

## Nanomagnetic organic-inorganic hybrid (CuFe<sub>2</sub>O<sub>4</sub>@Si-Imid-PMo): an efficient green catalyst for the synthesis of 2,4,5-trisubstituted imidazoles

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### Abstract

In this research, a new magnetic nanocatalyst CuFe<sub>2</sub>O<sub>4</sub>@Si-Imid-PMo containing acidic ionic liquid based on imidazolium cation and phosphomolybdic acid anion immobilized on CuFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub> magnetic nanoparticles was prepared and characterized using FT-IR, EDX, SEM, and VSM techniques. Then, the catalytic activity of CuFe<sub>2</sub>O<sub>4</sub>@Si-Imid-PMo was evaluated in the synthesis of 2,4,5-trisubstituted imidazoles. The results showed that the catalyst had high activity and the desired products were obtained in high yields within short reaction times. The best result was obtained at 120 °C in the presence of 0.02 g of the catalyst under solvent-free conditions. The catalyst was also readily recovered by an external magnet and could be used for several times without substantial reduction in its catalytic activity.

**Keywords:** CuFe<sub>2</sub>O<sub>4</sub>@Si-Imid-PMo; immobilized ionic liquid; magnetic nanoparticles; magnetically separable; 2,4,5-trisubstituted imidazoles.

### Introduction

Separation and recycling of catalyst are essential steps in catalytic technology and frequently affect the overall process economy. Although the homogeneous catalysts are remarkably efficient, they share a common drawback: separation and reuse of the catalyst are extremely difficult. For these reasons, developing efficient heterogeneous catalysts is quite necessary and immobilization of homogeneous catalysts has therefore attracted a lot of attention. A possible method is immobilizing catalytically homogeneous species onto the surface

of core/shell materials with magnetic cores, which can be easily separated from the reaction medium by using an external permanent magnet and provides simple separation of the catalyst without the need to filtration, centrifugation or other tedious workup processes which is in line the principles of green chemistry [1]. In particular, besides the easy separation, the surface of magnetic nanoparticles (MNPs) could be modified by organic or inorganic materials, such as functionalized silica, polymers, biomolecules, metals, etc. and have been used in a wide range of catalytic

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reactions including C-C couplings [2], reductions [3], oxidations [4], and multicomponent reactions [5] with high level of activity.

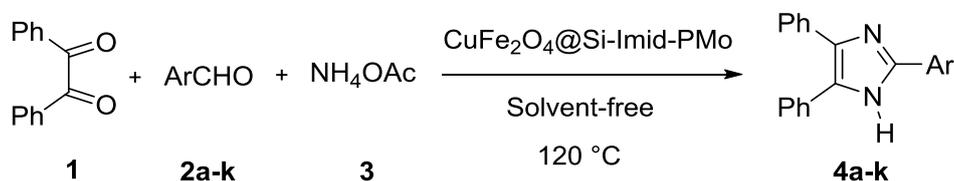
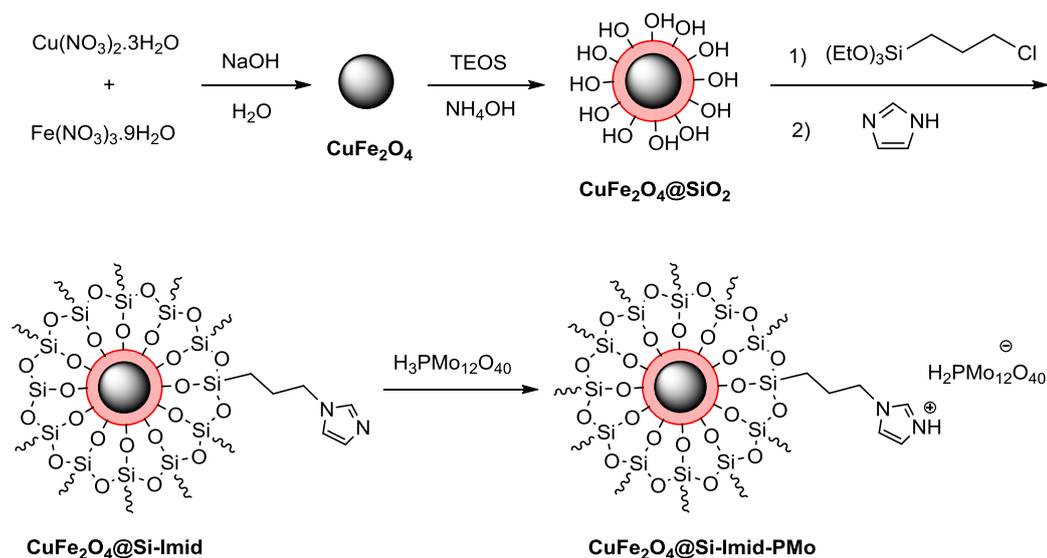
Heteropoly acids (HPAs) with strong acidity and redox properties, have been widely used in organic reactions as acid and oxidation catalysts [6]. However, the catalytic activity of bulk HPAs, can be improved by their immobilization on a large surface area support. In this regard, a few reports, firstly by Luo and co-workers [7], have recently appeared in the literature for immobilization of phosphotungstic acid with a Keggin structure, on MNPs materials [8]. The immobilized catalysts performed well and demonstrated a high level of catalytic activity in some organic reactions.

