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Preparation of a novel, efficient, and recyclable magnetic catalyst, Cu(II)-OHPC-Fe₃O₄ nanoparticles, and a solvent-free protocol for the synthesis of coumarin derivatives

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ABSTRACT

Cu(II) supported on 5-oxo-4,5-dihydro-pyrrole-3-carboxylic acid functionalized Fe₃O₄ nanoparticles (Cu(II)-OHPC-Fe₃O₄) as a new magnetic nanocatalyst was prepared and characterized by ICP-AES, FT-IR, XRD, SEM, TEM, TGA, XRD, VSM and EDX techniques. Prepared nanocatalyst (Cu(II)-OHPC-Fe₃O₄) is employed for Pechmann reactions between different substituted phenols and ethyl acetoacetate to obtain new products of coumarin derivatives in good to excellent yields. This green catalyst was easily removed, reused several times with no significant loss of its activity and provided clean synthesis with excellent yield and reduced time.

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Pechmann reactions; nanocatalyst; coumarin; nanomagnetic; Cu; 5-Oxo-4,5-dihydro-pyrrole-3-carboxylic acid



1. Introduction

Design of efficient, economical, useful, separable and biocompatible catalysts have attracted attention [1]. In fact, with expanding environmental and biological concerns, the development of reusable and recoverable heterogeneous catalysts developed a considerable research field. Nanomaterials specialty nanoparticles as heterogeneous catalysts with attractive structures and unique catalytic activities have been employed [2]. Also, nanoparticles could have higher catalyst loading capacity and higher dispersion than many common support matrices, resulting in enhanced catalytic activity of the supported catalysts [3].

Magnetic nanoparticles (MNPs) are potent, valuable and highly-efficient heterogeneous catalyst supports because of their response to a magnetic field, giving good

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Scheme 1. Pechmann reactions to prepare coumarin derivatives with Cu(II)-OHPC-Fe₃O₄ as nano magnetic catalyst.

recyclability, reusability, easy separation and great specific surface area [4–8]. Also, MNPs have other unique characteristics such as good biocompatibility and biodegrad-ability, efficiency, easy accessibility and low toxicity [9, 10].

The construction of novel magnetically separable catalytic systems has developed as an alternative for improving the effective separation of heterogeneous catalysts [11]. Surface-functionalization of MNPs can occur via immobilization of various organic or inorganic non-magnetic active new materials in biotechnology and catalysis [12, 13]. Some of these different chemical materials include types of metal complexes, functional groups and metal nanoparticles (e.g. Pd, Si or Cu) [14].

Particular additives, which can be copper ligands, make better reaction rates and lead to couplings carried out at milder temperatures in the presence of decreased amounts of copper or with a higher support area. At the present, many ligands have been employed such as 1,10-phenanthroline and its derivatives [15], ethylene glycol [16], N,N-dimethylglycine [17], diethylsalicylamide, oxime-type and Schiff-base ligands [18], amino acids [19], aminoarenethiolate [20], phosphine ligands [21], etc.

Coumarin and its derivatives are a valuable class of benzopyrones bound in structural units of several natural products and exhibit applications in pharmacologic, pharmaceutics, agricultural and perfume industry [22]. They have displayed considerable biological activities, such as antitumor [23], anti-HIV [24] and antioxidative [25] activities. Hence, to broaden biological activities of coumarin derivatives, researchers have interest in the development of new methods for their preparation. In general, coumarins have been synthesized by Pechmann [26], Perkin [27], Knoevenagel [28], Reformatsky [29], Wittig reactions [30] and Flash Vacuum Pyrolysiso methods [31].

The Pechmann reaction is a significant method for synthesizing coumarins that proceeds from very simple starting materials, phenols and keto esters or unsaturated carboxylic acids using different catalysts such as nanocrystalline sulfated-zirconia [32], Zr-TMS-TFA-25 [33], furic acid [26], Fe₃O₄@SiO₂@Et-PhSO₃H [34], trifluoroacetic acid [35], Bi(NO₃)₃-5H₂O [36], TiCl₄ [37], ZrOCl₂·8H₂O/SiO₂ [38], ionic liquids [39] and sulfonic acid nanoreactor [40].

