Article

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Polyethylene Glycol-(*N*-Methylimidazolium) Hydroxide-Grafted γ-Fe_2O_3@HAp: A Novel Nanomagnetic Recyclable Basic Phase-Transfer Catalyst for the Synthesis of Tetrahydrobenzopyran Derivatives in Aqueous Media

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Polyethylene glycol-(*N*-methylimidazolium) hydroxide-grafted hydroxyapatite encapsulated γ-Fe_2O_3 nanoparticles, γ-Fe_2O_3@HAp@PEG(mim)OH, were prepared and characterized by FTIR, SEM, TEM, TGA, and EDAX. This nanocomposite was applied as a novel, green, nanomagnetic, and recyclable basic phase-transfer catalyst for the synthesis of tetrahydrobenzopyrans in high yields via the three-component reaction of aromatic aldehydes, malononitrile, and dimedone or 1,3-cyclohexanedione in aqueous media at ambient temperature.

Keywords: Phase-transfer catalyst; γ-Fe_2O_3@HAp@PEG(mim)OH; Nanomagnetic basic catalyst; Tetrahydrobenzopyrans; Green chemistry.

INTRODUCTION

Green chemistry is a concept that has been receiving great attention in recent years by chemists and researchers. It focuses on technological approaches to pollution prevention by the designing processes and products that minimize the use and production of hazardous chemicals, and also avoiding the use organic solvents and using alternative safer solvents.[1] One of the best solutions to the problem of solvent toxicity and disposal is the use of water as the medium for organic reactions.[2]

Since most of the organic reactants do not dissolve in water, phase-transfer catalysts (PTCs) can be used to overcome this problem.[3] Both homogeneous and heterogeneous PTCs improve the contact between inorganic reagents and organic substrates, but one of the major problems associated with the use of homogeneous catalysts is the recovery of the catalyst from the reaction medium. Immobilization of the PTC on an insoluble matrix can provide a simple solution to this problem.[4–7]

Because of the widespread application of hydroxyapatite as a robust material for drug and protein delivery agent and catalyst supporting material,[8–12] and based on our earlier success in the synthesis of novel catalysts,[13–16] in this study, for the first time, we prepared polyethylene glycol-(*N*-methylimidazolium) hydroxide-grafted hydroxyapatite encapsulated γ-Fe_2O_3 nanoparticles, which we denote as γ-Fe_2O_3@HAp@PEG(mim)OH. This novel, nanomagnetic, and recyclable basic PTC was characterized with several techniques, and, finally, its catalytic activity was tested in the synthesis of tetrahydrobenzopyrans via one-pot three-component reaction of aryl aldehydes, malononitrile, and 1,3-cyclohexadione or dimedone under aqueous conditions at room temperature.

RESULTS AND DISCUSSION

γ-Fe_2O_3@HAp@PEG(mim)OH was prepared by the concise route outlined in Scheme 1. The addition of $Ca(NO_3)_2{\cdot}4H_2O$ and $(NH_4)_2HPO_4$ solutions to the Fe_3O_4 magnetic nanoparticles (MNPs) led to its oxidation and coating with hydroxyapatite. Hexamethylenediisocyanate (HMDI) was used for conjugating polyethylene glycol monobromide onto the surface of the γ-Fe_2O_3@HAp NPs. After that, *N*-methylimidazole was immobilized onto the modified MNPs, leading to the formation of the nanomagnetic PTC γ-Fe_2O_3@HAp@PEG(mim)Br. Ultimately, a mixture of the prepared nanocomposite and sodium hydroxide in water was stirred at room temperature, and a novel nanomagnetic basic PTC was produced.

