalysts used for ERO reactions (Table 3). The comparative study table clearly reveals that our as synthesized nano-catalyst shows excellent catalytic activity for the synthesis of β -amino alcohols starting from styrene oxide and aniline. Plant extract mediated synthesis of metal-based NP always produces finer nanoparticles. As polyphenolic moeity helps to stabilize the metal NPs the latter do not

Comparative study table for the synthesis methods of $\beta\mbox{-amino}$ alcohols using various catalysts.

Entry	Catalyst	Reaction Condition	Time	Yield	Ref
1	CeO ₂ -ZrO ₂ (20 wt%)	TBHP, CCl ₄ , 80 °C,	5 h	92	29
2	MoO ₂ (acac) ₂ (5 mol%)	CCl ₄ , 50 °C	2.5 h	95	30
3	TiO ₂ –ZrO ₂	H_2O , RT,	1.2 h	86	31
4	Mesoporous-Zr-beta catalyst	35 °C	0.5 h	81	32
5	CoFe@rGO (20%)	Neat, 80 °C	6 min	90	33
6	Nano Fe ₃ O ₄ (10 mol%)	RT, Neat,	20 h	83	34
7	CoFe ₂ O ₄	Neat, 80 °C	10 min	89	35
8	MTF-1E (0.04 mmol Fe),	Neat, RT,	3 h	91	36
9	IONs(0.00249 mmol of Fe, 2.493 \times 10-4 mol% of Fe)	RT, Neat	5 h	90	This work

undergo agglomeration during synthesis. Therefore, the NPs can provide larger surface area and hence their catalytic activity becomes higher. The higher turnover frequency (TOF in min⁻¹) of the synthesized products using our freshly prepared IONs clearly justify this fact. Moreover, the comparative study with several iron oxide-based catalysts also supports this fact that our polyphenol coated IONs show comparatively better catalytic activity.

Table 2

ERO reaction of various epoxides with different anilines using IONs.^a.

Entry	Epoxide	Amine	Product	Time (h)	Yield (%) ^b	TOF ^c (min ⁻¹)
1		NH ₂	HO	5	90	1203
2	ciO	NH ₂	CI OH H CI	4.5	89	1190
3		NH ₂	CI OCH H	5	87	1163

^a Conditions: Epoxide (1.0 mmol), Amine (1.0 mmol), IONs (20 mg, 0.00249 mmol of Fe, 2.493×10⁴ mol% of Fe),

without solvent, RT.

^b Isolated yield.

°TOF = mol of product / (mol of total metal × time)

3.3. Recyclability of the catalyst

Recycling efficiency is the most significant characteristic property of heterogeneous catalyst. In order to check the stability of IONs, HR-TEM was studied of the reused catalyst after 3rd run (Fig. 5). The HR-TEM analysis data clearly specifies that the nature of the catalyst remains significantly unaltered after reuse as is reflected in the shadow around the dark spots of metal ions. The FTIR spectrum of the reused IONs (Fig. S1) depicts a slight degradation after three successive runs. The broad peak at 3347 cm⁻¹ for stretching of -OH is slightly shifted to 3343 cm⁻¹. The peak at 1619 cm⁻¹ due to the carbonyl bond now appears at 1622 cm⁻¹ and the peaks at 1519, 1438, and 1372 cm⁻¹ owing to aromatic -C=C-, -C-H- bonds of alkanes and phenolic -OH, respectively have undergone slight shifts to 1516, 1442 and 1366 cm⁻¹. The Fe-O stretching vibration bands of amorphous IONs near 671 and 533 cm⁻¹ also are shifted to 673 and 528 cm⁻¹. These changes reflect that although there are slight degradation of the catalyst after reuse and regeneration, the main functionalities of the polyphenols remain to be attached in the nanoparticles.

Fig. 6 showed the recycling activity of IONs for the ERO reaction of styrene oxide and aniline. The figure clearly indicates that after the third run the yield percentage decreases from 90 to 82%.

4. Conclusion

The present work describes the biogenic production of Fe₂O₃ nanocatalyst using peanut skin extract. A successful application of the catalyst is reported towards ring opening of epoxides for the generation of β -amino alcohol derivatives in presence of aromatic amines. The IONs showed good chemical stability and appreciable catalytic activity. The promising advantages presented by this protocol are the solventless neat condition, simple operational method, universal applicability, mild and green reaction conditions, recyclability of the catalyst with considerably good product yields. The overall green and cost-effective methodology of the catalytic process using iron oxide nano-catalyst reported herein is a



Fig. 5. HR-TEM of the reused catalyst after 3rd run.



Fig. 6. Recyclability chart of IONs catalyst.

potential avenue towards large scale synthesis of a broad variety of valueadded fine chemicals.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://do i.org/10.1016/j.jics.2021.100056.

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