ISSN 1070-3632, Russian Journal of General Chemistry, 2017, Vol. 87, No. 10, pp. 2436–2443. © Pleiades Publishing, Ltd., 2017.

Preparation, Characterization, and First Catalytic Application of a Novel Phosphotungstic Acid-Containing Ionic Liquid Immobilized on $CuFe_2O_4$@SiO_2 Magnetic Nanoparticles in the Synthesis of 1*H*-Pyrazolo[1,2-*b*]phthalazine-5,10-diones[1]

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Received June 24, 2017

Abstract—A novel heterogeneous acidic ionic liquid based on functionalized imidazolium salt of phosphotungstic acid ($H_3PW_{12}O_{40}$, denoted as PW), immobilized on $CuFe_2O_4$@SiO_2 magnetic nanoparticles, denoted as $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW, was prepared and characterized using FT-IR, SEM, EDX, and VSM techniques. High activity of the prepared material as a novel catalyst was evaluated in one-pot synthesis of 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones by reaction of phthalhydrazide with an aromatic aldehyde and malononitrile under solvent-free conditions. The process gave high yields of the products over short reaction time. The catalyst was efficiently recovered by magnetic decantation and used repeatedly without significant loss of its activity.

Keywords: $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW, immobilized ionic liquid, magnetic nanoparticles, magnetically separable, pyrazolo[1,2-*b*]phthalazines

DOI: 10.1134/S1070363217100267

INTRODUCTION

Several disadvantages of conventional homogeneous acids such as $AlCl_3$, $FeCl_3$, HF, and H_2SO_4, including toxicity, volatility, corrosion, and difficulties in separation, make those incompatible with environment. Over the recent decade, acidic ionic liquids (ILs), especially those based on imidazolium cation, have attracted much attention as green catalysts that could substitute conventional acids [1–3]. They possess a number of unique physicochemical properties such as extremely low vapor pressure, high thermal stability and low toxicity. Several organic reactions have been reported to proceed in acidic ILs with high selectivity and yields [4–8]. However, danger of catalyst leaching and difficulty of extracting polar products from ILs were still big challenges to overcome.

Immobilization of liquid catalysts on a solid support such as magnetic nanoparticles (MNPs) is a possible route for developing novel heterogeneous catalysts with easier recovery and reusability than those of homogeneous systems. In this regard, there are several reports on immobilizing ILs using MNPs supports [9–12]. The main advantage of MNPs supported catalysts is that they can be isolated efficiently from the reaction medium by a simple magnetic decantation that eliminates a catalyst filtration and/or centrifugation. A number of applications in biomolecular sensors [13], drug and gene delivery [14, 15], and magnetic resonance imaging (MRI) [16] have been also reported for MNPs.

Polyoxometalates (POMs) with strong acidity and redox properties have been widely used in organic reactions as acidic and oxidation catalysts [17, 18]. Catalytic activity of bulk POMs can be improved by their immobilization on a developed surface support. In this regard, few reports, firstly by Luo and coworkers [19], have recently presented immobilization of phosphotungstic acid ($H_3PW_{12}O_{40}$, denoted as PW in the present paper), with a Keggin structure, on MNPs materials [20–22]. The immobilized catalysts