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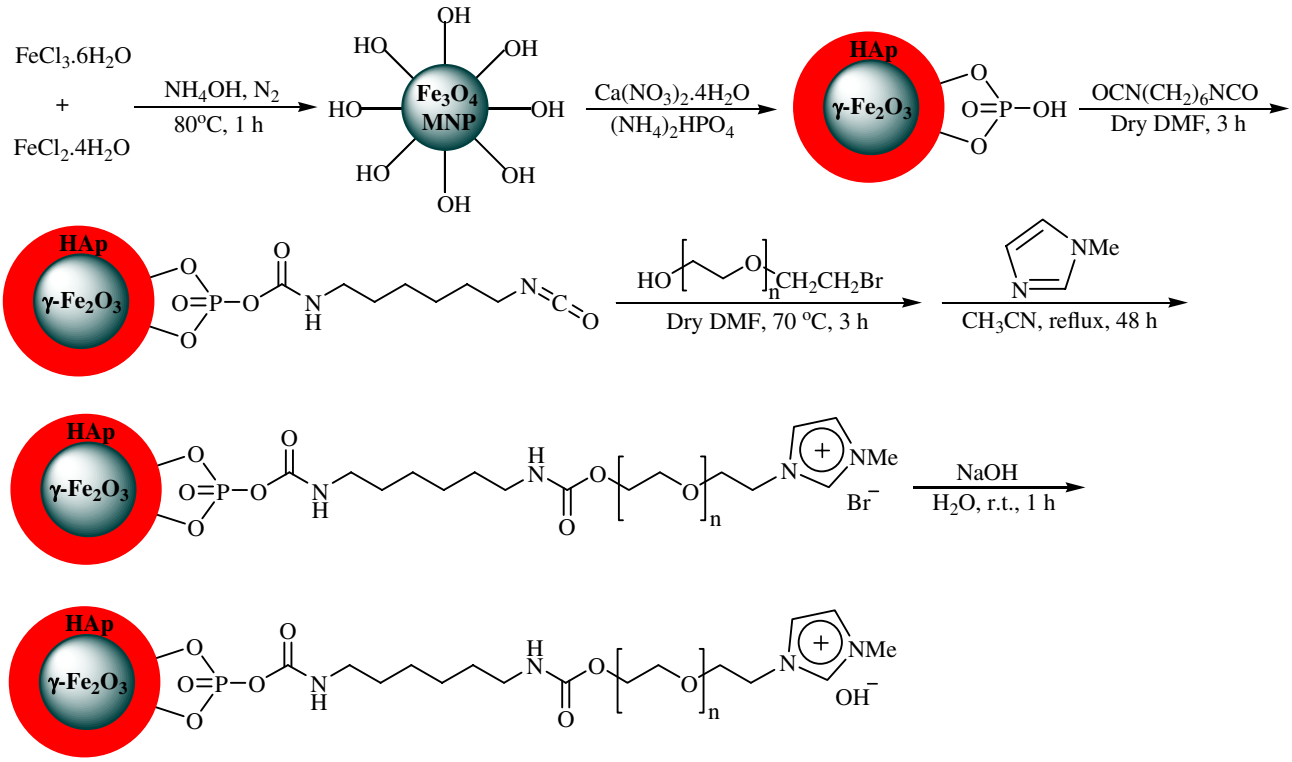


Scheme 1. Synthesis of γ-Fe_2O_3@HAp@PEG(mim)OH.

The catalyst was characterized by the various techniques including Fourier transform infrared (FTIR) spectroscopy (Figure 1), transmission electron microscopy (TEM, Figure 2), scanning electron microscopy (SEM, Figure 3), energy dispersive X-ray (EDX, Figure 4) spectroscopy, and thermogravimetric analysis (TGA, Figure 5). According to the FTIR spectrum of the catalyst (Figure 1), the characteristic absorption bands due to the bending vibration mode of O–P–O surface phosphate groups in the hydroxyapatite shell were observed at 563 and 601 cm^{-1} which overlap with the Fe–O stretching band. In addition, the absorption

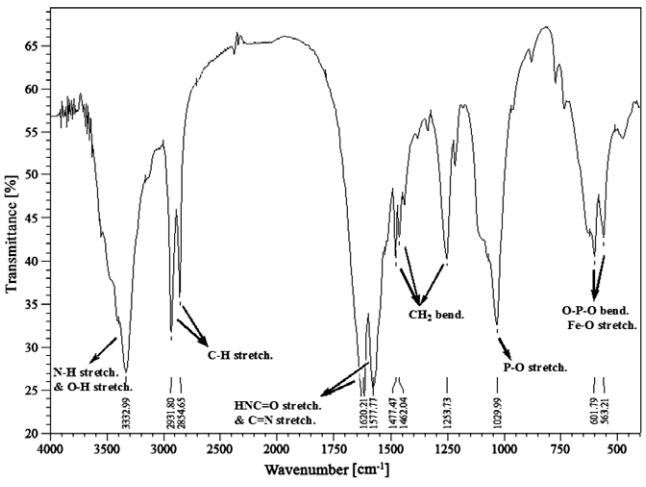


Fig. 1. FTIR spectra of γ-Fe_2O_3@HAp@PEG (mim)OH.

