

Fe²⁺ Supported on Hydroxyapatite-core-shell- γ -Fe₂O₃ Nanoparticles as an Inexpensive and Magnetically-recoverable Catalyst for Rapid Synthesis of Benzimidazoles and Benzoxazole Derivatives

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(Received 16 March 2016, Accepted 8 June 2016)

A simple and facile method for the preparation of Fe²⁺ supported on hydroxyapatite-core-shell- γ -Fe₂O₃ nanoparticles (γ -Fe₂O₃@HAp-Fe²⁺ NPs) as an environmentally friendly and recyclable green catalyst is described and used for the one-pot synthesis of benzimidazoles and benzoxazole derivatives via reactions between aromatic aldehydes and ortho-phenylenediamine or ortho-aminophenol in aqueous media conditions at room temperature. This green method offers significant advantages in terms of its simplicity, very low loading of catalyst, high catalytic efficiency, good to excellent product yields, short reaction time, simple experimental and work-up procedure. Also, after the reaction, γ -Fe₂O₃@HAp-Fe²⁺ NPs can be easily recovered and reused for at least ten runs. This magnetic nanoparticle was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscope (SEM) and vibrating sample magnetometry (VSM) spectra.

Keywords: γ -Fe₂O₃@HAp-Fe²⁺ NPs, Lewis acid, Magnetic nanoparticle, Benzimidazole, Benzoxazole

INTRODUCTION

Recently, the application of nanoparticles (NPs) as attractive and interesting materials has been more and more increased, because of their high surface area and unique magnetic properties. Moreover, they have a wide range of usage in various fields, such as biology and medical applications [1], environmental remediation [2], magnetic fluids [3], data storage [4], magnetic resonance imaging [5], and their application as catalysts in organic transformations [6-7]. Recently, the use of functionalized magnetic nanoparticles (MNPs) in organic synthesis has been developed because such reagents not only cause to simplify the purification processes but also help to prevent the releasing of toxic reaction residues into the environment. Furthermore, these MNPs are readily available, chemically

stable and can be prepared by simple methods. A large number of benzimidazole moieties are found in various biologically active and naturally occurring compounds having antiviral [8], antiulcer [9], antihypertensive [10], antihistaminic [11] and anticancer properties [12]. Moreover, some benzimidazole derivatives have been demonstrated to be potent antiparasitic agents [13], potential antitumour agents [14], selective neuropeptide Y Y1 receptor antagonists [15], inhibitors of HCMV replication [16], angiotensin II (AII) inhibitors [17], topoisomerase I inhibitors [18], antimicrobial agents [19], and inhibitors of the hepatitis C virus RNA polymerase [20]. Therefore their preparations have received an increasing attention to synthetic organic chemists and biologists. The widespread interest in benzimidazole-containing structures has prompted extensive studies for their synthesis. There are two general methods for the synthesis of 2-substituted benzimidazoles. One is the coupling of ortho-phenylenediamines and carboxylic acids [21], which often

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requires strong acidic conditions and sometimes combines with very high temperatures (*i.e.*, PPA, 180 °C) or using the microwave irradiation [22]. The other way involves a two-step procedure including the oxidative cyclodehydrogenation of aniline Schiff's bases, often generated in situ from the condensation of *ortho*-phenylenediamines and aldehydes. Various oxidative and catalytic reagents such as sulfamic acid [23], Yb(OTf)₃ [24], *N*-halosuccinamide (X = Cl, Br, I) [25], PPA [26], Zeolite [27], sulfur/ultrasonic [28], polyaniline-sulfate [29], ionic liquids [30], L-Proline [31], SOCl₂/SiO₂ [32], TiCl₄ [33], and Sc(OTf)₃ [34] have been employed. Many of the aforementioned methods of the benzimidazole derivatives synthesis involve expensive reagents, long reaction times, low yields, the use of an excess of reagents/catalysts, or the use of toxic organic solvents. Therefore, to avoid these limitations, the discovery of a new and efficient catalyst with high catalytic activity, and simple reaction working-up for the preparation of benzimidazoles and benzoxazole derivatives under mild and practical conditions is of prime interest. The aim of this study was to utilize γ -Fe₂O₃@HAp-Fe²⁺ NPs as a new, highly efficient and reusable Lewis acid catalyst for the synthesis of benzimidazoles and benzoxazole derivatives in good to excellent yields and short reaction time under green solvent and room temperature (Scheme 1).