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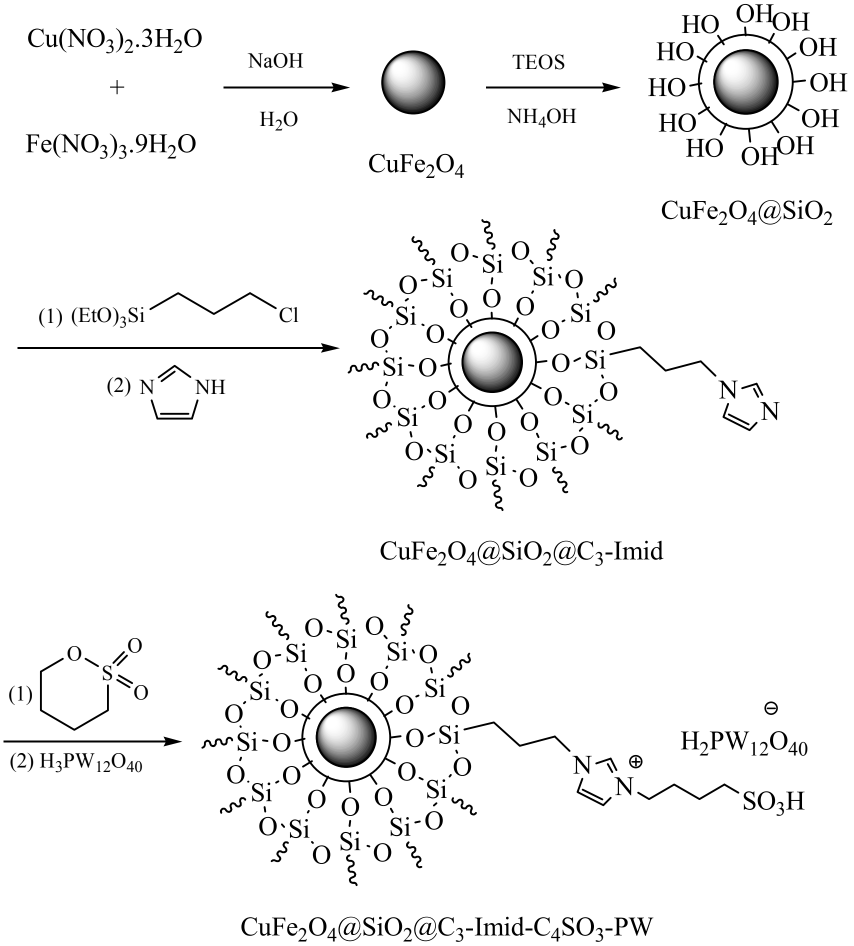
[1] The text was submitted by the authors in English.

Scheme 1.



performed well and demonstrated a high catalytic activity in some organic reactions.

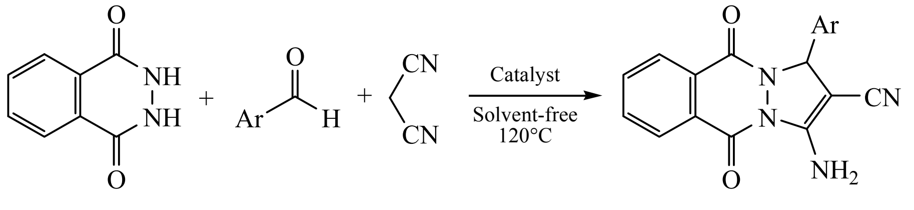
Recently, the titled compounds, 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones, containing two active pharmacophores, pyrazole and phthalazine, have attracted attention due to their important biological activities [23,24]. Such compounds are generally synthesized via a one-pot three-component reaction of phthalhydrazide with an aldehyde and malononitrile or ethyl cyanoacetate initiated by various catalysts [25–32]. Synthesis of these compounds using [bmim]OH or Et_3N under microwave or ultrasonic irradiation, respectively, have been also reported [33, 34]. Nevertheless, development of new efficient recyclable catalysts for the synthesis of 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones was of certain demand.

The presented above information, our earlier studies in heterocycles [35–37] and application of reusable catalysts in organic reactions [38–42] inspired our development of a novel acidic ionic liquid immobilized on $CuFe_2O_4$@SiO_2 magnetic nanoparticles that contained imidazolium salt of PW (Scheme 1). Catalytic activity of this new heterogeneous catalyst, denoted as $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW, was studied in one-pot synthesis of 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones by reaction of phthalhydrazide with an aromatic aldehyde and malononitrile (Scheme 2).

RESULTS AND DISCUSSION

$CuFe_2O_4$ MNPs prepared by a chemical co-precipitation method using $Cu(NO_3)_2 \cdot 3H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ as precursors [43] were easily coated with a layer of SiO_2 by sonication in a mixture of aqueous ammonia with tetraethyl orthosilicate (TEOS) and ethanol via sol-gel method [44] that led to $CuFe_2O_4$@SiO_2 MNPs. These MNPs reacted with (3-chloropropyl)triethoxysilane and then with an excess of imidazole to give $CuFe_2O_4$@SiO_2@C_3-Imid MNPs. Finally, interac-

Scheme 2.



