The First Pyrazolium-Based Ionic Liquid Containing Phosphotungstic Acid Immobilized on CuFe$_2$O$_4$@SiO$_2$: A Recyclable Organic-Inorganic Nanohybrid Catalyst for the Synthesis of Polyhydroquinolines

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ABSTRACT: *A new magnetically separable organic-inorganic nanohybrid catalyst denoted as CuFe$_2$O$_4$@SiO$_2$@C$_3$-Pyrazole-C$_4$SO$_3$-H$_2$PW was successfully prepared by grafting of a functionalized ionic liquid containing a pyrazolium cation with a phosphotungstic counter-anion H$_2$PW$_{12}$O$_{40}^-$ (H$_2$PW) on silica-coated copper ferrite magnetic nanoparticles (CuFe$_2$O$_4$@SiO$_2$). The prepared catalyst was fully characterized using scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray analysis, inductively coupled plasma optical emission spectrometry, Fourier transform infrared spectroscopy, and vibrating sample magnetometry. The catalytic activity of CuFe$_2$O$_4$@SiO$_2$@C$_3$-Pyrazole-C$_4$SO$_3$-H$_2$PW as a novel heterogeneous catalyst was probed in the synthesis of polyhydroquinolines by one-pot condensation of dimedone, an aromatic aldehyde, ammonium acetate, and ethyl acetoacetate. The results demonstrated a significant catalytic performance of the catalyst for this transformation under solvent-free conditions, giving high yields of the products over short reaction time. Also, the magnetic nanocatalyst could be easily recovered from the reaction mixture and reused many times with no significant loss of its catalytic activity.*

KEYWORDS: *CuFe$_2$O$_4$@SiO$_2$@C$_3$-Pyrazole-C$_4$SO$_3$-H$_2$PW; Ionic liquid; Magnetic nanoparticles; Polyhydroquinolines.*

INTRODUCTION

Although, acidic Ionic Liquids (ILs) with high thermal stability, extremely low vapor pressure and low toxicity are suitable substitute catalysts for conventional acids such as AlCl$_3$, FeCl$_3$, HF, and H$_2$SO$_4$ [1-8], the danger of catalyst leaching and the difficulties of product isolation from ILs remain. The preparing organic-inorganic hybrid catalysts by linking ILs with organic linkers to inorganic solid supports can solve these

problems [9-12]. These immobilized ILs maintain the advantages of both IL and support and thus help reduce the cost and overcome the viscosity and leaching of ILs. The choice of efficient support could significantly improve the activity, selectivity, recycling, and reproducibility of catalyst systems. For this purpose, recently, Magnetic NanoParticles (MNPs) with high thermal and mechanical stability have attracted much attention not only for their high surface area which enhances the contact between reactants and catalyst and thus increase the activity but also for their simple separation from the reaction medium by an external permanent magnet, preventing the loss of catalyst [13-17]. In this regard, a few MNPs supports immobilized ILs that have been prepared which showed good catalytic activity in some organic transformations [18-22]. These facts prompted us to prepare and investigate the catalytic behavior of a novel MNPs immobilized acidic ionic liquid.

Polyhydroquinolines are a class of fused 1,4-dihydropyridines which have received less attention than other fused 1,4-dihydropyridines and comparatively very few methods for their preparation have been reported. Polyhydroquinolines are generally synthesized by unsymmetrical Hantzsch reaction which involves the one-pot four-component condensation of dimedone, aldehydes, ammonium acetate, and ethyl acetoacetate using a catalyst [23-37]. Synthesis of these compounds using microwave irradiation [38], and solar thermal energy [39] has also been reported. Nevertheless, the development of new efficient recyclable catalysts for the synthesis of polyhydroquinolines was of a certain demand.

Heteropolyacids (HPAs) have been particularly used as a catalyst in organic transformations due to their strong acidity [40, 41]. Among the Keggin HPAs, phosphotungstic acid ($H_3PW_{12}O_{40}$, denoted as H_3PW in the present paper) has the highest acidity approaching the superacid region and exhibits stronger acidity as compared to mineral acids [42, 43]. Since the catalytic activity of a catalyst can be improved by its immobilization on a large surface area support, a few reports, firstly by Luo and co-workers [44], have recently appeared in the literature for immobilization of H_3PW, on MNPs materials [45-47]. The immobilized catalysts performed well and demonstrated a high level of catalytic activity in some organic reactions.