EXPERIMENTAL

General

All reagents were purchased from Aldrich or SD Fine Chemicals and were used without further purification. Products were separated and purified by different chromatographic techniques and were identified by the comparison of their Melting point and NMR with those reported for the authentic samples. The products are characterized by recording their ¹H and ¹³C NMR spectroscopy by using Bruker 300 MHz apparatus. Chemical shifts are given in ppm with respect to internal TMS, and J values are quoted in Hz. Melting points were determined using an electrothermal apparatus and are uncorrected. The progress of reaction was followed with thin-layer chromatography (TLC) using silica gel SILG/UV 254 and 365 plate. IR spectra were recorded on a Frontier

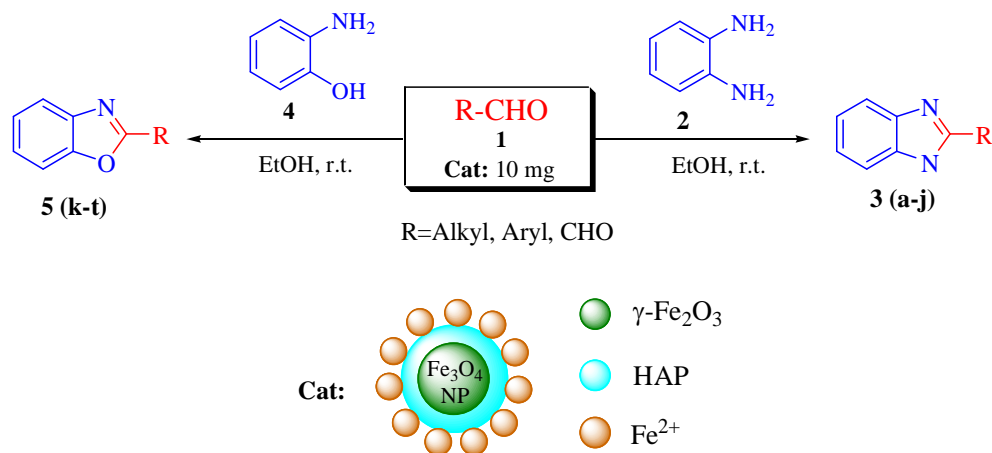
FT-IR (Perkin Elmer) spectrometer using a KBr disk. The phases present in the magnetic materials were analyzed using a powder XRD, Philips (Holland), model X0 Pert with X' Pert with CuK α 1 radiation ($\lambda = 1.5401 \text{ \AA}$), and the X-ray generator was operated at 40 kV and 30 mA. Diffraction patterns were collected from 2 $\theta = 20^\circ$ -80 $^\circ$.

Preparation of γ -Fe₂O₃@HAp-Fe²⁺NPs. In this study, γ -Fe₂O₃@HAp-Fe²⁺ NPs was prepared in two steps. The Iron Oxide Magnetic Particles (IOMP) were synthesized by chemical coprecipitation technique of ferric and ferrous chlorides in aqueous solution. Solutions of FeCl₃.6H₂O (0.25 M) and FeCl₂.4H₂O (0.125 M) were mixed and precipitated with NH₄OH solution (25%) at pH 12, while stirring vigorously. The black suspension, which formed immediately, was maintained at 70 °C for approximately one hour and washed several times with ultrapure water until the pH decreased to 7. IOMP/HAP was prepared by the impregnation method according to the known procedures with some modifications [35]. Then, Hydroxyapatite-Encapsulated γ -Fe₂O₃ (0.6 g) was introduced into 100 ml of distilled water containing 6.4 mmol of FeCl₂.4H₂O. The mixture was stirred (500 rpm) for 24 h, filtered, and washed several times with ethanol. The recovered solid was dried at 70 °C overnight (Scheme 2). The mean size and the surface morphology of the γ -Fe₂O₃@HAp-Fe²⁺ NPs were characterized by TEM, SEM, VSM, XRD and FTIR techniques [36].