However, each of these has its own advantages but also suffers from one or more disadvantages, such as long reaction times, low yields, use of harmful organic solvents, requirement of excess of catalyst and reagents, and harsh reaction conditions. Researchers are endeavoring to develop effective alternative catalysts to synthesize coumarin derivatives via the Pechmann method.



Figure 1. FT-IR spectra of Fe₃O₄, OHPC, OHPC-Fe₃O₄ and Cu(II)-OHPC-Fe₃O₄.

In this study, we synthesize Cu(II) supported on 5-oxo-4,5-dihydro-pyrrole-3-carboxylic acid functionalized Fe_3O_4 nanoparticles (Cu(II)-OHPC-Fe_3O_4) as a new magnetic nanocatalyst and tested its catalytic application for synthesis of coumarin derivatives from two component reactions of various substituted phenols and ethyl acetoacetate in solvent-free conditions (Scheme 1). The prepared nanocatalyst is characterized by XRD, ICP-AES, SEM, TEM, FT-IR, TGA, VSM and EDX techniques.

2. Results and discussion

2.1. Characterization of the prepared Cu(II)-OHPC-Fe₃O₄ magnetic nanoparticles

2.1.1. Fourier transforms infrared (FT-IR) analysis

FT-IR spectra of the nanoparticles of Fe₃O₄, OHPC, OHPC-Fe₃O₄ and Cu(II)-OHPC-Fe₃O₄ are displayed in Figure 1. In FT-IR spectrum OHPC-Fe₃O₄ NPs show two absorption peaks at 2924 and 2853 cm⁻¹ which can be assigned to the symmetric stretching of C–H group. The adsorption peaks at 1633 and 1441 cm⁻¹ correspond to the asymmetric and symmetric stretching vibration of COO (carboxylate group) and C = N of 5-oxo-



Figure 2. XRD patterns of Fe₃O₄ (a), OHPC-Fe₃O₄ (b) and Cu(II)-OHPC-Fe₃O₄ (c) nanoparticles.

4,5-dihydro-pyrrole-3-carboxylate moiety. Also, adsorption bands at 590 and 620 cm⁻¹ attributed to Fe-O groups confirm the presence of Fe₃O₄ nanoparticles in the prepared catalyst. Hence, the obtained data from FT-IR spectroscopy prove the existence of the nonmagnetic particle and heterocyclic moiety in the structure of OHPC-Fe₃O₄ nanoparticle (Figure 1). In the FT-IR spectra of Cu(II)-OHPC-Fe₃O₄ (Figure 1), the C = N and COO (1639 and 1445 cm⁻¹) stretching bands were shifted to the higher wavenumbers, which exhibited coordination of nitrogen and oxygen to the metal center (Figure 1).

2.1.2. X-ray diffraction (XRD) analysis

Powder X-ray diffraction patterns of Fe₃O₄ nanoparticle, OHPC-Fe₃O₄ and Cu(II)-OHPC-Fe₃O₄ nanoparticle are shown in Figure 2. As can be seen in Figure 2(c), the peaks at $2\theta = 42.87^{\circ}$, 50.26° and 74.56° assigned with the (111), (200) and (220) were assigned to Cu(II) [41]. Also $2\theta = 30.2^{\circ}$, 35.30°, 43. 3°, 53.65°, 57.3° and 62.8° peaks corresponding to the (220), (311), (400), (422), (511) and (440) were obtained due to the cubic spinel structure of Fe₃O₄ NPs. Therefore, the results obtained from XRD spectra confirmed the presence of the Cu on organic group moiety in the nanoparticles containing Cu(II)-OHPC-Fe₃O₄.

2.1.3. EDX analysis of the catalyst

EDX analysis of Cu(II)-OHPC-Fe₃O₄ is displayed in Figure 3. As it can be seen, Cu(II)-OHPC-Fe₃O₄ is composed of the expected elements in the structure of the catalyst including Carbon (C), Oxygen (O), Nitrogen (N), Iron (Fe), Copper (Cu) and Chlorine (Cl), indicating that Cu has been grafted to OHPC-Fe₃O₄.



Figure 3. EDX spectrum of Cu(II)-OHPC-Fe₃O₄.