In this view and line with our interest in heterocycles [48-50], ILs [4-6,51,52], and catalysis [53-55], in this paper,
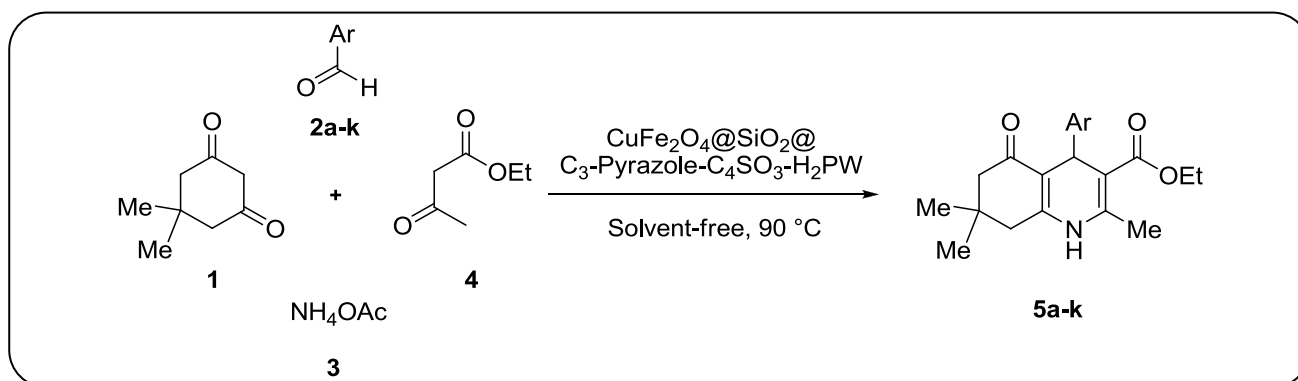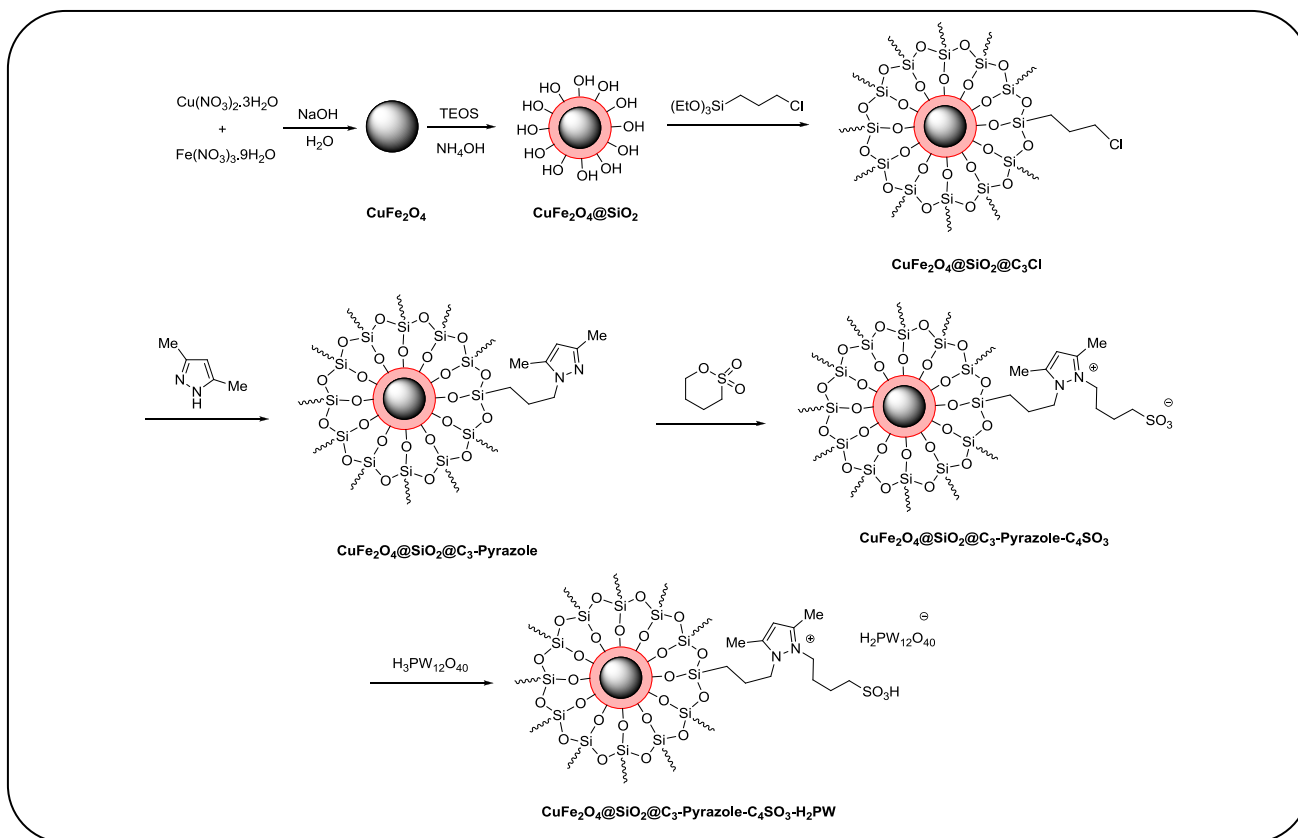
for the first time, a novel functionalized pyrazolium-based ionic liquid containing a phosphotungstic counter-anion $H_2PW_{12}O_{40}^-$ (H_2PW) immobilized on $CuFe_2O_4@SiO_2$ MNPs was prepared and fully characterized (Scheme 1). The catalytic activity of this new material which was denoted as $CuFe_2O_4@SiO_2@C_3$-Pyrazole-C_4SO_3-H_2PW was also investigated in the one-pot synthesis of polyhydroquinolines by condensation of dimedone, an aldehyde, ammonium acetate, and ethyl acetoacetate (Scheme 2).

EXPERIMENTAL SECTION

3,5-Dimethyl-1*H*-pyrazole was prepared according to the literature procedure [56]. All other chemicals were available commercially and used without additional purification. Melting points were recorded with a Stuart SMP3 melting point apparatus. The ^1H NMR (300 MHz) spectra were recorded on a Bruker 300 FT spectrometer, in DMSO-d_6 as the solvent using tetramethylsilane (TMS) as an internal standard. 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. Scanning electron microscopy (SEM) analysis was done using a MIRA3 TESCAN scanning electron microscope operated at an accelerating voltage of 30 kV. Transmission Electron Microscopy (TEM) analysis was performed using a Leo 912 AB microscope (Zeiss, Germany) with an accelerating voltage of 120 kV. Energy-Dispersive X-ray (EDX) analysis was performed using a SAMX model instrument. The amount of tungsten in the catalyst was determined using Inductively Coupled Optical Emission Spectroscopy (ICP-OES) conducted with a Spectro Arcos model spectrometer. Magnetization curves were obtained with a MDKFT Vibrating Sample Magnetometer (VSM).