The imidazole ring system is an important nitrogen-containing substructure that plays an important role in numerous biochemical processes, and this system can be found in a large number of natural products and pharmacologically active compounds [9]. Several substituted imidazoles have been also reported as inhibitors of p38 MAP kinase [10] and B-Raf kinase [11]. Despite the availability of a wide variety of synthetic routes for the construction of imidazoles, very few methods exist for the synthesis of 2,4,5-trisubstituted imidazoles.

2,4,5-Trisubstituted imidazoles are generally synthesized *via* a one-pot three-component cyclocondensation of a 1,2-diketone with an aromatic aldehyde and ammonium acetate in the presence of several catalysts such as Wells-Dawson heteropolyacid supported on silica (WD/SiO<sub>2</sub>) [12], InCl<sub>3</sub>.3H<sub>2</sub>O [13], Al-

MCM-41 [14], BiFeO<sub>3</sub>/CuWO<sub>4</sub> [15], zirconium modified silica gel [16], KH<sub>2</sub>PO<sub>4</sub> [17], KAl(SO<sub>4</sub>)<sub>2</sub> [18], *p*-dodecylbenzenesulfonic acid (*p*-DBSA) [19], Yb(OTf)<sub>3</sub> [20], L-proline [21], ionic liquid [22], magnetic titanium dioxide nanoparticles [23], 2,6-dimethylpyridinium trinitromethanide [24], and [TBA]<sub>2</sub>[W<sub>6</sub>O<sub>19</sub>] [25]. Methods utilizing microwave irradiation in the presence of Al<sub>2</sub>O<sub>3</sub> [26] or ultrasonic irradiation using zinc (II) [tetra (4-methylphenyl)] porphyrin ([ZnT(4-CH<sub>3</sub>)PP]) [27] as catalyst, have also been reported. However, some of these synthetic methods have been limited in terms of their application because of poor yields or their requirement for expensive catalysts, long reaction time, and tedious isolation procedures. With this in mind, there is therefore an urgent need for the development of a new environmentally friendly method using an inexpensive catalyst with high catalytic activity for the synthesis of 2,4,5-trisubstituted imidazoles.

Inspired by the above facts and due to our interest in heterocycles [28] and application of reusable catalysts in organic reactions [29] in this paper for the first time, a novel acidic ionic liquid immobilized on CuFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub> MNPs, containing imidazolium salt of PMo was prepared (Scheme 1). The catalytic activity of this new heterogeneous catalyst which was denoted as CuFe<sub>2</sub>O<sub>4</sub>@Si-Imid-PMo was also investigated in one-pot synthesis of 2,4,5-trisubstituted imidazoles by reaction of benzil, an aromatic aldehyde, and ammonium acetate (Scheme 2).



## Materials and characterization

### Experimental

All chemicals were available commercially and used without additional purification. Melting points were recorded on a Stuart SMP3 melting point apparatus. The Fourier transform infrared (FT-IR) spectra were obtained using a Tensor 27 Bruker spectrophotometer as KBr disks. Ultrasonication was performed using a Soltec sonicator at a frequency of 40 kHz and a nominal power of 260 W. The scanning electron microscopy (SEM) analysis was done using a MIRA3 TESCAN scanning electron microscope operated at 30 kV accelerating voltage. The energy-dispersive X-ray (EDX) analysis was performed using a SAMX model

instrument. Magnetization curve was obtained by a MDKFT vibrating sample magnetometer (VSM).

### Preparation of $\text{CuFe}_2\text{O}_4$ MNPs

$\text{CuFe}_2\text{O}_4$  MNPs were prepared by coprecipitation method according to the literature procedure [30]. Briefly, to a solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.60 g, 2.5 mmol) and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (2.02 g, 5 mmol) in distilled water (10 mL), aqueous NaOH (4M, 7.5 mL, 30 mmol) was added at room temperature over a period of 10 min. The reaction mixture containing reddish-black precipitate was warmed to 90 °C and stirred for 2 h and then cooled to room temperature. Magnetic particles were collected by a magnet, washed several times with water, dried in air oven overnight at 80 °C, and finally ground with a pestle and

mortar and kept in a furnace at 800 °C for 5 h at a heating rate of 20 °C min<sup>-1</sup>. After slowly cooling to room temperature CuFe<sub>2</sub>O<sub>4</sub> MNPs were formed.