2.1.4. ICP-AES analysis

The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis shows the weight percentage of the Cu to be 9% in Cu(II)-OHPC-Fe₃O₄.

2.1.5. Thermogravimetric analysis (TGA)

The thermal behavior of Cu(II)-OHPC-Fe₃O₄ was investigated by thermogravimetric analysis (TGA) under an air atmosphere with a heating rate of 10 °C min⁻¹ from 0 to 800 °C (Figure 4). The composition ratio of the catalyst can be appraised from the residual mass percentage. As displayed in Figure 4, the small weight loss of about 0.51% at temperatures lower than 120 °C is likely due to the removal of the adsorbed water and remaining organic solvents. Other weight loss steps with a total loss of about 8.14% from 120 to 760 °C can be related to the decomposition of the organic group and Cu(II) the Cu(II)-OHPC-Fe₃O₄. Based on these results, grafting of Cu(II)-OHPC-Fe₃O₄ on the Fe₃O₄ nanoparticles is asserted. The amount of adsorbed Cu(II)-OHPC calculated by Equation (1) is 0.5 mmol g⁻¹.

$$mmolCu(II) - OHPC = (weightloss/100 \times MwCu(II) - OHPC) \times 1000 = 0.4 mmol$$
 (1)

2.1.6. Transmission electron microscopy (TEM)

The morphology of the OHPC-Fe₃O₄ nanoparticles and Cu(II)-OHPC-Fe₃O₄ nanoparticles were investigated by TEM (Figure 5). The average particle size distribution increases from 14 nm in OHPC-Fe₃O₄ nanoparticles to 17 nm in Cu(II)-OHPC-Fe₃O₄ nanoparticles, which is in good agreement with the crystallite size estimated from XRD. Comparison of experimental results showed grafting of OHPC and Cu(II)-OHPC



Figure 4. TGA diagram of Cu(II)-OHPC-Fe₃O₄ nanoparticles.



Figure 5. TEM micrographs of (a) OHPC-Fe₃O₄ and (b) Cu(II)-OHPC-Fe₃O₄ nanoparticles.

groups on the Fe_3O_4 nanoparticles. The TEM images of OHPC- Fe_3O_4 and Cu(II)-OHPC- Fe_3O_4 displayed a sphere-like structure.

2.1.7. Scanning electron microscopy (SEM)

The morphological features and size details of synthesized OHPC-Fe₃O₄ nanoparticles and Cu(II)-OHPC-Fe₃O₄ nanoparticles were studied by scanning electron microscopy (SEM) (Figure 6). The SEM image shows that OHPC-Fe₃O₄ nanoparticles have a mean diameter of about 16 nm and Cu(II)-OHPC-Fe₃O₄ nanoparticles with more than 20 nm in size. Comparison of experimental results showed grafting of OHPC and Cu(II)-OHPC



(a)

(b)

Figure 6. The SEM images of OHPC-Fe₃O₄ and Cu(II)-OHPC-Fe₃O₄ nanoparticles.



Figure 7. Room temperature magnetization curves of Fe_3O_4 , OHPC- Fe_3O_4 and Cu(II)-OHPC- Fe_3O_4 nanoparticle.

groups on the Fe_3O_4 nanoparticles. The SEM images of OHPC- Fe_3O_4 and Cu(II)-OHPC- Fe_3O_4 displayed a sphere-like structure.

2.1.8. Magnetic properties of the catalyst

A vibrating sample magnetometer (VSM) was employed for characterizing the magnetic properties of Fe_3O_4 , OHPC- Fe_3O_4 and Cu(II)-OHPC- Fe_3O_4 at 300 K (Figure 7). The magnetization curves for these nanoparticles display no hysteresis in their magnetizations. As shown in Figure 7, the saturation magnetization values for Fe_3O_4 , OHPC-

	Amount of catalyst			
Entry	(mol %)	Temperature (°C)	Time (h)	Yield (%) ^a
1	0.5	25	10	_
2	1	25	10	Trace
3	2	25	10	26
4	0.5	70	5	50
5	1	70	4	60
6	2	70	4	76
7	0.2	100	2	88
8	0.5	100	1.5	95
9	1	100	1.5	96
10	OHPC-Fe ₃ O ₄ (3 mol%)	100	10	Trace
11	Fe ₃ O ₄ (3 mol%)	100	10	Trace
12	Without catalyst	100	10	-

Table 1. Optimization conditions for reactions of ethyl acetoacetate (1 mmol) and catechol (1 mmol) in the presence of different amounts of the Cu(II)-OHPC-Fe₃O₄ as nanocatalyst at various temperatures under solvent-free conditions.