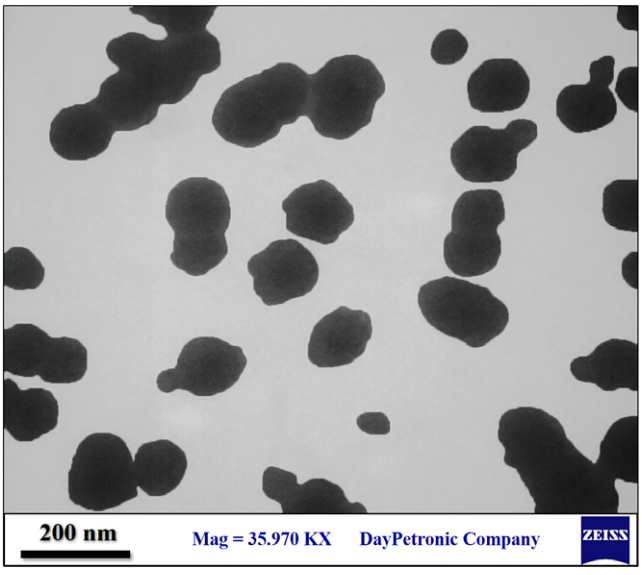


Fig. 2. TEM image of γ-Fe_2O_3@HAp@PEG (mim)OH.

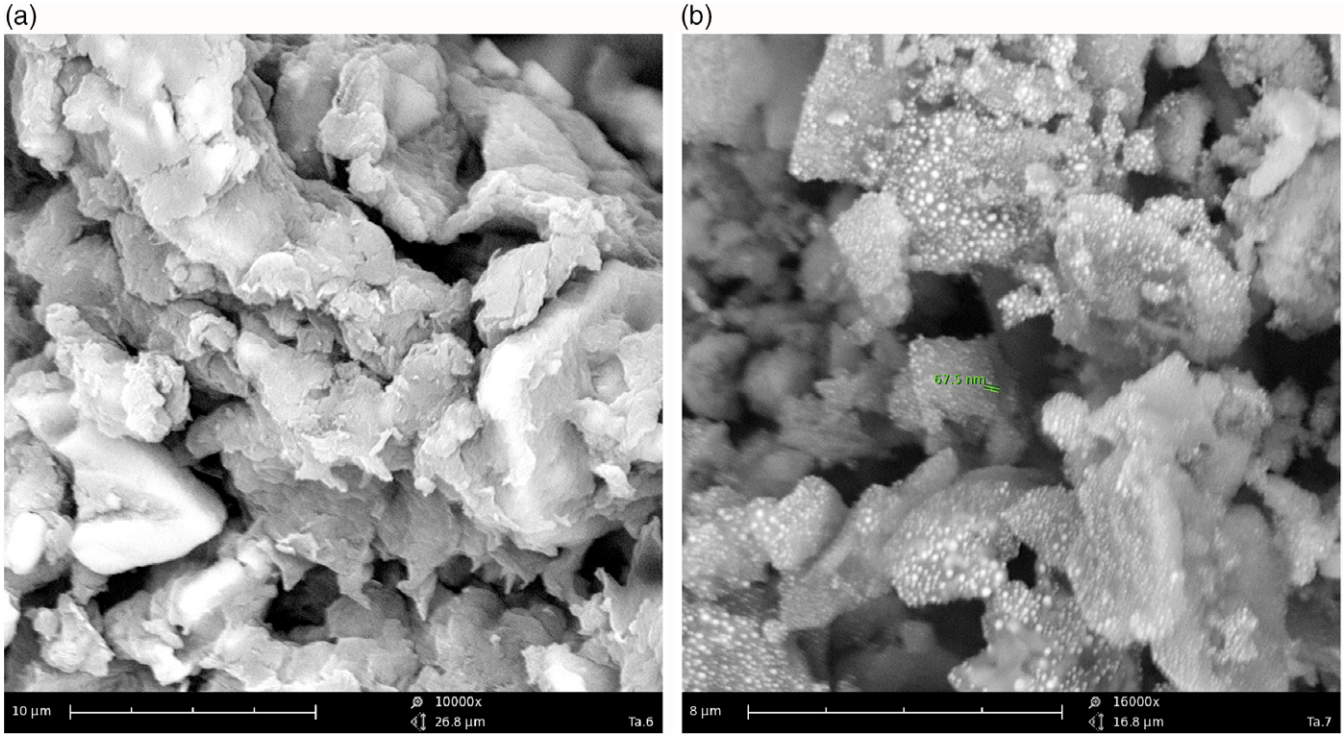


Fig. 3. SEM images of (a) γ-Fe_2O_3@HAp and (b) γ-Fe_2O_3@HAp@PEG(mim)OH (b).