1 **2a–2j** **3** **4a–4j**

Ar = C_6H_5 (**a**), 2-ClC_6H_4 (**b**), 3-ClC_6H_4 (**c**), 4-ClC_6H_4 (**d**), 4-FC_6H_4 (**e**), 2-$O_2NC_6H_4$ (**f**), 3-$O_2NC_6H_4$ (**g**), 4-$O_2NC_6H_4$ (**h**), 4-MeC_6H_4 (**i**), 4-$MeOC_6H_4$ (**j**).

tion of obtained $CuFe_2O_4$@SiO_2@C_3-Imid MNPs with 1,4-butane sultone followed by reaction with PW gave the final PW-containing IL immobilized on $CuFe_2O_4$@SiO_2 MNPs which is denoted as $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW (Scheme 1). The latter was characterized using FT-IR, scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), and vibrating sample magnetometry (VSM).

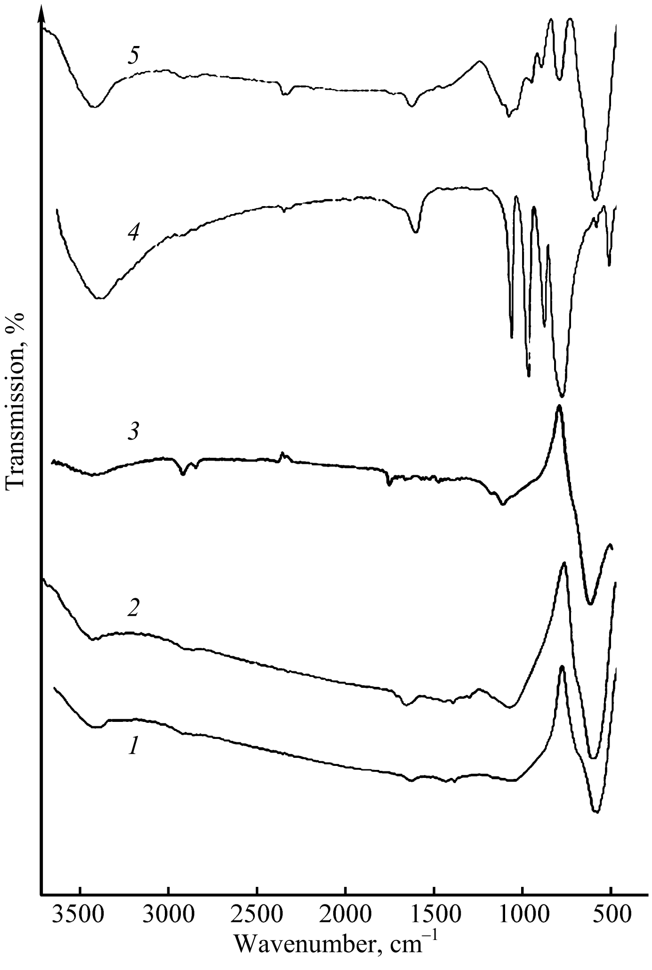


Fig. 1. FT-IR spectra of (*1*) $CuFe_2O_4$ MNPs, (*2*) $CuFe_2O_4$@SiO_2 MNPs, (*3*) $CuFe_2O_4$@SiO_2@C_3-Imid MNPs, (*4*) PW, and (*5*) $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW MNPs.

FT-IR spectra of $CuFe_2O_4$, $CuFe_2O_4$@SiO_2, $CuFe_2O_4$@SiO_2@C_3-Imid, PW and $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW MNPs are presented in Fig. 1. A strong band in the range of 579–594 cm^{-1} appeared in the spectra of all MNPs (Fig. 1, curves *1*–*3*, *5*) and was assigned to the stretching vibration of Fe–O bond. The additional peak in the range of 1065–1117 cm^{-1} recorded for MNPs having a SiO_2 layer (Fig. 1, curves *2*, *3*, and *5*) was due to Si–O–Si antisymmetric stretching vibrations. The characteristic bands at 1400–1650 cm^{-1} and 2850–2930 cm^{-1} recorded for $CuFe_2O_4$@SiO_2@C_3-Imid (Fig. 1, curve *3*) were attributed to imidazole and C–H stretching vibrations, respectively, and confirmed efficient grafting of imidazole and alkyl silane groups on $CuFe_2O_4$@SiO_2. Appearance of all characteristic peaks of PW (Fig. 1, curve *4*) and $CuFe_2O_4$@SiO_2@C_3-Imid (Fig. 1, curve *3*) as well as the SO_2 stretching vibrations (overlapped with PW and Si-O-Si in the range of 1000–1200 cm^{-1}) proved the formation of $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW MNPs (Fig. 1, curve *5*).