^aYields refer to isolated pure product.

 Fe_3O_4 and Cu(II)-OHPC-Fe₃O₄ were 72.1, 56.02 and 52.1 emu g⁻¹, respectively. A decrease of the saturation magnetization of Cu(II)-OHPC-Fe₃O₄ is observed due to the grafting of Cu on the surface of OHPC-Fe₃O₄ nanoparticles. These differences are because of the various coating layers and their thicknesses on the surface of MNPs. The prepared catalyst has excellent magnetic characteristics and can be quickly separated from the reaction media by an external magnet.

2.2. Catalytic application of Cu(II)-OHPC-Fe $_3O_4$ as nanocatalyst for Pechmann reactions to prepare coumarin derivatives

To find optimum conditions, the reaction of ethyl acetoacetate (1 mmol) and catechol (1 mmol) in the presence of the Cu(II)-OHPC-Fe₃O₄ as nanocatalyst was selected as a model reaction. The reaction was carried out with various amounts of Cu(II)-OHPC-Fe₃O₄ as catalyst (0.2, 0.5, 1 and 2 mol %) at several temperatures (25, 70, 100 °C) in the absence of solvent. According to the obtained results (Table 1), optimum conditions were 0.5 mol % of Cu(II)-OHPC-Fe₃O₄ as catalyst at 100 °C in the absence of solvent (Table 1, entry 8).

Then, different phenols were used in the reactions to prepare the corresponding products in high to excellent yields (Table 2). As can be seen in Table 2, the reactions with the electron-donating or electron-withdrawing substituents on phenols give the products in high to excellent yields (Table 2). According to a literature survey [22], the suggested mechanism for the formation of the products is shown in Scheme 2.

In order to compare the present work with reported results for the preparation of coumarin derivatives, the data are provided in Table 3. The obtained results exhibited that Cu(II)-OHPC-Fe₃O₄ is the better catalyst because of the short time reaction, good yields and low temperature of the product.

We also investigated recycling of the Cu(II)-OHPC-Fe₃O₄ as catalyst under solventfree conditions using the model reaction of ethyl acetoacetate (1 mmol) and catechol (1 mmol) (Table 2, entry 1). After completion of the reaction, the reaction mixture was dissolved in dichloromethane. Then, Cu(II)-OHPC-Fe₃O₄ as catalyst were separated by an external magnet for subsequent experiments to check reusability under similar

						Meltin	g point (°C)
Entry	Phenols	Time (h)	Yield (%)	TON	TOF (1/h)	Found	Reported [Ref.
1	ОН	1.5	94	188	125	182–184	183–185 [42]
2	H ₃ C CH ₃	3	90	180	60	89–90	87–89 [43]
3	OH	1.5	95	190	127	166	163–165 [43]
4	ЮН	1.5	93	186	124	280	279–281 [42]
5	OH CH ₃ OH	2	94	188	94	140–141	139–142 [35]
6	И ОН	2	90	180	90	261–263	260–262 [44]
7	НО ОН	2	92	184	92	240–241	239–240 [44]
8	OH CH ₃	2	91	182	91	170–171	171–173 [45]
9	OH	2.5	91	182	73	152–154	153–155 [45]
10	OH	2.5	89	178	71	180–181	178–180 [45]
11	CH ₃	2	93	186	93	130–131	129–132 [46]
12	OH	3	89	178	59	137–138	135–139 [47]

Table 2. Three-component reactions of ethyl acetoacetate (1 mmol) and various phenols in the presence of Cu(II)-OHPC-Fe₃O₄ (0.5 mol %) as nanocatalyst under solvent-free conditions at 100 $^{\circ}$ C.

^aYields refer to the isolated pure products.



Scheme 2. The suggested mechanism for formation of coumarin derivatives in the presence of Cu(II)-OHPC-Fe₃O₄ as nanocatalyst.