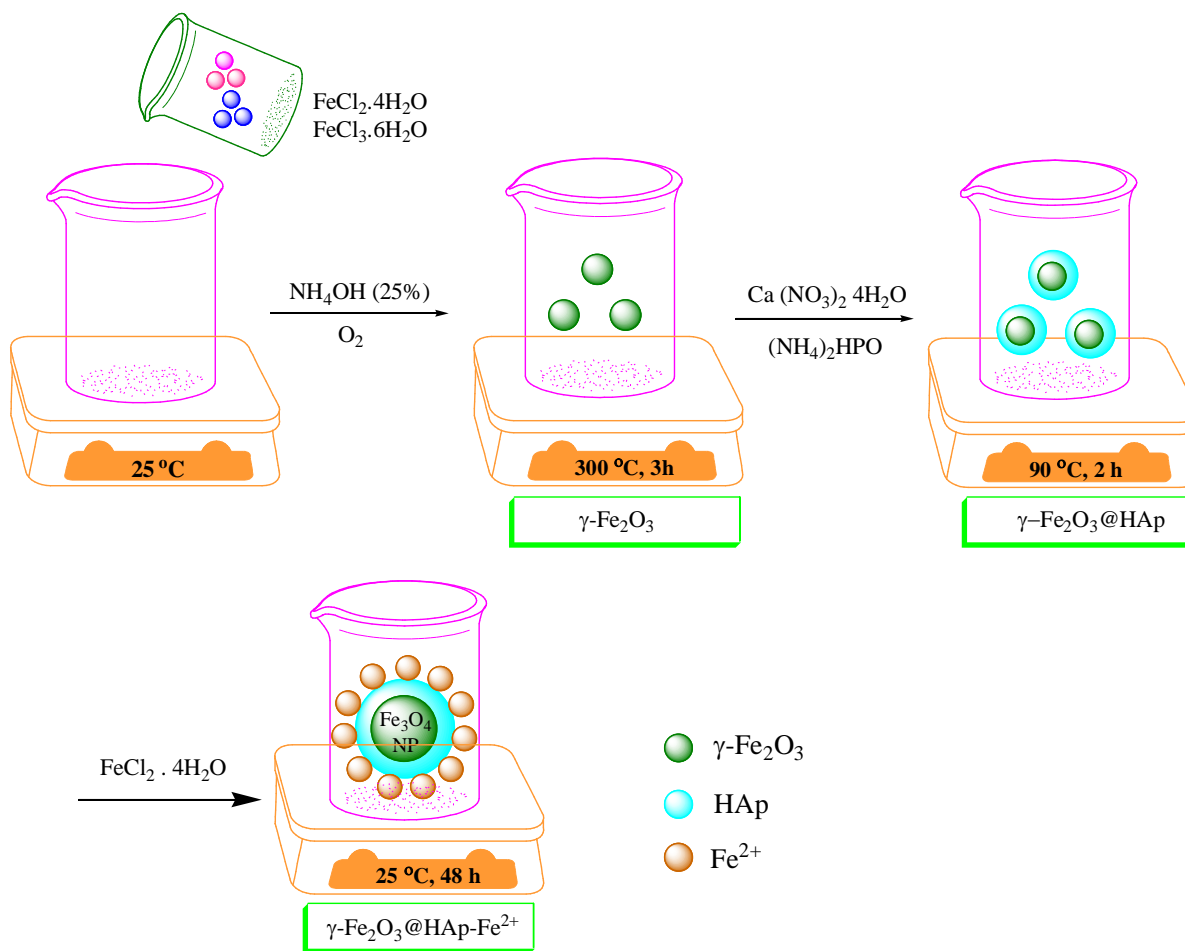
General Procedure for the Synthesis of Benzimidazole derivative

In a 50 ml round bottom flask, a mixture of *ortho*-phenyldiamine/*ortho*-aminophenol (1 mmol) and aldehydes (1 mmol) in ethanol (5 ml) were mixed and stirred in the presence of γ -Fe₂O₃@HAp-Fe²⁺ NPs (10 mg) at room temperature for an appropriate time (Table 2). The progress of the reaction was monitored by TLC. On completion of reaction, the catalyst was recovered by filtration and filtrate was extracted with ethyl acetate (2 \times 10 ml). By evaporation of the solvent, the crude product was recrystallized from hot ethanol to obtain the pure compound. All the products were characterized by Melting point, ¹H NMR and ¹³C NMR.