According to SEM image of the prepared $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW MNPs (Fig. 2), nanoparticles of the catalyst had spherical shape with an average diameter ca 30 nm and large surface area.

Appearance of P and W along with other elements in EDX spectrum of $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW catalyst demonstrated successful immobilization of PW-containing IL on $CuFe_2O_4$@SiO_2 MNPs (Fig. 3). No impurities were recorded in the spectrum.

Magnetic properties of $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW nanoparticles were assessed using VSM at ambient temperature in an applied magnetic field, with the field sweeping from –10000 to +10,000 Oe, and compared with bare $CuFe_2O_4$ (Fig. 4). The saturation magnetization (M_s) of bare $CuFe_2O_4$ nanoparticles

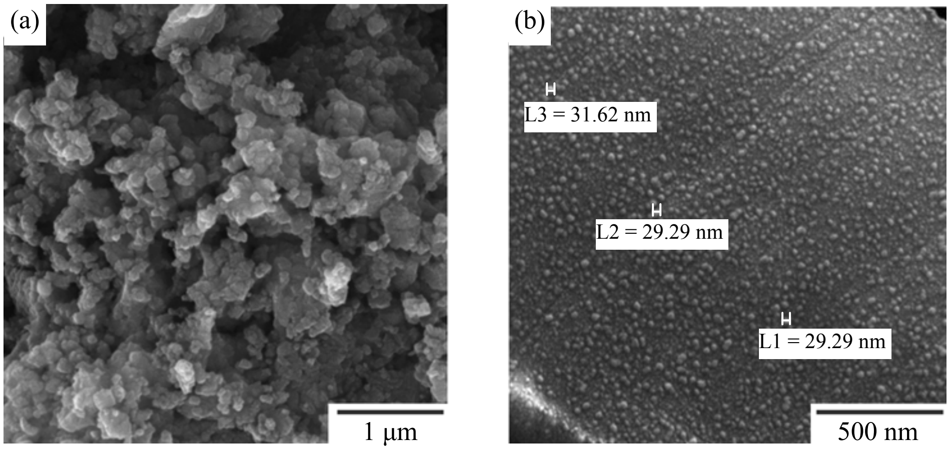


Fig. 2. SEM images of (a) $CuFe_2O_4$ MNPs and (b) $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW MNPs.

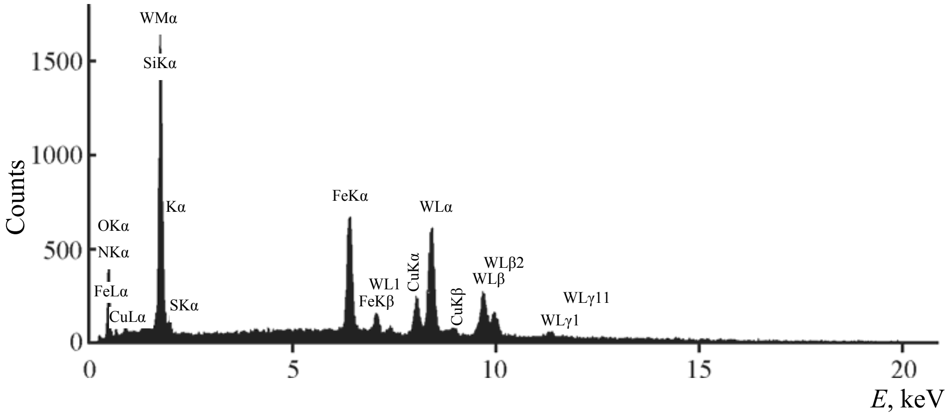


Fig. 3. EDX pattern of $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW MNPs.

(25.85 emu/g) decreased to 11.57 emu/g in $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW nanoparticles. This effect was attributed to the contribution of non-magnetic silica shell and immobilized IL. However, although the M_s value of the catalyst decreased, it still could be efficiently separated from solution with a permanent magnet. On the other hand, the hysteresis loops in both MNPs were irreversible confirming the ferromagnetic nature of those. The remanent magnetization (M_r) and the coercivity (H_c) values for $CuFe_2O_4$ and $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW were 15.30 and 6.77 emu/g, and 1008 and 699 Oe, respectively.