**Preparation of CuFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub> MNPs**  
Sol-gel method was used for preparation of CuFe<sub>2</sub>O<sub>4</sub>/SiO<sub>2</sub> MNPs according to the literature procedure.[31] A mixture of 25% aqueous ammonia (10 mL) and the CuFe<sub>2</sub>O<sub>4</sub> MNPs (2.0 g, 8.5 mmol), that had been ultrasonically dispersed in ethanol (25 mL) for 2 h at 60 °C, was stirred at 60 °C for 40 min. TEOS (1.0 mL) was then added (as the silica source) to the mixture and stirring was continued at the same temperature for 24 h. The suspended silica-coated MNPs were collected by a permanent magnet, washed three times with methanol and dried in vacuum at 50 °C for 48 h. After calcinating at 800 °C for 4 h, the CuFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub> MNPs were ready to use in the next step.

#### **Preparation of CuFe<sub>2</sub>O<sub>4</sub>@Si-Imid MNPs**

A mixture of CuFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub> (2.0 g), dispersed ultrasonically, and (3-chloropropyl)triethoxysilane (2.0 mL) in dry toluene (10 mL) (similar to the method reported by Soni et al. [32]) was stirred at room temperature for 15 min and then refluxed for 24 h. After this time, the reaction mixture was cooled to room temperature and the solid was isolated by a magnet and repeatedly washed with toluene and dried under vacuum at 80 °C for 7 h to form CuFe<sub>2</sub>O<sub>4</sub>@Si-Cl MNPs. The later MNPs were ultrasonically dispersed in dry toluene (7 mL) for 20 min at 60 °C and then imidazole (15 mmol) was added and the mixture was heated under reflux for 14 h. After cooling to room temperature, the new MNPs were collected and repeatedly washed with

toluene and diethyl ether and dried under vacuum at 70 °C for 3 h to form CuFe<sub>2</sub>O<sub>4</sub>@Si-Imid MNPs.

#### **Preparation of CuFe<sub>2</sub>O<sub>4</sub>@Si-Imid-PMo MNPs**

The CuFe<sub>2</sub>O<sub>4</sub>@Si-Imid MNPs (1.0 g) were sonicated in dry toluene (5 mL) for 15 min at 60 °C and then 1,4-butane sultone (10 mmol) was added dropwise during 20 min and the mixture was refluxed for 6 h. After cooling to room temperature, the solid was collected using a permanent magnet and repeatedly washed with dry toluene and dried under vacuum at 70 °C for 2 h to form functionalized CuFe<sub>2</sub>O<sub>4</sub>@Si-Imid sultone MNPs. These MNPs (1.0 g) were then ultrasonically dispersed in dry THF (5 mL) for 15 min at 60 °C and PMo (3 mmol) was added and sonication continued for another 1 h. The resulting MNPs were isolated by magnetic decantation and washed with dry THF and dried under vacuum at 60 °C for 12 h to form CuFe<sub>2</sub>O<sub>4</sub>@Si-Imid-PMo MNPs.

#### **General procedure for the synthesis of 2,4,5-trisubstituted imidazoles 4a-k**

A mixture of benzil **1** (1 mmol), an aromatic aldehyde **2a-k** (1 mmol), ammonium acetate **3** (2 mmol), and CuFe<sub>2</sub>O<sub>4</sub>@Si-Imid-PMo MNPs (0.02 g) was heated in an oil bath at 120 °C for 10-15 min. After completion of the reaction, monitored by TLC, the mixture was cooled to room temperature and hot ethanol was added. The catalyst was recycled by magnetic decantation and washed with dry THF and dried under vacuum at 60 °C for 2 h. The combined filtrates were concentrated and allowed to stand at room temperature until precipitation occurred. The precipitate was recrystallized from ethanol to give compounds **4a-k** in high yields. All the

products were known and characterized by comparison of their melting points with those of authentic samples and for some cases using  $^1\text{H}$  NMR and IR spectral data.

#### Selected $^1\text{H}$ NMR data

##### **2,4,5-Triphenyl-1H-imidazole (4a).**

$^1\text{H}$  NMR (300 MHz,  $\text{d}_6\text{-DMSO}$ , ppm):  $\delta$  7.20-7.60 (m, 13H,  $\text{H}_{\text{Ar}}$ ), 8.10 (d, 2H,  $J = 7.5$  Hz,  $\text{H}_{\text{Ar}}$ ), 12.71 (s, 1H, NH).

**2-(2-Chlorophenyl)-4,5-diphenyl-1H-imidazole (4b).**  $^1\text{H}$  NMR (300 MHz,  $\text{d}_6\text{-DMSO}$ , ppm):  $\delta$  7.20-7.65 (m, 13H,  $\text{H}_{\text{Ar}}$ ), 7.78-7.85 (m, 1H,  $\text{H}_{\text{Ar}}$ ), 12.65 (s, 1H, NH).