Preparation of CuFe$_2$O$_4$ MNPs

$CuFe_2O_4$ MNPs were prepared by co-precipitation of $Cu(NO_3)_2$ and $Fe(NO_3)_3$ in water in the presence of sodium hydroxide according to the literature procedure [57]. Briefly, to a solution of $Fe(NO_3)_3 \cdot 9H_2O$ (2.02 g, 5 mmol) and $Cu(NO_3)_2 \cdot 3H_2O$ (0.60 g, 2.5 mmol) in distiller water (10 ml), aqueous NaOH (4M, 7.5 mL, 30 mmol) was added at room temperature over 10 min

Scheme 1: Preparation of CuFe₂O₄@SiO₂@C₃-Pyrazole-C₄SO₃-H₂PW MNPs.

Scheme 2: CuFe₂O₄@SiO₂@C₃-Pyrazole-C₄SO₃-H₂PW MNPs catalyzed synthesis of polyhydroquinolines.

to form a reddish-black precipitate. Then, the reaction mixture was warmed to 90 °C and stirred for 2 h. After cooling to room temperature, magnetic particles were collected by a magnetic separator, washed several times with water and kept in air oven overnight at 80 °C. The resulting particles were finely 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), and then slowly cooled to room temperature to form CuFe₂O₄ MNPs.

Preparation of CuFe₂O₄@SiO₂ MNPs

CuFe₂O₄@SiO₂ MNPs were prepared by the sol-gel method according to the literature procedure [58]. The nano CuFe₂O₄ (2.0 g, 8.5 mmol) was ultrasonically dispersed in ethanol (25 mL) for 2 h at 60 °C and then a 25% aqueous ammonia (10 mL) was added to the mixture and stirred at 60 °C for 40 min. Then tetraethyl orthosilicate (TEOS) (1.0 mL) was 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 a vacuum at 50 °C for 48 h. The resulting $CuFe_2O_4@SiO_2$ MNPs were then calcinated at 800 °C for 4 h.

Preparation of $CuFe_2O_4@SiO_2@C_3$-Pyrazole MNPs

Similar to the method reported by *Soni et al.* [59], firstly, $CuFe_2O_4@SiO_2$ MNPs (2.0 g) were ultrasonically dispersed in dry toluene (5 mL) and then (3-chloropropyl) triethoxysilane (2.0 mL) was added. The mixture was stirred at room temperature for 15 min and then refluxed for 24 h. After cooling to room temperature, the obtained solid was isolated using an external permanent magnet and repeatedly washed with toluene and dried under vacuum at 80 °C for 8 h to form $CuFe_2O_4@SiO_2@C_3Cl$ MNPs. These MNPs (2.0 g) were ultrasonically dispersed in dry toluene (5 ml) for 15 min at 60 °C and then 3,5-dimethyl-1*H*-pyrazole (8 mmol) was added and the mixture was heated under reflux for 24 h. After cooling to room temperature, the new MNPs were collected and repeatedly washed with toluene and dried under vacuum at 80 °C for 5 h to form $CuFe_2O_4@SiO_2@C_3$-Pyrazole MNPs.

Preparation of $CuFe_2O_4@SiO_2@C_3$-Pyrazole-C_4SO_3-H_2PW MNPs

The $CuFe_2O_4@SiO_2@C_3$-Pyrazole MNPs (2.0 g) were sonicated in dry toluene (7 mL) for 20 min at 60 °C and then 1,4-butane sultone (12 mmol) was added dropwise for 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 3 h to form $CuFe_2O_4@SiO_2@C_3$-Pyrazole-C_4SO_3 MNPs. These MNPs (2.0 g) were then ultrasonically dispersed in dry THF (8 mL) for 20 min at 60 °C and $H_3PW_{12}O_{40}$ (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 24 h to form $CuFe_2O_4@SiO_2@C_3$-Pyrazole-C_4SO_3-H_2PW MNPs.

General procedure for the synthesis of polyhydroquinolines 5a-k catalyzed by $CuFe_2O_4@SiO_2@C_3$-Pyrazole-C_4SO_3-H_2PW MNPs

A mixture of dimedone **1** (1.0 mmol), an aromatic aldehyde **2a-k** (1.0 mmol), ammonium acetate **3** (1.0 mmol),

ethyl acetoacetate **4** (1.0 mmol), and $CuFe_2O_4@SiO_2@C_3$-Pyrazole-C_4SO_3-H_2PW MNPs (0.02 g) was heated in an oil bath at 90 °C for a few minutes. The reaction was monitored by TLC. Upon completion of the transformation, the reaction mixture was cooled to room temperature and hot ethanol was added. The catalyst was recycled by magnetic decantation and washed with ethanol and dried under vacuum at 60 °C for 1 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 **5a-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}H NMR and IR spectral data. The spectral data of the products have also been reported in references [27, 29, 31 and 34].