Performance of $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW as an acidic immobilized IL catalyst was tested in the synthesis of 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones. The reaction of phthalhydrazide (**1**) (1 mmol) with 4-chlorobenzaldehyde (**2d**) (1 mmol) and malononitrile (**3**) (1 mmol) that led to compound (**4d**) was selected as a model for optimizing the reaction conditions. Advantages of performing organic reactions under solvent-free conditions prompted us to study efficiency of $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW MNPs under solvent-free conditions with various amounts of the catalyst and different temperature. According to

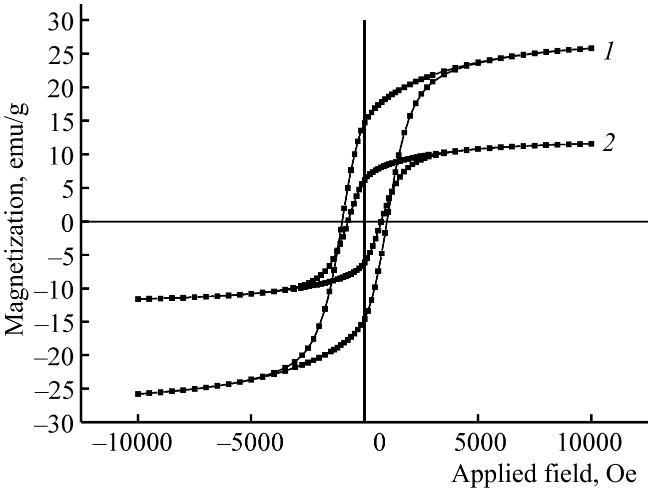


Fig. 4. Hysteresis loops of (*1*) $CuFe_2O_4$ MNPs and (*2*) $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW MNPs at room temperature.

Table 1. Screening of reaction conditions catalyzed by $CuFe_2O_4@SiO_2@C_3$-Imid-C_4SO_3-PW MNPs[a] in the synthesis of **4d**

Entry	Catalyst, g	Solvent	*T*, °C	Time, min	Isolated yield, %
1	–	–	120	120	Trace
2	0.02	–	80	60	70
3	0.02	–	100	30	82
4	0.02	–	120	30	85
5	0.04	–	80	50	75
6	0.04	–	100	25	84
7	0.04	–	120	25	91
8	0.06	–	80	30	81
9	0.06	–	100	25	89
10	0.06	–	120	10	95
11	0.08	–	120	15	94
12	0.06	–	140	15	95
13	0.06	H_2O	Reflux	90	65
14	0.06	EtOH	Reflux	150	58
15	0.06	MeOH	Reflux	120	75
16	0.06	CH_3CN	Reflux	200	35
17	0.06	$CHCl_3$	Reflux	250	20

[a] Reaction conditions: phthalhydrazide **1** (1 mmol), and 4-chlorobenzaldehyde **2d** (1 mmol), and malononitrile **3** (1 mmol).

the accumulated data (Table 1), the best result was obtained at 120°C in the presence of 0.06 g of $CuFe_2O_4@SiO_2@C_3$-Imid-C_4SO_3-PW MNPs (entry 10). A blank, no catalyst, reaction that proceeded at 120°C for 120 min did not lead to a significant yield of **4d**. The reaction performed in the presence of 0.06 g of the catalyst in different solvents (H_2O, EtOH, MeOH, CH_3CN, and $CHCl_3$) gave various yields of the product but not as high as under solvent-free conditions. Therefore, all subsequent reactions were carried out using 0.06 g of the catalyst at 120°C under solvent-free conditions.

The optimized conditions were extended to the reaction of various aromatic aldehydes (Table 2). All aromatic aldehydes with substituents carrying either electron-donating or electron withdrawing groups or none reacted efficiently and gave the products in high yields within short reaction time. Nature of a substituent on the aromatic aldehydes did not influence significantly on the reaction time and yield.

Recycling and reusing of $CuFe_2O_4@SiO_2@C_3$-Imid-C_4SO_3-PW MNPs were examined in the same model reaction under the aforementioned optimized reaction conditions. Upon completion of the first run, hot ethanol was added and the catalyst was collected with the aid of a magnet. The recycled catalyst was washed with dry THF, dried under vacuum at 60°C for 2 h and then used in the next run. The catalyst could be used at least four times with only a slight reduction in activity (respective yields 95, 94, 92, and 90%) which clearly demonstrated the practical reusability of the catalyst.