2-(*p*-Tolyl)-1H-benzo[d]imidazole (Table 2, entry 2). M.p.: 273-275 °C; ¹H NMR (300 MHz, CDCl₃) δ : 12.79 (s,



Scheme 1. Synthesis of the benzimidazole and benzoxazole derivatives



Scheme 2. Synthesis of Fe²⁺ supported on hydroxyapatite-core-shell γ -Fe₂O₃

1H, -NH), 8.05-8.08 (d, $J = 10.2$ Hz, 2H), 7.56-7.59 (m, 2H), 7.34-7.36 (d, $J = 10.2$ Hz, 2H), 7.17-7.21 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, DMSO- d_6) δ : 20.9, 114.9, 121.9, 126.3, 127.4, 129.4, 139.5, 151.3.

2-(4-Methoxyphenyl)-1H-benzo[d]imidazole (Table 2, entry 3). M.p.: 222-224 °C; ^1H NMR (300 MHz, CDCl_3) δ : 7.99-8.02 (m, 2H), 7.54-7.57 (m, 2H), 7.20-7.22 (m, 2H), 7.03-7.08 (m, 2H), 3.83 (s, 3H). ^{13}C NMR (75 MHz, CD_3OD) δ : 56.0, 115.6, 123.5, 123.7, 129.5, 153.6, 163.0.

2-(4-Chlorophenyl)-1H-benzo[d]imidazole (Table 2, entry 5). M.p.: 285-287 °C; ^1H NMR (300 MHz, CDCl_3) δ : 13.13 (broad s, 1H), 8.23 (d, $J = 8.5$ Hz, 2H), 7.64-7.58 (m, 2H), 7.34-7.18 (m, 4H). ^{13}C NMR (75 MHz, DMSO- d_6) δ : 115.8, 115.9, 124.2, 129.3, 129.7, 130.3, 137.3, 152.1.

2-Phenylbenzo[d]oxazole (Table 2, entry 11). M.p.: 101-102 °C; ^1H NMR (300 MHz, CDCl_3) δ : 8.21-8.27 (m, 2H), 7.75-7.79 (m, 1H), 7.48-7.58 (m, 4H), 7.31-7.36 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ : 110.8, 120.2, 124.7, 125.3, 127.3, 127.8, 129.1, 131.7, 142.3, 150.9, 163.2.

RESULT AND DISCUSSION

In continuation of our ongoing efforts on the applications of cheap and ecofriendly materials as catalysts for the development of new synthetic methodologies our ongoing [37-42], $\gamma\text{-Fe}_2\text{O}_3\text{@HAp-Fe}^{2+}$ NPs has been prepared according to the reported procedures, and characterized by FT-IR, XRD, TEM, SEM, and VSM [36]. The IR spectrum of the $\gamma\text{-Fe}_2\text{O}_3\text{@HAp-Fe}^{2+}$ NPs showed a broad peak at 3580 cm^{-1} related to OH groups in the hydroxyapatite structure. Also, the three peaks at 1098, 1030 and 961 cm^{-1} were attributed to the asymmetric and symmetric stretching vibration of the phosphate group (PO_4^{3-}), and the bending modes of Fe-O were observed at 608 , 565 and 475 cm^{-1} (Fig. 1).