Table 3. Comparison the results of Cu(II)-OHPC-Fe₃O₄ as nanocatalyst for pechmann reactions to prepare coumarin derivatives with other catalysts.

Entry	Catalyst	Conditions	Time	Yield (%) ^a [Ref]
1	Fe ₃ O ₄ @SiO ₂ @Et-PhSO ₃ H (0.3 mol%)	Solvent free, 120 °C	2 h	93 [34]
2	Cu-BTC@SiO ₂ @Fe ₃ O ₄ (5 mol%)	Solvent free, 130 °C	5 h	95 [48]
3	$ZrO_{2}-Al_{2}O_{3}-Fe_{3}O_{4}$ (1.00 g)	Toluene, reflux	4 h	65 [49]
4	PANF-PAMSA (5 mol%)	Toluene, reflux	4h	95 [50]
5	Cu(II)-OHPC-Fe ₃ O ₄ (0.5 mol%)	Solvent free, 100 °C	1.5	95
				[Present work]

^aYields refer to isolated pure products.

reaction conditions. The results showed that Cu(II)-OHPC-Fe₃O₄ are a stable catalyst in reaction media and can be reused four times without significant loss of catalytic activity. The yield of the product obtained in the final cycle was almost 88%, indicating that Cu leaching of the recovered catalyst was negligible. This high recyclability of Cu(II)-OHPC-Fe₃O₄ demonstrated the significance of this catalyst for practical applications (Figure 8).

However, the ICP-AES, FT-IR, SEM, EDX, XRD and TEM analysis of recycled Cu(II)-OHPC-Fe₃O₄ (after four times recycling) are provided and shown in Figures 9–13.

The FT-IR spectra of recovered Cu(II)-OHPC-Fe₃O₄ are illustrated in Figure 9. The peaks around 2930 and 2852 cm⁻¹, for asymmetric and symmetric vibrations of C–H stretching can be obviously found. The adsorption peaks at 1630 and 1450 cm⁻¹ corresponds to the asymmetric and symmetric stretching vibration of the C = N and C-H (aromatic) of organic moiety. The adsorption bands at 586 and 447 cm⁻¹ were



Figure 8. The recycling of the Cu(II)-OHPC-Fe₃O₄ as nanocatalyst.



Figure 9. FT-IR spectrum of Cu(II)-OHPC-Fe₃O₄ nanoparticles after four times recycling.

attributed to Fe-O stretching band and 3443 cm⁻¹ corresponded to broad OH groups on magnetic surface of Fe₃O₄. Therefore, the obtained data from FT-IR spectroscopy can be proved the existence of the nonomagnetic particle, heterocyclic moiety and Cu in the structure of Cu(II)-OHPC-Fe₃O₄ magnetic nanoparticle. (Figure 9).

Morphology of synthesized of Cu(II)-OHPC-Fe₃O₄ nanoparticles were investigated by TEM that shown in Figure 10. Particles are observed to have spherical morphology from Figure 10. Average particle size is estimated about 17 nm from the TEM micrographs. Also, the SEM image of the Cu (II)-OHPC-Fe₃O₄ nanoparticle is shown (Figure 11). The SEM image of Cu (II)-OHPC-Fe₃O₄ showed a spherelike structure. The EDX analysis and XRD spectrum of recycled Cu (II)-OHPC-Fe₃O₄ (after four times recycling) was provided and compared with fresh catalyst (Figures 12 and 13). Therefore, based on



Figure 10. TEM analysis of Cu(II)-OHPC-Fe₃O₄ nanoparticles after four times recycling.



Figure 11. SEM analysis of Cu (II)-OHPC-Fe₃O₄ nanoparticles after four times recycling.



Figure 12. EDX analysis of Cu (II)-OHPC-Fe $_3O_4$ nanoparticles after four times recycling.



Figure 13. XRD patterns of Cu (II)-OHPC-Fe₃O₄ nanoparticles after four times recycling.

the obtained results, the Cu (II)-OHPC-Fe₃O₄ catalyst has not changed after four recycling and its activity is similar to the new prepared catalyst.

The results demonstrated that Cu(II)-OHPC-Fe₃O₄ catalyst could be reused without losing its efficiency after four times. It should be said that there was low Cu leaching (about 9%) during the reaction and the catalyst showed high stability even after four cycles.