Selected ^{1}H NMR and FT-IR data
*Ethyl 4-(2-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate **5b** (Table 2, entry 2).*

^{1}H NMR (ppm): δ 0.84 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 1.07 (t, J = 7.2 Hz, 3H, CH_3), 1.91 (d, J = 15.9 Hz, 1H, one proton of diastereotopic protons in CH_2), 2.14 (d, J = 15.9 Hz, 1H, one proton of diastereotopic protons in CH_2), 2.25 (s, 3H, CH_3 overlapped with one proton of diastereotopic protons in CH_2), 2.27 (d, J = 16.8 Hz, 1H, one proton of diastereotopic protons in CH_2 overlapped with CH_3), 2.42 (d, J = 16.8 Hz, 1H, one proton of diastereotopic protons in CH_2), 3.85-4.00 (m, 2H, diastereotopic protons in OCH_2), 5.20 (s, 1H, CH), 7.05 (td, J = 7.5, 1.5 Hz, 1H, H_{arom}), 7.14 (td, J = 7.5, 1.2 Hz, 1H, H_{arom}), 7.21 (dd, J = 7.8, 1.2 Hz, 1H, H_{arom}), 7.29 (dd, J = 7.8, 1.5 Hz, 1H, H_{arom}), 9.08 (s br., 1H, NH); FT-IR (cm^{-1}): υ 3293, 3209, 3073, 2961, 1698, 1609, 1482, 1379, 1279, 1213, 1152, 1107, 1071, 1032, 755.

*Ethyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate **5d** (Table 2, entry 4)*

^{1}H NMR (ppm): δ 0.82 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.11 (t, 3H, J = 7.2 Hz, CH_3), 1.96 (d, J = 15.9 Hz, 1H, one proton of diastereotopic protons in CH_2), 2.16 (d, J = 16.2 Hz, 1H, one proton of diastereotopic protons in CH_2), 2.23-2.31 (m, 4H, a doublet for one proton of diastereotopic protons in CH_2 ovelapped with a singlet for CH_3), 2.41 (d, J = 17.1 Hz, 1H, one proton of

diastereotopic protons in CH_2), 3.96 (q, J = 7.2 Hz, 2H, OCH_2), 4.83 (s, 1H, CH), 7.14 (d, J = 8.7 Hz, 2H, H_{arom}), 7.26 (d, J = 8.7 Hz, 2H, H_{arom}), 9.10 (s br., 1H, NH); FT-IR (cm^{-1}): υ 3276, 3205, 3078, 2963, 1706, 1648, 1606, 1492, 1382, 1280, 1216, 1155, 1108, 1072, 1031, 846, 755.

Ethyl 4-(3-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate 5e (Table 2, entry 5)

^{1}H NMR (ppm): δ 0.85 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 1.12 (t, 3H, J = 7.2 Hz, CH_3), 1.99 (d, J = 16.2 Hz, 1H, one proton of diastereotopic protons in CH_2), 2.17 (d, J = 16.2 Hz, 1H, one proton of diastereotopic protons in CH_2), 2.30 (s, 3H, CH_3 overlapped with one proton of diastereotopic protons in CH_2), 2.31 (d, J = 16.8 Hz, 1H, one proton of diastereotopic protons in CH_2 overlapped with CH_3), 2.42 (d, J = 16.8 Hz, 1H, one proton of diastereotopic protons in CH_2), 3.90-4.10 (m, 2H, diastereotopic protons in OCH_2), 4.84 (s, 1H, CH), 7.13-7.18 (m, 2H, H_{arom}), 7.23-7.28 (m, 1H, H_{arom}), 7.31 (s, 1H, H_{arom}), 9.13 (s br., 1H, NH); FT-IR (cm^{-1}): υ 3277, 3208, 3075, 2959, 1702, 1643, 1606, 1488, 1381, 1281, 1214, 1153, 1110, 1073, 1029, 879, 771, 738.

Ethyl 4-(4-methylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate 5i (Table 2, entry 9)

^{1}H NMR (ppm): δ 0.85 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 1.13 (t, 3H, J = 7.2 Hz, CH_3), 1.96 (d, J = 16.2 Hz, 1H, one proton of diastereotopic protons in CH_2), 2.12-2.21 (m, 4H, a doublet for one proton of diastereotopic protons in CH_2 ovelapped with a singlet for CH_3), 2.27 (s, 3H, CH_3 overlapped with one proton of diastereotopic protons in CH_2), 2.28 (d, J = 16.8 Hz, 1H, one proton of diastereotopic protons in CH_2 overlapped with CH_3), 2.41 (d, J = 16.8 Hz, 1H, one proton of diastereotopic protons in CH_2), 3.96 (q, J = 7.2 Hz, 2H, OCH_2), 4.81 (s, 1H, CH), 6.97 (d, J = 7.8 Hz, 2H, H_{arom}), 7.03 (d, J = 8.1 Hz, 2H, H_{arom}), 9.01 (s br., 1H, NH); FT-IR (cm^{-1}): υ 3276, 3206, 3078, 2960, 1702, 1647, 1606, 1492, 1381, 1281, 1216, 1154, 1108, 1072, 1031, 849, 822.

Ethyl 4-(4-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate 5k (Table 2, entry 11)

^{1}H NMR (ppm): δ 0.85 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.13 (t, 3H, J = 7.2 Hz, CH_3), 1.97 (d, J = 15.9 Hz, 1H, one proton of diastereotopic protons in CH_2), 2.15 (d, J = 16.2 Hz, 1H, one proton of diastereotopic protons in CH_2), 2.26 (d, J = 16.8 Hz, 1H, one proton of diastereotopic protons in CH_2 overlapped with CH_3), 2.27 (s, 3H, CH_3 overlapped with one proton of diastereotopic protons in CH_2), 2.39 (d, J = 16.8 Hz, 1H, one proton of diastereotopic protons in CH_2), 3.92-4.02 (m, 2H, diastereotopic protons in OCH_2), 4.76 (s, 1H, CH), 6.57 (d, J = 8.7 Hz, 2H, H_{arom}), 6.95 (d, J = 8.7 Hz, 2H, H_{arom}), 8.96 (s br., 1H, NH or OH), 9.03 (s br., 1H, OH or NH); FT-IR (cm^{-1}): υ 3459, 3277, 3201, 3073, 2959, 1683, 1607, 1488, 1381, 1283, 1218, 1167, 1109, 1072, 1028, 852, 769.