EXPERIMENTAL

All chemicals were available commercially and used without additional purification. Melting points were measured on a Stuart SMP3 melting point apparatus. FT-IR spectra were recorded for KBr discs on a Tensor 27 Bruker spectrophotometer. ^1H NMR spectra were measured on a Bruker 300 FT spectrometer in DMSO-d_6 using TMS as the internal standard. Ultrasonication was performed using a Soltec sonicator at a frequency of 40 kHz and a nominal power of 260 W. SEM analysis was carried out on a MIRA3 TESCAN

Table 2. Synthesis of 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones **4a–4j** catalyzed by $CuFe_2O_4@SiO_2@C_3$-Imid-C_4SO_3-PW MNPs[a]

Products	Ar	Time, min	Isolated yields, %	mp, ºC	
				found	calculated
4a	C_6H_5	15	89	247–249	249–251 [25]
4b	2-ClC_6H_4	10	91	256–257	256–258 [25]
4c	3-ClC_6H_4	15	88	264–266	265–267 [25]
4d	4-ClC_6H_4	10	95	265–266	269–271 [30]
4e	4-FC_6H_4	10	92	265–267	267–268 [30]
4f	2-$O_2NC_6H_4$	15	88	264–266	262–264 [27]
4g	3-$O_2NC_6H_4$	10	90	254–257	258–260 [29]
4h	4-$O_2NC_6H_4$	10	92	262–264	264–266 [20]
4i	4-MeC_6H_4	10	89	253–255	254–256 [30]
4j	4-$MeOC_6H_4$	10	89	242–243	240–242 [28]

[a] Reaction conditions: phthalhydrazide **1** (1 mmol), an aromatic aldehyde **2a–2j** (1 mmol), malononitrile **3** (1 mmol), $CuFe_2O_4@SiO_2@C_3$-Imid-C_4SO_3-PW MNPs (0.06 g), 120ºC, solvent-free.

scanning electron microscope operated at 30 kV accelerating voltage. The energy-dispersive X-ray (EDX) analysis was performed on a SAMX model instrument. Magnetization curve was obtained by a MDKFT vibrating sample magnetometer (VSM).

$CuFe_2O_4$ MNPs were prepared by co-precipitation method according to the developed earlier procedure [43]. Briefly, to a solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.60 g, 2.5 mmol) and $Fe(NO_3)_3\cdot 9H_2O$ (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 up to 90°C and stirred for 2 h and then cooled down to room temperature. Magnetic particles were collected by a magnet, washed several times with water, dried in an air oven overnight at 80°C, and finally ground with a pestle and mortar and stored in a furnace at 800°C for 5 h. Upon slow cooling down to room temperature $CuFe_2O_4$ MNPs were formed.

$CuFe_2O_4@SiO_2$ MNPs were prepared according to the sol-gel method [44]. A mixture of 25% aqueous ammonia (10 mL) and $CuFe_2O_4$ 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 following stirring at the same temperature lasted for 24 h. The suspended silica-coated MNPs were collected by a permanent magnet, washed three times with methanol and dried under vacuum at 50°C for 48 h. After calcinating at 800°C for 4 h, $CuFe_2O_4@SiO_2$ MNPs were ready to be used in the following process.

Preparation of $CuFe_2O_4@SiO_2@C_3$-Imid MNPs. A mixture of $CuFe_2O_4@SiO_2$ (2.0 g) dispersed ultrasonically with (3-chloropropyl)triethoxysilane (2.0 mL) in dry toluene (10 mL) (similar to the method reported by Soni et. al. [45]) was stirred at room temperature for 15 min and then refluxed for 24 h. The reaction mixture was cooled down 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 give $CuFe_2O_4@SiO_2@C_3Cl$ MNPs. The latter 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 refluxed for 14 h. After cooling down 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 give $CuFe_2O_4@SiO_2@C_3$-Imid MNPs.