In the present paper, we wish to report a simple, efficient and high-yielding method for the synthesis of benzimidazoles 3(a-j) and benzoxazole 5(k-t) derivatives by treatment of various aldehydes with (2) or *ortho*-

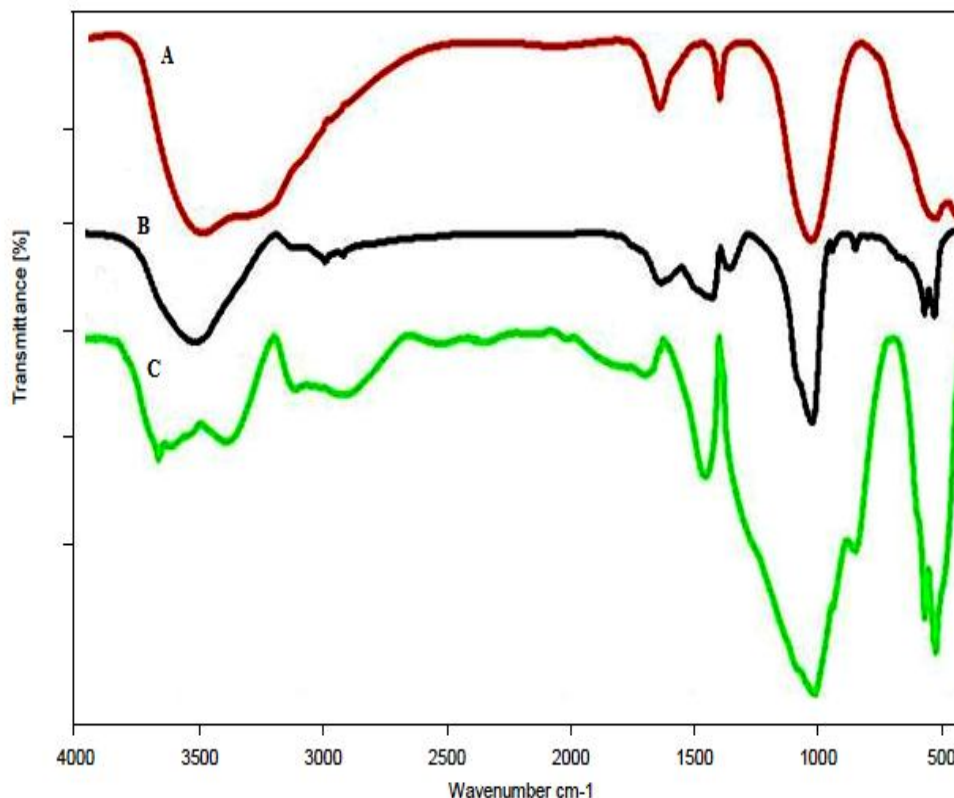


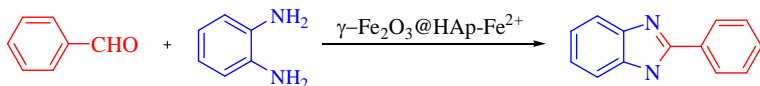
Fig. 1. FT-IR spectra of (A) $\gamma\text{-Fe}_2\text{O}_3\text{@HAp-Fe}^{2+}$ NPs, (B) $\gamma\text{-Fe}_2\text{O}_3\text{@HAp}$, (C) HAp.

aminophenol (4) catalyzed by γ -Fe₂O₃@HAp-Fe²⁺ NPs as an eco-friendly catalyst in ethanol as green solvent at room temperature (Scheme 1). To find the optimal conditions, the reaction between benzaldehyde 1 (1 mmol) and *ortho*-phenylenediamine 2 (1 mmol) was used as a reaction model to develop a protocol for the optimization of the reaction (Table 1). To improve the yield of the target product, we carried out the test reaction in the presence of various solvents such as ethanol, acetonitrile, dichloromethane, toluene, and chloroform and the results are presented in Table 1. As shown in Table 1, in the absence of the catalyst, the reaction was not completed after 24 h (Table 1, entry 1). Within the optimization of catalyst amount, we found that 10 mg of γ -Fe₂O₃@HAp-Fe²⁺ NPs could effectively catalyze the reaction for the synthesis of the desired product. When 5 mg of γ -Fe₂O₃@HAp-Fe²⁺ NPs was used, the yield of the desired product and reaction time decreased considerably (Table 1, entry 2). A higher percentage of loading the catalyst neither increased the yield