band at 1029 cm^{-1} can be attributed to the stretching of the P–O bond. The IR spectrum of the catalyst also showed the characteristic absorption bands at 3332 and 1620 cm^{-1} corresponding to the NH and C=O groups. The NHCO stretching was also observed at 1577 cm^{-1}. It is worth noting the disappearance of the isocyanate peak in the IR spectrum of the catalyst at about 2200–2300 cm^{-1}. The introduction of PEG-substituted *N*-methylimidazolium on

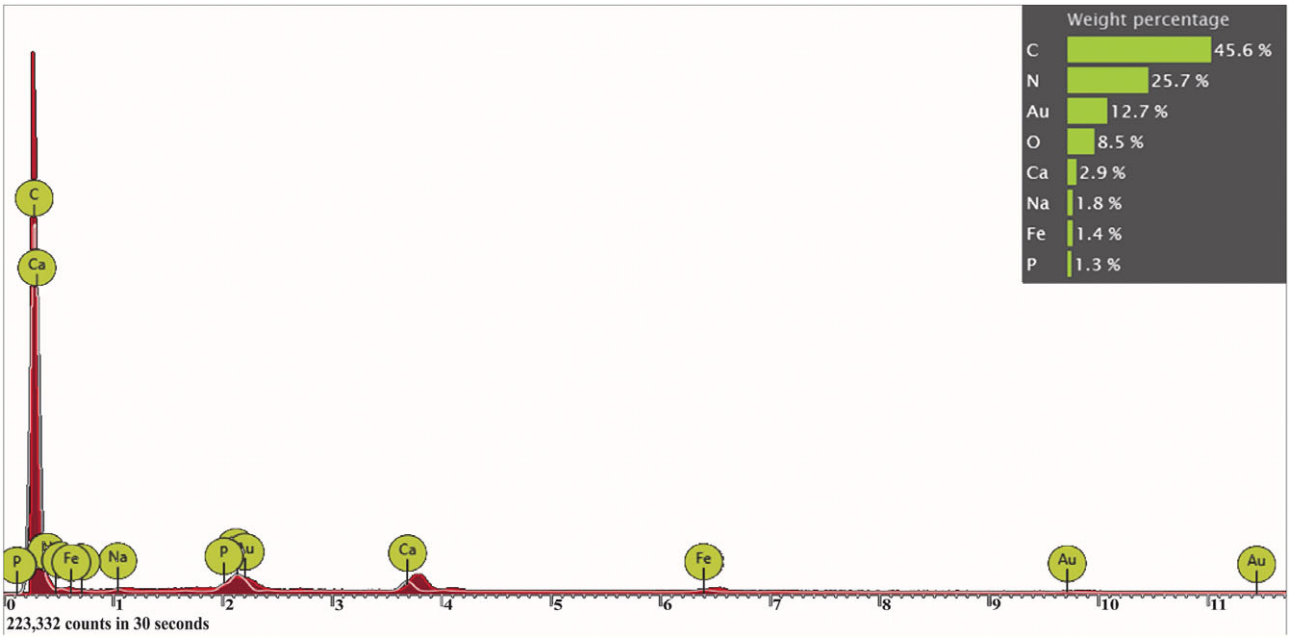


Fig. 4. EDAX pattern of γ-Fe_2O_3@HAp@PEG(mim)OH.

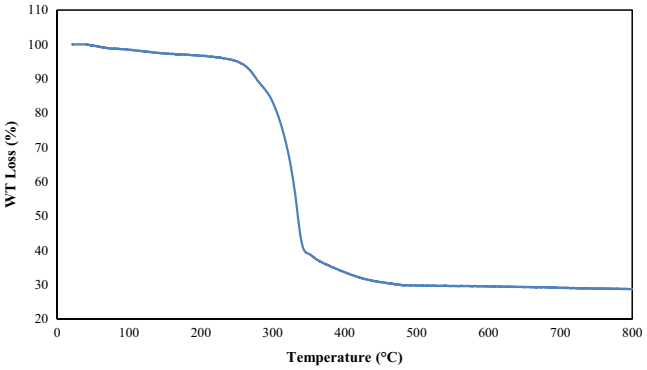


Fig. 5. TGA diagram of γ-Fe_2O_3@HAp@PEG (mim)OH.

the surface of γ-Fe_2O_3@HAp was confirmed by the C—H stretching and bending bands, which could be observed at 2850–2950 and 1400–1500 cm^{-1}, respectively. In addition, the bands at 1620 and 1577 cm^{-1} were assigned to the imidazole C=N bending and ring-stretching vibrations, respectively, which overlap with the NHCO stretching bands. This spectrum showed a broad peak at 3200–3600 cm^{-1}, which includes the O—H stretching vibration.