**2-(4-Methylphenyl)-4,5-diphenyl-1H-imidazole (4c).**  $^1\text{H}$  NMR (300 MHz,  $\text{d}_6\text{-DMSO}$ , ppm):  $\delta$  2.35 (s, 3H,  $\text{CH}_3$ ), 7.18-7.58 (m, 12H,  $\text{H}_{\text{Ar}}$ ), 8.11 (d, 2H,  $J = 8.1$  Hz,  $\text{H}_{\text{Ar}}$ ), 12.59 (s, 1H, NH).

**2-(4-Chlorophenyl)-4,5-diphenyl-1H-imidazole (4d).**  $^1\text{H}$  NMR (300 MHz,  $\text{d}_6\text{-DMSO}$ , ppm):  $\delta$  7.18-7.63 (m, 12H,  $\text{H}_{\text{Ar}}$ ), 8.11 (d, 2H,  $J = 7.8$  Hz,  $\text{H}_{\text{Ar}}$ ), 12.79 (s, 1H, NH).

**2-(4-Hydroxyphenyl)-4,5-diphenyl-1H-imidazole (4j).**  $^1\text{H}$  NMR (300 MHz,  $\text{d}_6\text{-DMSO}$ , ppm):  $\delta$  7.20-7.64 (m, 13H,  $\text{H}_{\text{Ar}}$ ), 8.11 (d, 2H,  $J = 7.5$  Hz,  $\text{H}_{\text{Ar}}$ ), 8.30 (s, 1H, OH), 12.82 (s, 1H, NH).

#### Results and discussions

At first,  $\text{CuFe}_2\text{O}_4$  MNPs prepared by a chemical co-precipitation method using  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  as precursors [30] were easily coated with a layer of  $\text{SiO}_2$  by sonication in a mixture of aqueous ammonia, tetraethyl orthosilicate (TEOS) and ethanol *via* sol-gel method [31] to give  $\text{CuFe}_2\text{O}_4@ \text{SiO}_2$  MNPs. These MNPs was allowed to react with (3-chloropropyl)triethoxysilane and then with an excess amount of imidazole to form  $\text{CuFe}_2\text{O}_4@ \text{Si-Imid}$  MNPs. Finally, the interaction of obtained  $\text{CuFe}_2\text{O}_4@ \text{Si-Imid}$  MNPs with

$\text{H}_3\text{PMo}_{12}\text{O}_{40}$  (PMo) to prepare the final PMo-containing IL immobilized on  $\text{CuFe}_2\text{O}_4@ \text{SiO}_2$  MNPs which is denoted as  $\text{CuFe}_2\text{O}_4@ \text{Si-Imid-PMo}$  (Scheme 1) and characterized using different techniques including Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), and vibrating sample magnetometry (VSM).

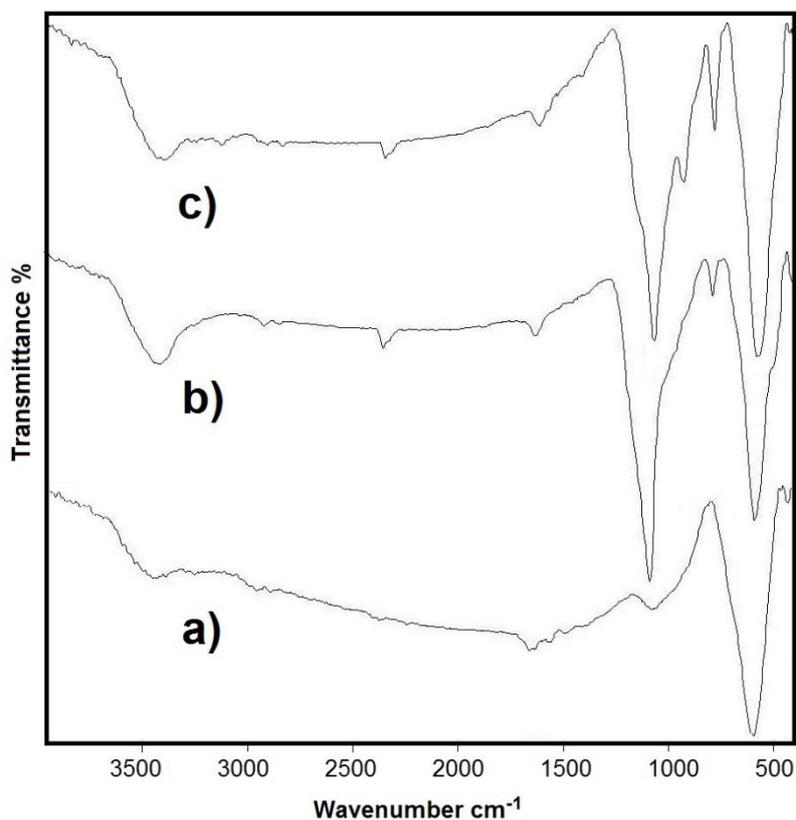
The FT-IR spectra of  $\text{CuFe}_2\text{O}_4$ ,  $\text{CuFe}_2\text{O}_4@ \text{SiO}_2$ , and  $\text{CuFe}_2\text{O}_4@ \text{Si-Imid-PMo}$  MNPs are compared in Figure 1. A strong band at around 579-594  $\text{cm}^{-1}$  appeared in all the MNPs (a, b, and c) can be assigned to the stretching vibration of Fe-O bond. The additional peak at around 1065-1117  $\text{cm}^{-1}$  in MNPs having a  $\text{SiO}_2$  layer (curves b and c) is due to Si-O-Si antisymmetric stretching vibration band. In  $\text{CuFe}_2\text{O}_4@ \text{Si-Imid-PMo}$  (Figure 1(c)), the characteristic peaks at 1400-1650  $\text{cm}^{-1}$  and 2850-2930  $\text{cm}^{-1}$  attributed to imidazole and C-H stretching vibrations, respectively, confirm successful grafting of imidazole and alkyl silane groups on  $\text{CuFe}_2\text{O}_4@ \text{SiO}_2$ . Also, the appearance of characteristic peaks of PMo around 797, 943 and 1630  $\text{cm}^{-1}$  prove the formation of  $\text{CuFe}_2\text{O}_4@ \text{Si-Imid-PMo}$  MNPs.