Preparation of $CuFe_2O_4@SiO_2@C_3$-Imid-C_4SO_3-PW MNPs. $CuFe_2O_4@SiO_2@C_3$-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 in the course of 20 min and the mixture was refluxed for 6 h. After cooling down 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 give $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3 MNPs. These MNPs (1.0 g) were then ultrasonically dispersed in dry THF (5 mL) for 15 min at 60°C and PW (3 mmol) was added and following sonication continued for 1 h. The resulting MNPs were isolated by magnetic decantation, washed with dry THF and dried under vacuum at 60°C for 12 h to give $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW MNPs.

Synthesis of 1*H*-pyrazolo[1,2-b]phthalazine-5,10-diones (4a-j) catalyzed by $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW MNPs. A mixture of phthalhydrazide **1** (1 mmol) with an aromatic aldehyde **2a–2j** (1 mmol), malononitrile (**3**) (1 mmol) and $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW MNPs (0.06 g) was heated in an oil bath at 120°C for 10–15 min. Upon completion of the reaction, monitored by TLC, the mixture was cooled down to room temperature and hot ethanol was added. The catalyst was recycled by magnetic decantation, 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–4j** in high yields. All compounds were known and characterized by comparison of their melting points with those of authentic samples and in some cases using ^{1}H NMR and IR spectral data.

3-Amino-5,10-dioxo-1-phenyl-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (4a). IR spectrum, ν, cm^{-1}: 3361 and 3260 (NH_2), 2197 (CN), 1660 (C=O). ^{1}H NMR spectrum, δ, ppm: 6.14 s (1H, CH), 7.30-7.53 m (5H, H_{arom}), 7.95–8.03 m (2H, H_{arom}), 8.08–8.17 m (3H, H_{arom} and NH_2), 8.25–8.31 m (1H, H_{arom}).

3-Amino-1-(4-chlorophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (4d). IR spectrum, ν, cm^{-1}: 3376 and 3265 (NH_2), 2200 (CN), 1660 (C=O). ^{1}H NMR spectrum, δ, ppm: 6.16 s (1H, CH), 7.44 d (*J* = 8.4 Hz, 2H, H_{arom}), 7.54 d (*J* = 8.4 Hz, 2H, H_{arom}), 7.96–8.02 m (2H, H_{arom}), 8.08–8.19 m (3H, H_{arom} and NH_2), 8.25–8.30 m (1H, H_{arom}).

3-Amino-1-(4-methylphenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (4i). IR spectrum, ν, cm^{-1}: 3366 and 3265 (NH_2), 2201 (CN), 1662 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.31 s (3H, CH_3), 6.10 s (1H, CH), 7.18 d (*J* = 7.8 Hz, 2H, H_{arom}), 7.35 d (*J* = 7.8 Hz, 2H, H_{arom}), 7.95–8.01 m (2H, H_{arom}), 8.05–8.15 m (3H, H_{arom} and NH_2), 8.23–8.29 m (1H, H_{arom}).

3-Amino-1-(4-methoxyphenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (4j). IR spectrum, ν, cm^{-1}: 3372 and 3267 (NH_2), 2190 (CN), 1651 (C=O). ^{1}H NMR spectrum, δ, ppm: 3.76 s (3H, OCH_3), 6.11 s (1H, CH), 6.92 d (*J* = 8.4 Hz, 2H, H_{arom}), 7.40 d (*J* = 8.4 Hz, 2H, H_{arom}), 7.93–8.02 m (2H, H_{arom}), 8.07–8.16 m (3H, H_{arom} and NH_2), 8.23–8.29 m (1H, H_{arom}).

CONCLUSIONS

Novel $CuFe_2O_4$@SiO_2@C_3-Imid-C_4SO_3-PW ferromagnetic nanoparticles were prepared by immobilization of PW-containing IL on $CuFe_2O_4$@SiO_2 and characterized using FT-IR, SEM, EDX, and VSM techniques. The new MNPs with average diameter of 30 nm performed well as a catalyst in one-pot synthesis of 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones by reaction of phthalhydrazide with several aromatic aldehydes and malononitrile under solvent-free conditions, giving high yields of the products within short reaction times. The catalyst can be easily isolated by a magnet and reused in the next runs without significant loss of catalytic activity.

ACKNOWLEDGMENTS

The authors express their gratitude to the Islamic Azad University, Mashhad Branch for its financial support and also to Gonbad Kavous University for providing some laboratory facilities.

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