Both TEM (Figure 2) and SEM (Figure 3) results showed that the encapsulated nanoparticles were present as uniform particles and the size of encapsulated nanoparticles was less than 100 nm.

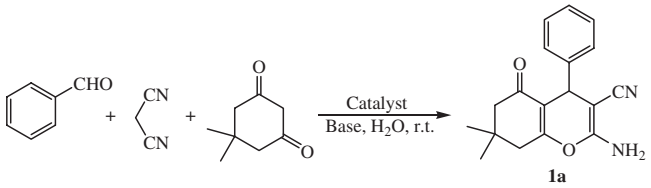
The data from EDAX analysis are consistent with our expectations and confirms the presence of carbon, oxygen, calcium, phosphorous, iron, and nitrogen in γ-Fe_2O_3@HAp@PEG(mim)OH (Figure 4).

TGA of the γ-Fe_2O_3@HAp@PEG(mim)OH was investigated by raising its temperature at the rate of 10 °C min^{-1} in air up to 800 °C to analyze its thermal decomposition behavior (Figure 5). Two main stages of weight loss are observed. The first small weight loss of 11% below 280 °C is due to the removal of physically adsorbed water as well as dehydration of the surface OH groups; the second one in the region of 280–360 °C is probably due to the decomposition of the organic groups. The curve shows a weight loss of about 52% from 280 to 360 °C, resulting from the decomposition of the organic spacer grafting to the magnetite surface.

After successful characterization of the catalyst, to evaluate the catalytic activity of γ-Fe_2O_3@HAp@PEG(mim)OH as a basic nanomagnetic PTC, initially a three-component reaction of benzaldehyde, malononitrile, and dimedone was carried out to determine the catalyst efficiency and to arrive at the optimized reaction conditions (Table 1).

After preliminary experiments, it was found that the condensation reaction of benzaldehyde, malononitrile, and dimedone was efficiently carried out in the presence

Table 1. Optimization of the reaction conditions for the synthesis of tetrahydrobenzopyran **1a**[a]

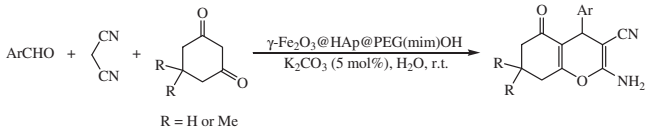


1a

Entry	Catalyst (g)	Base (mol%)	Time (min)	Yield[b] (%)
1	–	NaOH (10)	90	35
2	–	K_2CO_3 (10)	90	30
3	γ-Fe_2O_3@HAp@PEG(mim)Cl (0.05)	K_2CO_3 (10)	90	75
4	γ-Fe_2O_3@HAp@PEG(mim)Br (0.05)	K_2CO_3 (10)	90	80
5	γ-Fe_2O_3@HAp@PEG(mim)OH (0.05)	K_2CO_3 (10)	20	92
6	γ-Fe_2O_3@HAp@PEG(mim)OH (0.05)	K_2CO_3 (5)	20	91
7	γ-Fe_2O_3@HAp@PEG(mim)OH (0.05)	–	90	30
8	γ-Fe_2O_3@HAp@PEG(mim)OH (0.04)	K_2CO_3 (5)	20	92
9	γ-Fe_2O_3@HAp@PEG(mim)OH (0.05)	NaOH (10)	90	80

[a] Reaction conditions: benzaldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol), water (3 mL).
[b] Isolated yield.

Table 2. Synthesis of 4*H*-tetrahydrobenzopyrans catalyzed by γ-Fe_2O_3@HAp@PEG(mim)OH in water[a]



Entry	Ar	R	Time (min)	Product	Yield (%)[b]	M.p. (°C) Found	M.p. (°C) Reported[ref.]
1	C_6H_5	Me	20	**1a**	92	229–231	231–232[17]
2	4-$MeOC_6H_4$	Me	35	**1b**	90	192–193	197–199[18]
3	4-MeC_6H_4	Me	50	**1c**	87	215–216	219–221[19]
4	2-ClC_6H_4	Me	45	**1d**	88	204–206	208–210[20]
5	3-ClC_6H_4	Me	30	**1e**	85	226–228	226–227[20]
6	4-ClC_6H_4	Me	40	**1f**	86	214–215	217–219[20]
7	4-BrC_6H_4	Me	20	**1g**	89	202–204	201–203[20]
8	4-HOC_6H_4	Me	40	**1h**	85	225–237	226–228[19]
9	4-$Me_2NC_6H_4$	Me	60	**1i**	83	209–211	210–212[19]
10	3-$O_2NC_6H_4$	Me	30	**1j**	89	211–212	210–212[17]
11	2,5-$(MeO)_2C_6H_3$	Me	30	**1k**	91	171–173	–
12	2-Furyl	Me	55	**1l**	84	219–221	220–222[19]
13	C_6H_5	H	30	**2a**	88	237–240	238–240[17]
14	4-$MeOC_6H_4$	H	40	**2b**	91	195–197	192–193[17]
15	4-MeC_6H_4	H	65	**2c**	90	160–162	–
16	2-ClC_6H_4	H	50	**2d**	88	206–208	–
17	4-ClC_6H_4	H	40	**2e**	89	224–227	224–226[17]
18	4-BrC_6H_4	H	50	**2f**	87	236–237	238–240[18]
19	3-$O_2NC_6H_4$	H	40	**2g**	85	225–227	229–230[18]
20	2,5-$(MeO)_2C_6H_3$	H	40	**2h**	89	220–222	–