RESULTS AND DISCUSSION

Preparation and characterization of catalyst

At first, $CuFe_2O_4$ MNPs were prepared by chemical co-precipitation method using $Cu(NO_3)_2 \cdot 3H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ as precursors [57]. Sonication of these MNPs in a mixture of aqueous ammonia, tetraethyl orthosilicate (TEOS) and ethanol *via* sol-gel method [58] gave $CuFe_2O_4@SiO_2$ MNPs which were allowed to react with (3-chloropropyl)triethoxysilane and then with an excessive amount of 3,5-dimethyl-1H-pyrazole to give $CuFe_2O_4@SiO_2@C_3$-Pyrazole MNPs. The excess of 3,5-dimethyl-1H-pyrazole traps the HCl released in the reaction. The reaction of later MNPs with 1,4-butane sultone followed by interaction with H_3PW gave the final novel functionalized pyrazolium-based IL containing a phosphotungstic counter-anion H_2PW immobilized on $CuFe_2O_4@SiO_2$ MNPs which is denoted as $CuFe_2O_4@SiO_2@C_3$-Pyrazole-C_4SO_3-H_2PW (Scheme 1). The final prepared MNPs were characterized using different techniques including SEM, TEM, EDX analysis, ICP-OES, FT-IR spectroscopy, and VSM.

The surface morphology of the $CuFe_2O_4@SiO_2@C_3$-Pyrazole-C_4SO_3-H_2PW nanocatalyst was characterized using SEM analysis (Fig. 1b) and compared with $CuFe_2O_4$ MNPs (Fig. 1a). The SEM images exhibit that the particles have nearly spherical (between spherical and multifaceted cuboid) shapes with slight agglomeration due to magnetic dipole interactions between particles.

Furthermore, the TEM image of the nanocatalyst shown in Fig. 2 confirms the almost spherical shape of the nanoparticles with diameters of less than 25 nm with a narrow size distribution.
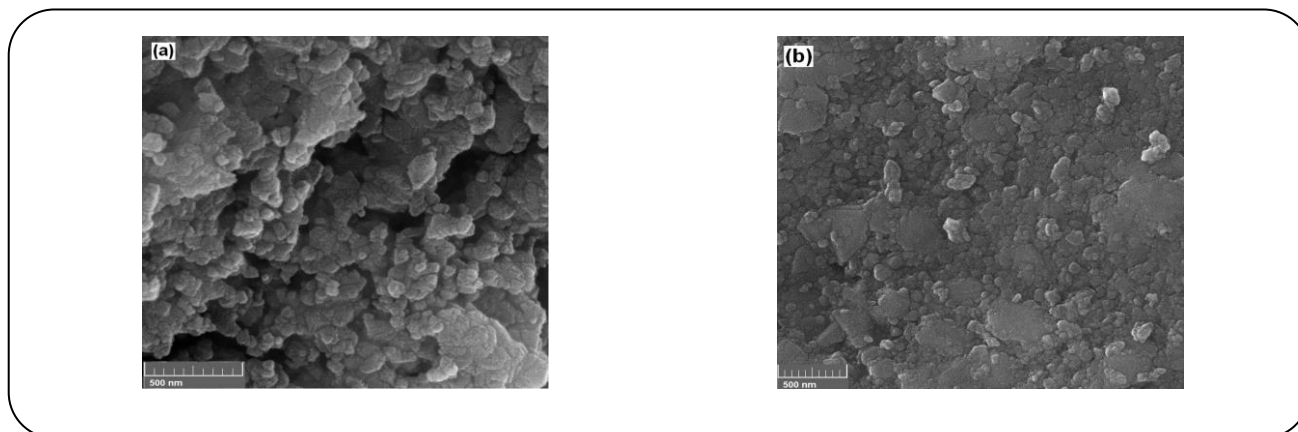
Fig. 1: The SEM images of (a) CuFe₂O₄ MNPs and (b) CuFe₂O₄@SiO₂@C₃-Pyrazole-C₄SO₃-H₂PW MNPs.
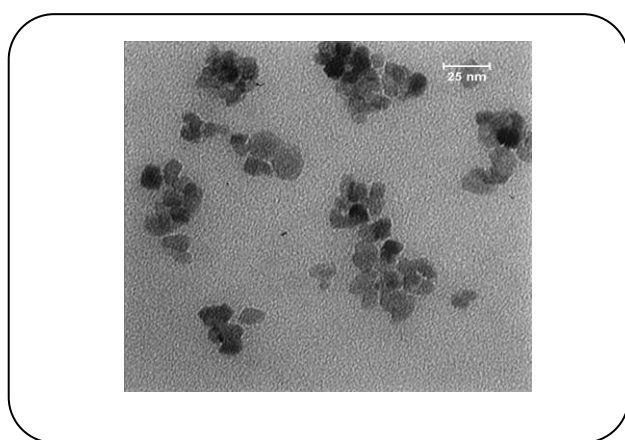
Fig. 2: The TEM image of CuFe₂O₄@SiO₂@C₃-Pyrazole-C₄SO₃-H₂PW MNPs.