nor shortened the conversion time (Table 1, entries 4 and 5). Use of acetonitrile (Table 1, entry 6) and dichloromethane (Table 1, entry 7) as solvent were much better than the other solvents including toluene (Table 1, entry 8) and chloroform (Table 1, entry 9). When the reaction was performed in solvent-free conditions, the reactions proceeded slowly and resulted in reduced product yields (Table 1, entry 10). Hence, performing the reaction in ethanol as green solvent and in the presence of 10 mg of γ -Fe₂O₃@HAp-Fe²⁺ NPs at room temperature was determined as the optimal condition (Table 1, entry 3). Using the optimized reaction condition, the scope and limitations of this methodology were evaluated using a variety of aromatic aldehydes (Table 2).

The reaction between benzaldehyde (Table 2, entry 1), 4-methyl benzaldehyde (Table 2, entry 2), 4-methoxy benzaldehyde (Table 2, entry 3), 4-bromobenzaldehyde (Table 2, entry 4), 4-chlorobenzaldehyde (Table 2, entry 5), 3-methyl benzaldehyde (Table 2, entry 10) with *ortho*-phenyldiamine resulted in the corresponding

Table 1. Optimization of γ -Fe₂O₃-HAp-Fe²⁺ NPs Catalyzed Model Reaction^a



Entry	Catalyst (mg)	Solvent	Time (min)	Yields (%) ^b
1	none	Ethanol	24 h	Not complete
2	5	Ethanol	60	78
3	10	Ethanol	30	94
4	15	Ethanol	90	85
5	20	Ethanol	90	65
6	10	Acetonitrile	120	71
7	10	Dichloromethane	120	65
8	10	Toluene	180	35
9	10	Chloroform	180	48
10	10	Solvent-free	120	51

^aModel reaction: *ortho*-phenylenediamine (1 mmol), benzaldehyde (1 mmol), γ -Fe₂O₃@HAp-Fe²⁺ NPs (10 mg) at room temperature. ^bIsolated yield.

Table 2. γ -Fe₂O₃@HAp-Fe²⁺ NPs Catalysed Synthesis of Benzimidazoles and Benzoxazoles

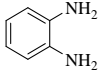
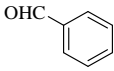
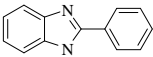
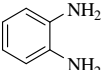
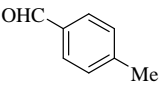
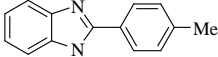
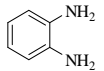
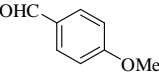
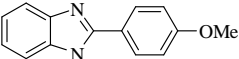
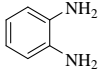
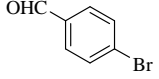
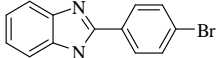
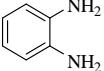
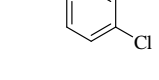
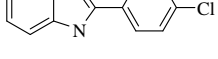
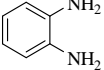
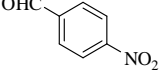
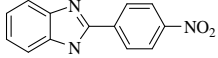
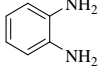
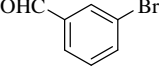
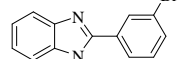
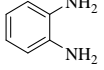
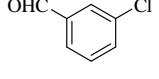
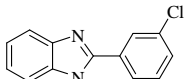
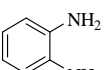
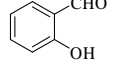
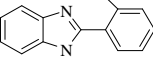
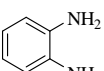
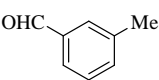
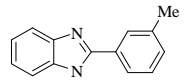
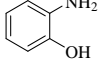
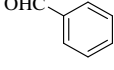
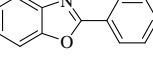
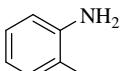
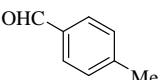
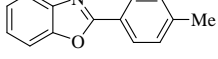
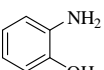
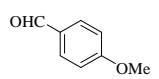
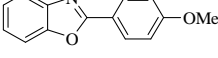
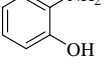
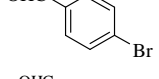
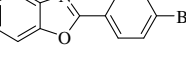
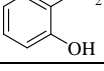
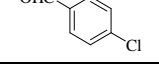
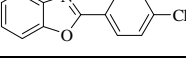
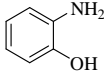
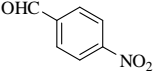
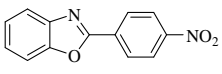
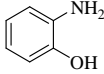
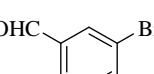
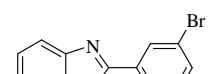
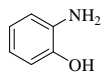
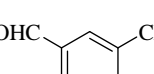
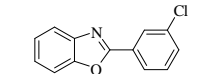
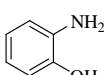
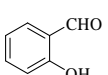
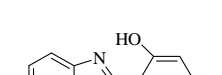
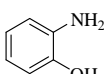
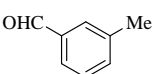
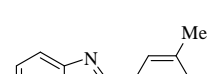
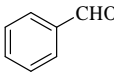
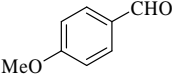
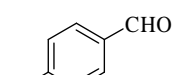
Entry	Diamines	Aldehyde	Product		Time (min)	Yield (%) ^a
1				3a	30	94
2				3b	30	91
3				3c	30	91
4				3d	15	96
5				3e	15	94
6				3f	10	89
7				3g	30	84
8				3h	30	82
9				3i	40	87
10				3j	10	92
11				5k	35	93
12				5l	35	89
13				5m	40	89
14				5n	25	87
15				5o	25	85