[a] Reaction conditions: aryl aldehyde (1 mmol), malononitrile (1 mmol), 1,3-dicarbonyl (1 mmol), K_2CO_3 (5 mol%), PTC (0.04 g), water (3 mL), room temperature.
[b] Isolated yield.

of 0.04 g of γ-Fe_2O_3@HAp@PEG(mim)OH and 5 mol% of potassium carbonate in water at room temperature to producedgive 2-amino-3-cyano-7,7-dimethyl-4-(4-methyl phenyl)-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo-pyran (**1a**) in excellent yield in a short reaction time (Table 1, entry 8). Lower amounts of catalyst gave 4*H*-pyranin lower yield, while higher amounts of the catalyst or base had no marked effect on the reaction time and yield (Table 1, entries 5 and 6). The reaction in the presence of NaOH and K_2CO_3 (10 mol%) without the catalyst led to the formation of the corresponding product in low yield after a long reaction time (Table 1, entries 1 and 2). Additionally, the reaction in the absence of the base (Table 1, entry 7) or in the presence of NaOH (Table 1, entry 9) did not reach completetion even after much longer reaction time. This coupling reaction in the presence of the chloride and bromide forms of the PTC gave the corresponding product in lower yields with longer reaction times (Table 1, entries 3 and 4).

Subsequently, the generality and synthetic scope of this three-component protocol for synthesizing a series of tetrahydrobenzopyrans were demonstrated by the reaction of various aryl aldehydes with malononitrile and dimedone or 1,3-cyclohexadione under optimal conditions (Table 2). As shown in Table 2, yields of products are good to excellent for aromatic aldehydes bearing both electron-donating and electron-withdrawing groups.

To investigate the reusability of the catalyst, it was recovered from the reaction mixture using an external magnet (Figure 6) and washed with acetone or methanol and dried in air. It was then reused for

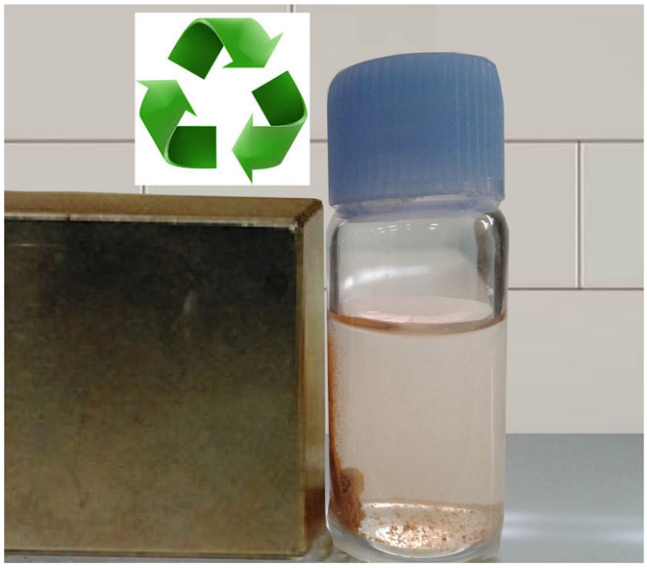
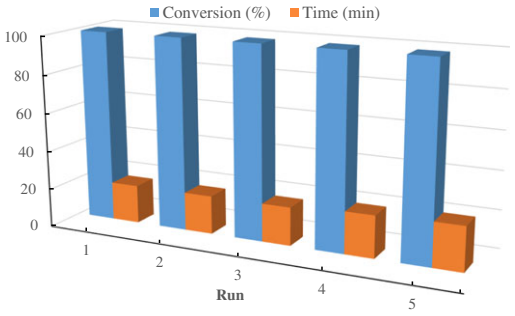


Fig. 6. Image showing the catalyst separation by an applied magnetic field.

subsequent experiments (up to five cycles) under similar reaction conditions. It was observed that the yields of the product remained comparable in these experiments (Figure 7), thereby establishing the recyclability and the reusability of the catalyst without any significant loss of activity.