The EDX spectrum depicted in Fig. 3 clearly shows the presence of copper (Cu), iron (Fe), oxygen (O), silicon (Si), nitrogen (N), and sulfur (S) elements in the catalyst with no extra peak related to other impurities confirming the successful immobilization of H_2PW-containing IL on $CuFe_2O_4@SiO_2$ MNPs.

Based on ICP-OES, the amount of W incorporated into the $CuFe_2O_4@SiO_2@C_3$-Pyrazole-C_4SO_3-H_2PW MNPs is 2.427%, which is another confirmation for immobilization of H_2PW-containing IL onto $CuFe_2O_4@SiO_2$ MNPs.

The FT-IR spectra of $CuFe_2O_4@SiO_2$, $CuFe_2O_4@SiO_2@C_3$-Pyrazole, and $CuFe_2O_4@SiO_2@C_3$-Pyrazole-C_4SO_3-H_2PW MNPs are also compared in Fig. 4. A strong band at around 582-590 cm^{-1} appeared in all the MNPs (**a**, **b**, and **c**) can be assigned to the stretching vibration of Fe-O bond. The additional characteristic peaks in Fig. 4**c** at 800-1185 cm^{-1} (overlapped SO_2, PW

and Si-O-Si stretching vibration bands), at 1400-1650 cm^{-1} as well as around 3000 cm^{-1} (attributed to the pyrazole and C-H stretching vibrations, respectively), confirm successful preparation of $CuFe_2O_4@SiO_2@C_3$-Pyrazole-C_4SO_3-H_2PW MNPs.

Finally, the magnetic property of $CuFe_2O_4@SiO_2@$ C_3-Pyrazole-C_4SO_3-H_2PW nanoparticles was studied using VSM at ambient temperature in an applied magnetic field, with the field sweeping from -10000 to +10,000 Oersted (Oe), and compared with bare $CuFe_2O_4$ (Fig. 5). It could be seen that the hysteresis loops in both MNPs are irreversible confirming the ferromagnetic nature of them. Although, due to the non-magnetic silica shell and immobilized IL, the saturation magnetization (M_s) of the $CuFe_2O_4@SiO_2@C_3$-Pyrazole-C_4SO_3-H_2PW nanoparticles has decreased from 34.12 emu/g for the bare $CuFe_2O_4$ nanoparticles to 30.37 emu/g, however, they still could be efficiently separated from the solution with a permanent magnet. While both $CuFe_2O_4$ and $CuFe_2O_4@SiO_2@C_3$-Pyrazole-C_4SO_3-H_2PW MNPs have the same remanent magnetization (M_r) of 10.49, the coercivity (H_c) values of them were found to be 240 and 421 Oe, respectively.

Catalytic application of CuFe₂O₄@SiO₂@C₃-Pyrazol-C₄SO₃-H₂PW MNPs

The performance of $CuFe_2O_4@SiO_2@C_3$-Pyrazol-C_4SO_3-H_2PW as catalyst was tested in the synthesis of polyhydroquinolines. The chosen model reaction between dimedone **1** (1 mmol), 4-chlorobenzaldehyde **2d** (1 mmol), ammonium acetate **3** (1 mmol), and ethyl acetoacetate **4** (1 mmol) was tested in various reaction conditions
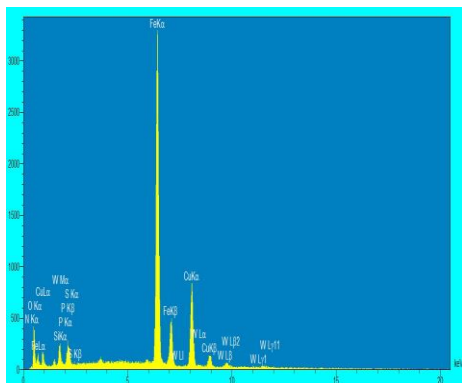
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Fig. 3: EDX analysis of CuFe₂O₄@SiO₂@C₃-Pyrazole-C₄SO₃-H₂PW MNPs.
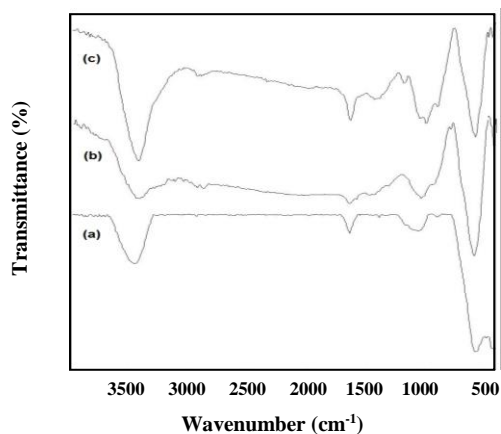
Fig. 4: FT-IR spectra of (a) CuFe₂O₄@SiO₂ MNPs, (b) CuFe₂O₄@SiO₂@C₃-Pyrazole MNPs, and (c) CuFe₂O₄@SiO₂@C₃-Pyrazole-C₄SO₃-H₂PW MNPs.
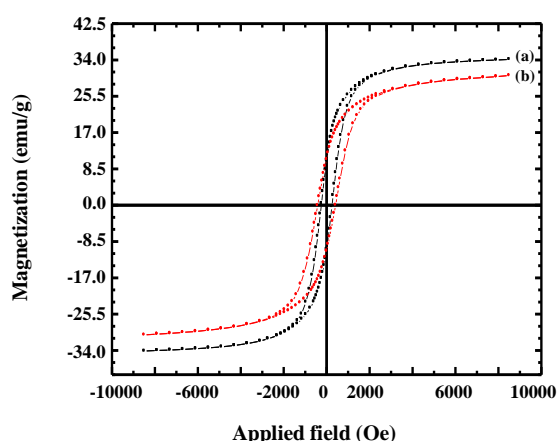
Fig. 5: Hysteresis loops of CuFe₂O₄ (black curve (a)) and CuFe₂O₄@SiO₂@C₃-Pyrazole-C₄SO₃-H₂PW MNPs (red curve (b)) at room temperature.