SEM analysis was applied for the characterization of synthesized catalyst from viewpoint of morphology, structure and size analysis (Figure 2). SEM image of the final catalyst ( $\text{CuFe}_2\text{O}_4@ \text{Si-Imid-PMo}$ ) was compared with  $\text{CuFe}_2\text{O}_4$  MNPs. As shown in Figure 2(b), nanoparticles in the prepared catalyst have spherical shape with an average diameter of approximately 30 nm, indicating the nanocatalyst has a large surface area.

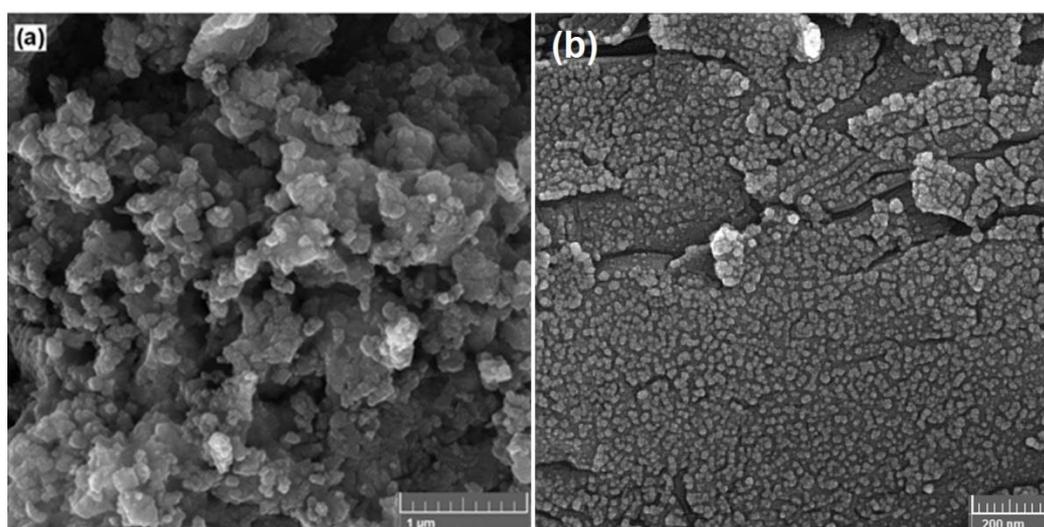
The appearance of phosphorous and molybdenum elements along with

other elements containing Cu, Fe, Si, O, N, and S in EDX spectrum of the  $\text{CuFe}_2\text{O}_4@\text{Si-Imid-PMo}$  catalyst shows the successful immobilization of PMo-containing IL on  $\text{CuFe}_2\text{O}_4@\text{SiO}_2$

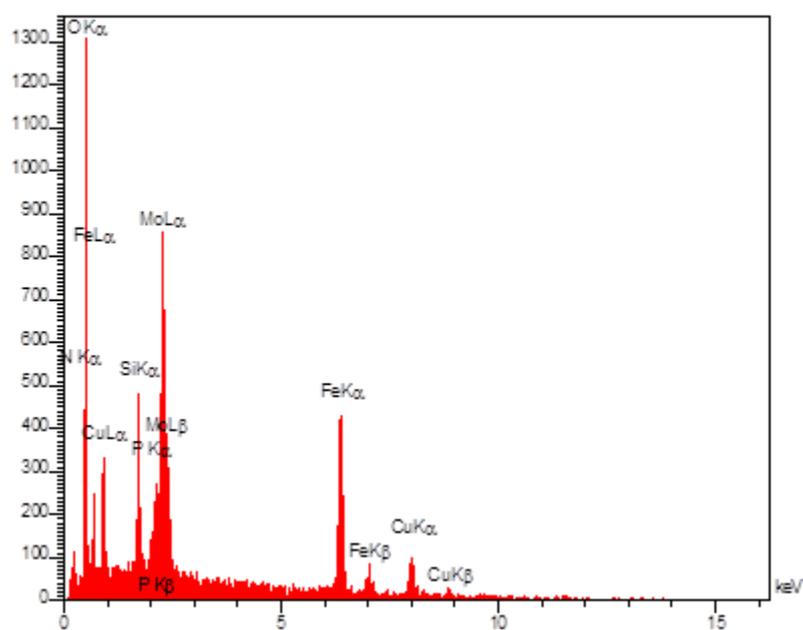
MNPs. As can be seen in Figure 3, no additional peak related to other impurities was appeared in the spectrum [33].