Comparison of the catalytic strength of γ-Fe_2O_3@HAp@PEG(mim)OH in the three-component condensation of benzaldehyde, malononitrile, and dimedone to produce the corresponding 4*H*-pyran with some of methods reported in the literature is given in Table 3. The results show that our procedure provides high yields of the products in short reaction times under mild and green conditions.



	1	2	3	4	5
Conversion (%)	100	100	100	100	100
Time (min)	20	20	20	22	23

Fig. 7. Recovery and reusability of the catalyst.

CONCLUSION

In conclusion, we described the synthesis and characterization of a novel nanomagnetic basic PTC, γ-Fe_2O_3@HAp@PEG(mim)OH and the catalytic activity of this magnetically separable catalyst in the one-pot three-component synthesis of tetrahydrobenzopyrans under aqueous media at room temperature. This novel catalytic method offers several advantages including environmental friendliness, high yield, short reaction time, the use of mild reaction conditions involving a simple work-up procedure, ease of separation, and recyclability of the magnetic catalyst. The immobilized catalyst could be easily recovered by easy magnetic decantation and reused at least five times without noticeable loss of activity. So this procedure can be considered a new and suitable addition to the present methodologies in this area.

EXPERIMENTAL

Materials and methods

All materials and reagents were purchased from Fluka and Merck and used without further purification. Products were characterized by comparison of their physical data as well as IR, ^{1}H-NMR, and ^{13}C-NMR spectra with those of known samples. NMR spectra were recorded in DMSO-d_6 on a Bruker Advance DPX 400 MHz spectrometer with TMS as the internal standard. IR spectra were recorded on a BOMEM MB-Series 1998 FTIR spectrometer. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/UV 254 plates. TGA curve of the catalyst was recorded on a BAHR SPA 503 at heating rates of 10 °C min^{-1} under air atmosphere, over the temperature range 25–800 °C. SEM-EDAX analyses were carried out using a Philips XL30 instrument. The TEM images were recorded using a Zeiss-EM10C-80 kV miroscope.

Synthesis of polyethylene glycol-(*N*-methylimidazolium) bromide-grafted hydroxyapatite encapsulated γ-Fe_2O_3 nanoparticles

γ-Fe_2O_3@HAp[30] and HO-PEG-Br[31] were prepared according to reported methods. To introduce isocyanate groups, the γ-Fe_2O_3@HAp core–shell nanoparticles (0.5 g) were dispersed in 15 mL dry DMF by sonication (30 min), and then HMDI (8 mmol, 1.28 mL) diluted in 5 mL dry DMF was added dropwise to the mixture.

Table 3. Comparison of synthesis of tetrahydrobenzopyrans with different methods

Entry	Base or/and catalyst	Solvent	Condition	Time (min)	Yield (%)	Ref.
1	$Yb(PFO)_3$	EtOH	60 °C	300	90	[21]
2	TBAF	H_2O	Reflux	30	97	[22]
3	MgO	EtOH, H_2O	Reflux	30	92	[23]
4	$[H_3N^+CH_2CH_2OH][HCO_2^-]$	Neat	r.t.	5	70	[24]
5	SiO_2 NPs	EtOH	r.t.	25	94	[25]
6	MSNs	EtOH	60 °C	15	94	[26]
7	MNPs-Guanidine	PEG, H_2O	r.t.	15	95	[27]
8	K_2CO_3, $[DiEG(mim)_2][OH]_2$	H_2O	r.t.	20	92	[28]
9	Cs_2CO_3	EtOH	Visible light	60	85	[29]
10	K_2CO_3, γ-Fe_2O_3@HAp@PEG(mim)OH	H_2O	r.t.	20	92	Present work

After mechanical stirring of the mixture for 3 h, to graft PEG onto the surface, HO-PEG-Br (2 g) dissolved in dry DMF (5 mL) was added dropwise to the reaction mixture and stirred at 70 °C for 3 h. The precipitate was separated by magnetic decantation and washed with CCl_4 several times. *N*-Methylimidazole (40 mmol, 3.28 g) in 30 mL acetonitrile was added to the obtained nanocomposite and stirred for 48 h under reflux condition. The solid was washed with CH_2Cl_2 and dried at room temperature.