to investigate the optimized conditions. Because of several advantages of solvent-free conditions in chemical reactions such as simplification of work-ups, formation of cleaner products, environmental compatibility, and reduction of by-products, we firstly decided to investigate the efficiency of $CuFe_2O_4@SiO_2@C_3$-Pyrazol-C_4SO_3-H_2PW in the model reaction under solvent-free conditions in different temperatures and employing different catalyst loadings. The results are summarized in Table 1. Our investigation clarified that $CuFe_2O_4@SiO_2@C_3$-Pyrazol-C_4SO_3-H_2PW is a suitable catalyst for the synthesis of compound **5d** under solvent-free conditions. The best result was conducted at 90 °C in the presence of 20 mg of $CuFe_2O_4@SiO_2@C_3$-Pyrazol-C_4SO_3-H_2PW (entry 6). The higher amount of the catalyst and temperature slightly reduce the yield of the product (entries 9-11). To prove the necessity of the catalyst, the model reaction was also performed in the absence of the catalyst at 90 °C. No significant yield of **5d** was obtained after 120 min (entry 1), indicating the importance of the catalyst in the reaction. Subsequently, our investigation showed that the compound **5d** can be obtained in good to high yield in different solvents including H_2O, EtOH, EtOH/H_2O, MeOH, CH_3CN, $CHCl_3$, and DMF. Although there is no significant difference between the use of EtOH, MeOH, and DMF as a solvent and also solvent-free conditions, however, because of the above-mentioned advantages, solvent-free conditions were selected in all subsequent reactions.

Furthermore, to show that whether the catalytic activity of $CuFe_2O_4@SiO_2@C_3$-Pyrazol-C_4SO_3-H_2PW is due to the ionic liquid or the presence of the phosphotungstic acid, the model reaction was also tested using $CuFe_2O_4@SiO_2@C_3$-Pyrazol-C_4SO_3. As depicted (Table 1, entry 19), $CuFe_2O_4@SiO_2@C_3$-Pyrazol-C_4SO_3-H_2PW proved to be a better catalyst than $CuFe_2O_4@SiO_2@C_3$-Pyrazol-C_4SO_3 in terms of reaction time and yield. We, therefore, believe that the catalytic activity of $CuFe_2O_4@SiO_2@C_3$-Pyrazol-C_4SO_3-H_2PW is more due to the presence of phosphotungstic acid.

Having successfully optimized the experimental conditions, we next explored the scope of the reaction. Therefore, a wide range of *ortho-*, *meta-* and *para-*substituted aromatic aldehydes undergo one-pot multicomponent reaction with dimedone, ammonium

Table 1: Optimization of reaction parameters for the synthesis of compound 5d catalyzed by
$CuFe_2O_4@SiO_2@C_3$-Pyrazole-C_4SO_3-H_2PW MNPs[a].

Entry	Catalyst[b] (mg)	Solvent	T (°C)	Time (min)	Isolated Yield (%)
1	-----	-----	90	120	Trace
2	A (10)	-----	80	5	73
3	A (10)	-----	90	3	83
4	A (10)	-----	100	3	82
5	A (20)	-----	80	3	80
6	A (20)	-----	90	2	90
7	A (20)	-----	100	3	86
8	A (40)	-----	80	3	78
9	A (40)	-----	90	2	84
10	A (40)	-----	100	3	83
11	A (60)	-----	100	3	82
12	A (20)	H_2O	Reflux	3	69
13	A (20)	EtOH	Reflux	3	86
14	A (20)	$EtOH/H_2O$	Reflux	3	80
15	A (20)	MeOH	Reflux	3	86
16	A (20)	CH_3CN	Reflux	6	78
17	A (20)	$CHCl_3$	Reflux	4	80
18	A (20)	DMF	Reflux	3	87
19	B (20)	-----	90	25	54

a) Reaction conditions: dimedone 1 (1 mmol), 4-chlorobenzaldehyde 2d (1 mmol), ammonium acetate 3 (1 mmol), and ethyl acetoacetate 4 (1 mmol)
b) A = $CuFe_2O_4@SiO_2@C_3$-Pyrazole-C_4SO_3-H_2PW, B = $CuFe_2O_4@SiO_2@C_3$-Pyrazole-C_4SO_3

acetate, and ethyl acetoacetate under optimized conditions to afford polyhydroquinoline derivatives (Table 2). As shown in Table 2, all electron-rich as well as electron-poor aromatic aldehydes reacted successfully and gave the products in high yields within short reaction time. The type of substituent on the aromatic aldehydes had no significant effect on the reaction time and yield. These results indicate that the $CuFe_2O_4@SiO_2@C_3$-Pyrazol-C_4SO_3-H_2PW acts as a highly active catalyst in this methodology.