Table 2. Continued

16				5p	40	86
17				5q	35	80
18				5r	35	78
19				5s	45	90
20				5t	20	92

^aIsolated yields.

Table 3. Comparing the Results of γ -Fe₂O₃@HAp-Fe²⁺ NPs with Cu-np/SiO₂, Silica Sulfuric Acid, Iron(III) Sulfate-silica, and Ceric Ammonium Nitrate in the Synthesis of Benzimidazole Derivatives

Entry	Substrate	Catalyst	Condition	Yield (%)
1		Cu-np/SiO ₂	Methanol/room temperature/4 h	93
		silica sulfuric acid	Water/room temperature/2 h	71
		iron(III)sulfate-silica	solvent-free/30 °C/2 h	89
		ceric ammonium nitrate	PEG/50 °C/2 h	98
		γ -Fe ₂ O ₃ @HAp-Fe ²⁺ NPs	Ethanol/room temperature/1 h	94
2		Cu-np/SiO ₂	Methanol/room temperature/6 h	85
		silica sulfuric acid	Water/room temperature/2.5 h	78
		iron(III)sulfate-silica	solvent-free/30 °C/2h	85
		ceric ammonium nitrate	PEG/50 °C/2 h	94
		γ -Fe ₂ O ₃ @HAp-Fe ²⁺ NPs	Ethanol/room temperature/ 1.5 h	91
3		Cu-np/SiO ₂	Methanol/room temperature/1.5 h	87
		silica sulfuric acid	Water/room temperature/2 h	82
		iron(III)sulfate-silica	solvent-free/30 °C/1.5 h	87
		ceric ammonium nitrate	PEG/50 °C/1.5 h	94
		γ -Fe ₂ O ₃ @HAp-Fe ²⁺ NPs	Ethanol/room temperature/1 h	94