**Figure 1.** FT-IR spectra of (a)  $\text{CuFe}_2\text{O}_4$  MNPs, (b)  $\text{CuFe}_2\text{O}_4@\text{SiO}_2$  MNPs and (c)  $\text{CuFe}_2\text{O}_4@\text{Si-Imid-PMo}$  MNPs



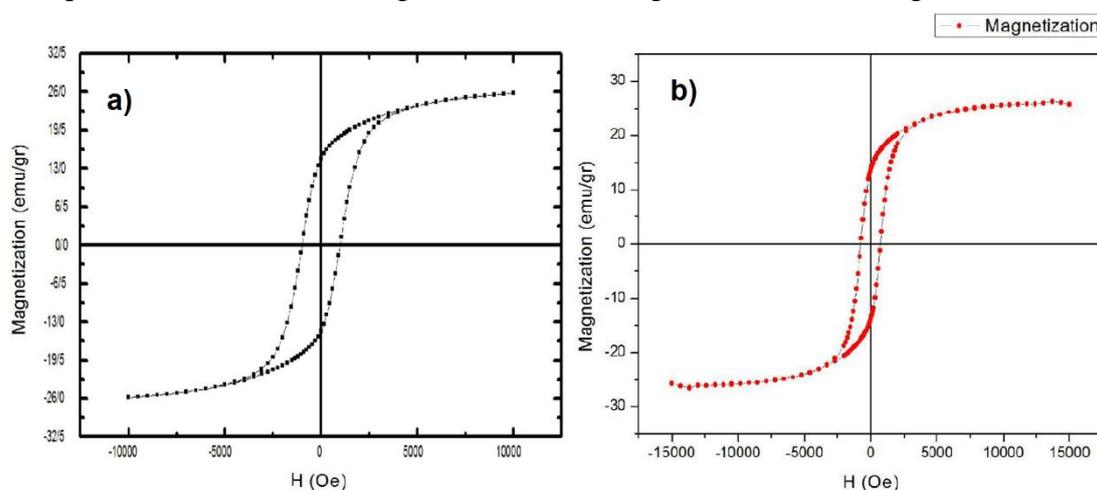
**Figure 2.** The SEM images of (a)  $\text{CuFe}_2\text{O}_4$  MNPs and (b)  $\text{CuFe}_2\text{O}_4@\text{Si-Imid-PMo}$  MNPs



**Figure 3.** EDX pattern of  $\text{CuFe}_2\text{O}_4@$ Si-Imid-PMo MNPs

The magnetic property of  $\text{CuFe}_2\text{O}_4$  and  $\text{CuFe}_2\text{O}_4@$ Si-Imid-PMo NPs was assessed using VSM at ambient temperature in an applied magnetic field, with the field sweeping from -10000 to +10000 Oersted (Oe) (Figure 4). As shown, the saturation magnetization ( $M_s$ ) of the bare  $\text{CuFe}_2\text{O}_4$  nanoparticles is 25.85 emu/g, which

decreased to 24.1 emu/g in  $\text{CuFe}_2\text{O}_4@$ Si-Imid-PMo nanoparticles. This decrease in the  $M_s$  is attributed to the contribution of the non-magnetic silica shell and immobilized IL. The particles showed high permeability magnetization, and their magnetization was sufficient for magnetic separation using a conventional magnet.



**Figure 4.** Hysteresis loops of a)  $\text{CuFe}_2\text{O}_4$  and b)  $\text{CuFe}_2\text{O}_4@$ Si-Imid-PMo MNPs

The one-pot synthesis of 2,4,5-trisubstituted imidazoles was achieved by the three-component condensation

of benzil, aromatic aldehydes, and ammonium acetate in the presence of  $\text{CuFe}_2\text{O}_4@$ Si-Imid-PMo MNPs as a heterogeneous nanocatalyst (Scheme