To evaluate the overall utility of the current methodology, the results were compared with those using other catalysts reported for the synthesis of polyhydroquinolines. As shown in Table 3, the current

procedure that involved nano $CuFe_2O_4@SiO_2@C_3$-Pyrazole-C_4SO_3-H_2PW as the catalyst gave high yields of the products in shorter reaction time than the other methods. Magnetic recyclability of our catalyst makes it superior over some of the other reported methods.

Because of the green chemistry, the catalyst was further explored for the reusability using the reaction of dimedone, 2-chlorobenzaldehyde, ammonium acetate, and ethyl acetoacetate for the synthesis of compound **5b** under the aforementioned optimized reaction conditions. Upon completion of the first run, hot ethanol was added and the catalyst was collected by simple magnetic decantation (Fig. 6). The recycled catalyst was washed with ethanol, dried under vacuum at 60 °C for 1 h, and

Table 2: Synthesis of polyhydroquinolines 5a-k catalyzed by CuFe₂O₄@SiO₂@C₃-Pyrazole-C₄SO₃-H₂PW MNPs.

Entry	Ar	Product	Time (min)	Isolated yield (%)	m.p. (ºC)	
					Found	Reported
1	C_6H_5	5a	5	98	216-219	220-224 [33]
2	$2-ClC_6H_4$	5b	2	96	208-210	208-210 [34]
3	$3-ClC_6H_4$	5c	1	82	229-231	231-234 [34]
4	$4-ClC_6H_4$	5d	2	90	246-248	246-250 [33]
5	$3-BrC_6H_4$	5e	2	87	229-230	235 [34]
6	$4-FC_6H_4$	5f	4	87	188-190	184-186 [37]
7	$2-O_2NC_6H_4$	5g	2	92	216-218	210-215 [34]
8	$3-O_2NC_6H_4$	5h	3	98	184-186	181-183 [27]
9	$4-MeC_6H_4$	5i	2	89	262-264	261-262 [34]
10	$4-MeOC_6H_4$	5j	4	84	259-261	257-259 [37]
11	$4-HOC_6H_4$	5k	5	92	239-240	239-241 [27]

Reaction conditions: dimedone 1 (2 mmol), an aromatic aldehyde 2a-k (1 mmol), ammonium acetate 3 (1 mmol), ethyl acetoacetate 4 (1 mmol), CuFe₂O₄@SiO₂@C₃-Pyrazole-C₄SO₃-H₂PW MNPs (20 mg), 90 ºC, solvent-free.

Table 3: Comparison of the efficiencies of different catalysts for the synthesis of polyhydroquinolines.

Catalyst	Solvent	T (ºC)	Catalyst amount* (mg)	Time (min)	Yield (%)	Ref.
$V-TiO_2$ NPs	----	80	3	10-20	65-94	[23]
$NS-[C_4(DABCO-SO_3H)_2].4Cl$	----	100	10	2-50	80-98	[24]
carbon-based solid acid	----	90	20	18-35	87-95	[25]
$BiFeO_3$ MNPs	----	110	20	10-30	70-95	[26]
$[TBA]_2[W_6O_{19}]$	----	110	110	20-40	67-95	[27]
β-Cyclodextrin–polyurethane polymer	----	80	150	10-30	84-93	[28]
1,3-Dibromo-5,5-Dimethylhydantoin	----	130	29	25-50	80-96	[29]
$SBA-Pr-SO_3H$	----	90	50	10-18	75-90	[30]
$PPA-SiO_2$	----	80	30	40-60	85-92	[31]
$[pyridine-SO_3H]Cl$	----	110	20	25-35	84-93	[32]
Nafion-H®	PEG 400-water	50	30	90-96	88-96	[33]
TiO_2 NPs	EtOH	reflux	8	105-240	50-93	[34]
$HClO_4/Zr-MCM-41$	EtOH	reflux	10	10-60	70-95	[35]
$Fe_3O_4@B-MCM-41$	EtOH	reflux	50	15-130	75-92	[36]
$CuFe_2O_4@SiO_2@C_3-Pyrazole-C_4SO_3-H_2PW$ MNPs	----	90	20	1-5	84-98	This work

The Catalyst amount is for 1 mmol of dimedone

Fig. 2: The reaction mixture in the synthesis of 5b after adding hot ethanol in the presence of a magnetic field.

then used in the next run. The catalyst could be used at least four times with only a slight reduction in activity (96, 94, 92, and 89 % yields for first to fourth use, respectively) which demonstrates the practical reusability of this catalyst.

CONCLUSIONS

A novel magnetically retrievable heterogeneous organic-inorganic nanocatalyst, denoted as $CuFe_2O_4@SiO_2@C_3$-Pyrazol-C_4SO_3-H_2PW, was successfully prepared by immobilization of H_2PW-containing functionalized pyrazolium-based IL on $CuFe_2O_4@SiO_2$ MNPs, and characterized using SEM, TEM, EDX analysis, FT-IR spectroscopy, and VSM. The average diameter of the newly prepared spherical shape ferromagnetic nanoparticles is found to be approximately less than 25 nm. The catalytic activity of the new MNPs as catalyst was also evaluated in the synthesis of polyhydroquinolines by the one-pot reaction of dimedone, an aromatic aldehyde, ammonium acetate, and ethyl acetoacetate. The results showed a significant catalytic performance of the catalyst for this transformation under solvent-free conditions, giving high yields of the products over short reaction time. Also, the catalyst is readily recovered by simple magnetic decantation and can be reused for subsequent reactions with no significant loss of its activity. Further applications of this new catalyst for other reactions, systems are currently under investigation.

Acknowledgment

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