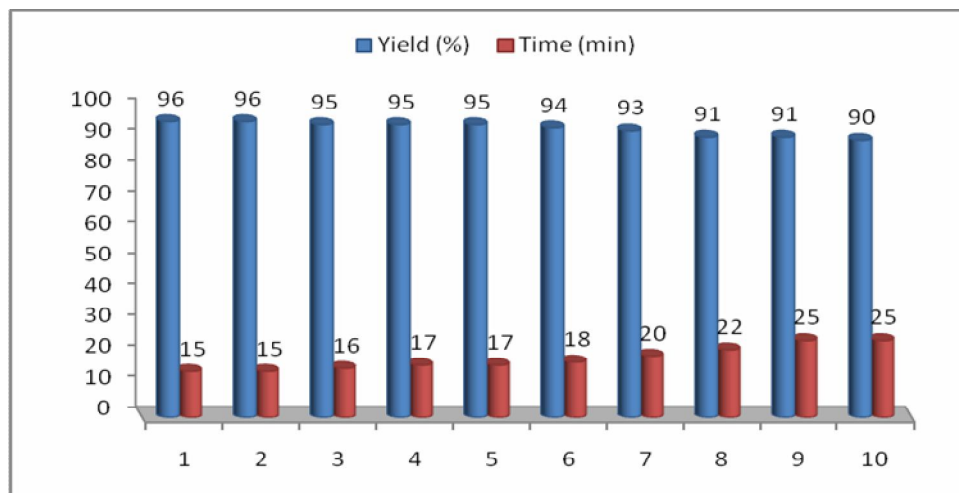


Fig. 2. Recyclability of $\gamma\text{-Fe}_2\text{O}_3\text{@HAp-Fe}^{2+}$ NPs for the 2-(4-Bromophenyl)-1H-benzo[d]imidazole.

benzimidazoles in excellent yields and short reaction time. Also the reaction between benzaldehyde (Table 2, entry 11), 2-hydroxy benzaldehyde (Table 2, entry 19), 3-methyl benzaldehyde (Table 2, entry 20) with *ortho*-aminophenol resulted in the corresponding benzoxazole in excellent yields and short reaction time. 3-bromobenzaldehyde (Table 2, entry 17) and 3-chlorobenzaldehyde (Table 2, entry 18) afforded low yields in short reaction times. Additionally, the reaction using 3-chlorobenzaldehyde and the corresponding product isolated in only 78% yield after 35 min (Table 1, entry 18). All products were identified by ^1H NMR and ^{13}C NMR spectroscopic methods and the results were confirmed by comparison with those available in the literature.

To show the merit of the present work in comparison with the reported results in the literature, we compared results of $\gamma\text{-Fe}_2\text{O}_3\text{@HAp-Fe}^{2+}$ NPs with Cu-np/SiO₂ [43], silica sulfuric acid [44], iron(III)sulfate-silica [45] and ceric ammonium nitrate [46] in the synthesis of benzimidazole derivatives (Table 3). It is thus evident that $\gamma\text{-Fe}_2\text{O}_3\text{@HAp-Fe}^{2+}$ NPs can act as an effective catalyst with respect to the reaction times and yields.

In another investigation, recyclability of $\gamma\text{-Fe}_2\text{O}_3\text{@HAp-Fe}^{2+}$ NPs was investigated. The recovery and reusability of the catalyst were studied using 4-bromo benzaldehyde (1 mmol) with *ortho*-phenyldiamine (1 mmol) in the presence of $\gamma\text{-Fe}_2\text{O}_3\text{@HAp-Fe}^{2+}$ NPs (10 mg) at room temperature as model reaction. Since the catalyst can be

separated from the reaction mixture using an external magnetic field, it was recovered with a simple magnet after dilution of the reaction mixture with water. The catalyst was consecutively reused ten times without any noticeable loss of its catalytic activity (Fig. 2).

CONCLUSIONS

In summary, the performance of $\gamma\text{-Fe}_2\text{O}_3\text{@HAp-Fe}^{2+}$ NPs as an environmentally friendly and recyclable green catalyst for the one-pot synthesis of benzimidazole and benzoxazole derivatives was investigated. The reactions were carried out using 10 mg of $\gamma\text{-Fe}_2\text{O}_3\text{@HAp-Fe}^{2+}$ NPs in short reaction times and affording good to excellent yields of the products in ethanol at room temperature. The catalyst was recyclable and has been reused for ten successive runs with little loss of the catalytic activities.

ACKNOWLEDGMENTS

We gratefully acknowledge funding from the National Elites Foundation of Iran for this research.

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