Synthesis of polyethylene glycol-(*N*-methylimidazolium) hydroxide-grafted hydroxyapatite encapsulated γ-Fe_2O_3 nanoparticles

A mixture of the nanocomposite (0.5 g) and sodium hydroxide (10 mmol, 0.4 g) in water (20 mL) was stirred at room temperature for 1 h. The produced precipitate was separated using an external magnet, washed with ethanol (3 × 10 mL), and dried in an oven at 80 °C to give γ-Fe_2O_3@HAp@PEG(mim)OH.

Basic capacity of the catalyst

To determine the basicity of the catalyst, γ-Fe_2O_3@HAp@PEG(mim)OH (0.1 g) was added to 25 mL of NaCl aqueous solution (1 M, pH = 5.9) and stirred for 24 h. The pH of the solution was increased to 9.76, which is equal to a basic capacity of 3.1×10^{-4} mmol basic sites/g of the catalyst.

General procedure for the synthesis of tetrahydrobenzopyrans

The basic PTC (40 mg) was added to a mixture of aromatic aldehydes (1 mmol), malononitrile (1 mmol), 1,3-cyclohexadione or dimedone (1 mmol), and K_2CO_3 (5 mol%, 6.9 mg) in water (3 mL). The reaction mixture was stirred at ambient temperature for an appropriate time as shown in Table 2. After completion of the reaction according to TLC analysis (*n*-hexane: ethyl acetate; 7:1), the mixture was filtered off in the presence of a magnet to separate the catalyst and the filtrate was washed with cool ethanol to obtain the corresponding 4*H*-pyrans. The crude products were purified by recrystallization from ethanol.

2-Amino-3-cyano-7,7-dimethyl-4-(4-methylphenyl)-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran (1c)

M.p. 215–216 °C; IR (KBr): ν = 3425, 3329, 2956, 2191, 1674, 1637, 1600 cm^{-1} (Figure S1, Supporting information); ^1H NMR (400 MHz, DMSO-d_6): δ = 0.96 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.07 (d, *J* = 16.0 Hz, 1H, CH-8), 2.23 (d, *J* = 16.0 Hz, 1H, CH-8), 2.27 (s, 3H, CH_3), 3.37 (m, 2H, CH-6), 4.14 (s, 1H, CH-4), 6.98 (s, 2H, NH_2), 7.04 (d, *J* = 8.0 Hz, 2H, ArH), 7.10 (d, *J* = 8.0 Hz, 2H, ArH) (Figure S2); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.56, 26.73, 28.39, 31.75, 35.15, 49.96, 58.43, 112.85, 119.73, 127.05, 128.84, 135.59, 141.79, 158.41, 162.25, 195.59 (Figure S3).

2-Amino-3-cyano-7,7-dimethyl-4-(furan-2-yl)-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran (1l)

M.p. 219–221 °C; IR (KBr): ν = 3398, 3325, 2951, 2187, 1678, 1651, 1604 cm^{-1} (Figure S4); ^1H NMR (400 MHz, DMSO-d_6): δ = 0.99 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 2.15 (d, 1H, *J* = 16.0 Hz, CH-8), 2.27 (d, 1H, *J* = 16.0 Hz, CH-8), 2.47–2.55 (m, 2H, CH-6), 4.33 (s, 1H, CH-4), 6.05 (m, 1H, ArH), 6.32 (m, 1H, ArH), 7.08 (s, 2H, NH_2), 7.48 (s, 1H, ArH) (Figure S5); ^{13}C NMR

(100 MHz, DMSO-d_6): δ_C = 26.52, 28.39, 28.95, 31.78, 46.43, 49.86, 55.36, 105.03, 110.32, 110.42, 119.53, 141.72, 155.69, 159.28, 163.24, 195.41 (Figure S6).

2-Amino-3-cyano-4-phenyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran (2a**)**

M.p. 237–240 °C; IR (KBr): ν = 3394, 3325, 3209, 2962, 2885, 2198, 1678, 1600 cm^{-1} (Figure S7); ^1H NMR (400 MHz, DMSO-d_6): δ = 1.95–2.00 (m, 2H, CH_2–6), 2.25–2.35 (m, 2H, CH_2–8), 2.61–2.64 (m, 2H, CH_2–7), 4.20 (s, 1H, CH-4), 7.00 (s, 2H, NH_2), 7.16–7.20 (m, 3H, ArH), 7.27–7.31 (m, 2H, ArH) (Figure S8); ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 19.77, 26.43, 35.41, 36.29, 58.18, 113.76, 119.75, 126.49, 127.09, 128.30, 144.76, 158.45, 164.44, 195.82 (Figure S9).

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Supporting information

Additional supporting information is available in the online version of this article.

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