1). The synthesis of compound **4d** was selected as a model, to optimize the reaction conditions. Because of several advantages of performing organic reactions under solvent-free conditions such as environmental compatibility, enhanced selectivity, reduction of by-products, and much improved reaction rates, we decided to investigate the efficiency of CuFe<sub>2</sub>O<sub>4</sub>@Si-Imid-PMo MNPs under solvent-free conditions. Therefore, at first, the effect of catalyst amount and influence of temperature were studied in the model reaction under solvent-free conditions (Table 1). To substantiate the important role of the catalyst, a blank reaction was carried out in the absence of the catalyst at 120 °C. After 120 min no significant yield of **4d** was obtained, indicating importance of the catalyst in the reaction (Entry 1). According to the

optimization experiments, the best result was obtained at 120 °C in the presence of 0.02 g of catalyst (Entry 5). Next, the reaction was performed in the presence of 0.02 g of the catalyst in different temperature and solvents including H<sub>2</sub>O, EtOH, MeOH, CH<sub>3</sub>CN, and CHCl<sub>3</sub>. As shown, the product yields in refluxing CH<sub>3</sub>CN, and CHCl<sub>3</sub> were low, even after prolonged reaction time (Entries 13 and 14), whereas relatively good yields were obtained in refluxing H<sub>2</sub>O, EtOH, or MeOH (Entries 10-12). However, the best results in terms of yield, as well as reaction time, were obtained under solvent-free conditions. Therefore, all subsequent reactions were carried out using 0.02 g of the catalyst at 120 °C under solvent-free conditions.

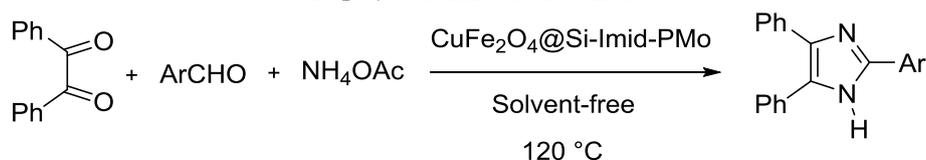
**Table 1.** Screening of reaction conditions for the formation of compound 4d catalyzed by CuFe<sub>2</sub>O<sub>4</sub>@Si-Imid-PMo MNPs<sup>a</sup>

Entry	Catalyst (g)	Solvent	T (°C)	Time (min)	Yield (%)
1	-----	solvent-free	100	140	trace
2	0.01	solvent-free	120	15	87
3	0.02	solvent-free	100	15	60
4	0.02	solvent-free	110	15	68
5	<b>0.02</b>	solvent-free	<b>120</b>	<b>10</b>	<b>97</b>
6	0.02	solvent-free	130	5	93
7	0.02	solvent-free	140	5	94
8	0.04	solvent-free	120	8	93
9	0.06	solvent-free	120	5	94
10	0.02	EtOH	Reflux	140	57
11	0.02	H <sub>2</sub> O	Reflux	120	45
12	0.02	CH <sub>3</sub> CN	Reflux	240	40
13	0.02	DMF	Reflux	120	35
14	0.02	CHCl <sub>3</sub>	Reflux	240	35

<sup>a</sup>Reaction conditions: Benzil 1 (1 mmol), and 4-chlorobenzaldehyde 2d (1 mmol), and ammonium acetate 3 (2 mmol)

Having these optimized reaction conditions in hand, the scope of reaction was extended to various aromatic aldehydes. According to the results shown in Table 2, all aromatic aldehydes with substituents carrying either electron-donating or electron

withdrawing groups or none reacted successfully and gave the products in high yields within short reaction time. The type substituent on the aromatic aldehydes had no significant effect on the reaction time and yield.

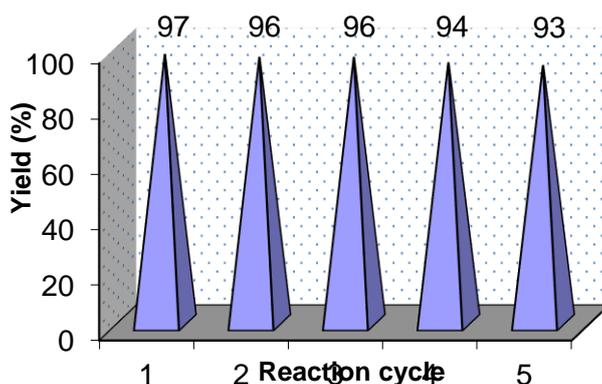
**Table 2.** Synthesis of 2,4,5-trisubstituted imidazoles 4a-k catalyzed by  $\text{CuFe}_2\text{O}_4@\text{Si-Imid-PMo}$  MNPs<sup>a</sup>

Entry	Ar	Products	Time (min)	Yields (%)	m.p. (°C)	
					Found	Reported
1	C <sub>6</sub> H <sub>5</sub>	<b>4a</b>	5	91	279-281	275-276 [25]
2	2-ClC <sub>6</sub> H <sub>4</sub>	<b>4b</b>	20	90	195-197	193-194 [25]
3	4-MeC <sub>6</sub> H <sub>4</sub>	<b>4c</b>	20	90	237-238	233-234 [25]
4	4-ClC <sub>6</sub> H <sub>4</sub>	<b>4d</b>	10	97	265-266	260-261 [25]
5	3-BrC <sub>6</sub> H <sub>4</sub>	<b>4e</b>	5	85	306-309	305-306 [25]
6	4-FC <sub>6</sub> H <sub>4</sub>	<b>4f</b>	10	92	231-233	189-190 [17]
7	3-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	<b>4g</b>	30	70	310-312	311-312 [25]
8	2-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	<b>4h</b>	25	82	221-224	220-222 [25]
9	4-MeOC <sub>6</sub> H <sub>4</sub>	<b>4i</b>	25	92	222-227	223-224 [25]
10	3-HOC <sub>6</sub> H <sub>4</sub>	<b>4j</b>	10	92	255-258	257-258 [25]
11	3-ClC <sub>6</sub> H <sub>4</sub>	<b>4k</b>	15	93	280-282	282-286 [18]

<sup>a</sup>Reaction conditions: benzil 1 (1 mmol), an aromatic aldehyde 2a-k (1 mmol), ammonium acetate 3 (2 mmol),  $\text{CuFe}_2\text{O}_4@\text{Si-Imid-PMo}$  MNPs (0.02 g), 120 °C, solvent-free

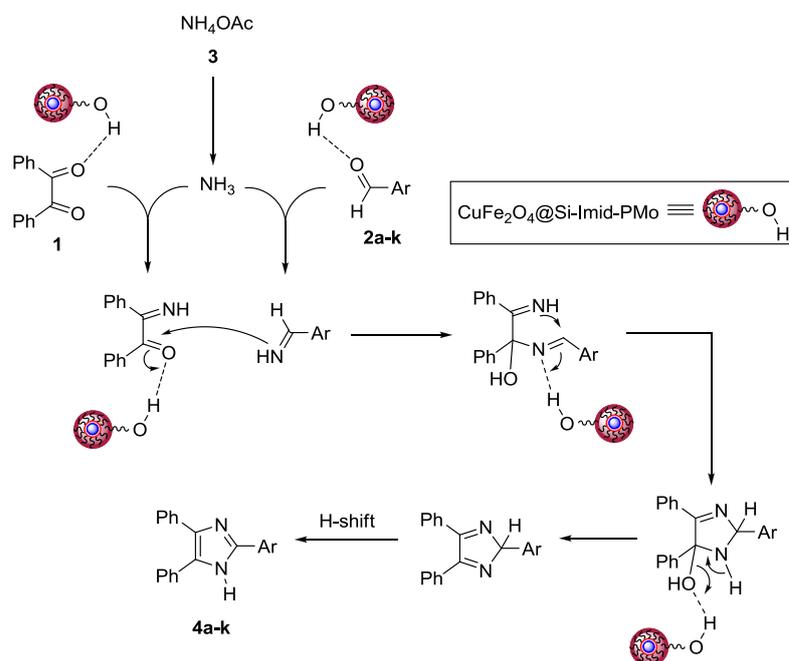
The reusability of  $\text{CuFe}_2\text{O}_4@\text{Si-Imid-PMo}$  was explored using the model reaction system under the optimized conditions. The catalyst was readily recovered from the reaction mixture using the procedure outlined in the experimental section. The separated

catalyst was washed with hot ethanol and subsequently dried at 70 °C under vacuum for 1 h before being reused in a similar reaction. The catalyst could be used at least five times without significant reduction in its activity (Figure 5).

**Figure 5.** Reusability of  $\text{CuFe}_2\text{O}_4@\text{Si-Imid-PMo}$  for the synthesis of compound **4d**

A plausible mechanism for the formation of the 2,4,5-trisubstituted imidazoles 4a-k is provided in Scheme 3. The  $\text{CuFe}_2\text{O}_4@\text{Si-Imid-PMo}$  MNPs can act as Brønsted acid centers, and therefore can promote the necessary reactions. As shown in Scheme 3, the catalyst plays a significant role in

increasing the electrophilic character of the electrophiles in the reaction and facilitates the formation of the intermediates in this reaction. Under these conditions, however, attempts to isolate the proposed intermediates failed even after careful monitoring of the reactions.



**Scheme 3.** Plausible mechanism for the formation of 2,4,5-trisubstituted imidazoles in the presence of  $\text{CuFe}_2\text{O}_4@\text{Si-Imid-PMo}$  as catalyst

### Conclusion

In conclusion, novel  $\text{CuFe}_2\text{O}_4@\text{Si-Imid-PMo}$  MNPs were successfully prepared by immobilization of PMo-containing IL on  $\text{CuFe}_2\text{O}_4@\text{SiO}_2$ , and characterized using FT-IR, SEM, EDX, and VSM techniques. The new MNPs with average diameter of 30 nm performed well as catalyst in one-pot synthesis of 2,4,5-trisubstituted imidazoles by reaction of benzil, several aromatic aldehydes, and ammonium acetate under solvent-free conditions, giving high yields of the products within short reaction times. In addition, the catalyst can be easily recovered by a magnet and reused in the next runs without significant loss of

catalytic activity. Further applications of this new catalyst for other reaction systems are currently under investigation.

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