3. Experimental

3.1. Chemicals and apparatus

The X-ray powder diffraction (XRD) of the prepared catalyst was carried out on a Philips PW 1830 X-ray diffractometer with CuK α source ($\lambda = 1.5418$ Å) in a range of Bragg's angle (10-80°) at temperature 25°C. Fourier transform infrared (FT-IR) spectrum was performed using a FT-IR spectrometer (Vector 22-Bruker) from 400-4000 cm⁻¹ at room temperature. Scanning electron microscopy (SEM) analysis was recorded using a VEGA//TESCAN KYKY-EM 3200 microscope (acceleration voltage 26 kV). Transmission electron microscopy (TEM) experiments were done on a Philips EM 208 electron microscope (EHT = 15.00 Kv). The elemental analysis of catalyst was appraised by energy dispersive X-ray (EDX), VEGA3 XUM/TESCAN. Thermogravimetric analysis (TGA) was performed on a Stanton Red craft STA-780 (London, UK). NMR spectra were performed with a Bruker DRX-400 AVANCE instrument (300.1 MHz for ¹H, 75.4 MHz for 13 C). The spectra were evaluated in DMSO-d₆ as a solvent. Magnetic measurements were carried out using a vibrating sample magnetometer (VSM, MDK, and Model 7400). The metal loading was determined by inductively coupled plasmaatomic emission spectrometry (ICP-AES). Melting points were evaluated on an Electrothermal 9100 apparatus.

3.2. General procedure

3.2.1. Preparation of 5-oxo-4,5-dihydro-pyrrole-3-carboxylic acid functionalized Fe_3O_4 nanoparticles (OHPC-Fe_3O_4)

First, FeCl₃· $6H_2O$ (4.865 g, 0.018 mol) and FeCl₂· $4H_2O$ (1.789 g, 0.0089 mol) were added to 100 ml deionized water and sonicated until the salts dissolved completely. After that, a specific amount of 5-oxo-4,5-dihydro-pyrrole-3-carboxylic acid (OHPC) (6.35 g,



Scheme 3. Preparation of OHPC-Fe₃O₄ nanoparticles.

0.05 mol) and NH₄OH (10 ml) solution were added until the pH was increased at which a black suspension formed. The prepared suspension was then refluxed at 100 °C for 6 h, with strong stirring. OHPC-Fe₃O₄ nanoparticles separated from the aqueous solution by magnetic decantation, washed with deionized water several times and then dried in an oven overnight (Scheme 3). All synthesis steps were done under N₂ atmosphere.

3.2.2. Preparation of Cu(II)-OHPC-Fe₃O₄ nanoparticles

To prepare Cu(II)-OHPC-Fe₃O₄ nanoparticles the obtained OHPC-Fe₃O₄ (0.5 g) was dispersed in 50 ml of ethanol by sonication for 30 min, and then 0.045 g of CuCl₂ was added to the above mixture, forming a brown suspension which was refluxed with strong stirring for 8 h. The catalyst (Cu(II)-OHPC-Fe₃O₄) was separated from the solution by an external magnetic field, washed with deionized water several times, and dried in an oven overnight (Scheme 4). All steps were carried out under N₂ flow.

3.2.3. General procedure for Pechmann reactions to prepare coumarin derivatives by Cu(II)-OHPC-Fe₃O₄ as nanoctalyst

To a mixture of ethyl acetoacetate (1 mmol) and phenol derivatives was added 0.5 mol % Cu(II)-OHPC-Fe₃O₄ as nanocatalyst at 100 °C under solvent-free conditions. When the reaction was completed (as monitored by TLC (*n*-hexane/EtOAc, 9:1, Rf valence: 0.52)), the reaction mixture was cooled to room temperature. After that, the reaction mixture was dissolved in dichloromethane (10 ml) and Cu(II)-OHPC-Fe₃O₄ nanoparticle catalyst was separated by an external magnet for 5 min. The solution containing the product was removed by vacuum and the residual solid was recrystallized using ethanol. The product was obtained as a powder. Eventually, the isolated catalyst was washed several times with dried CH₂Cl₂, dried under vacuum at 60 °C to give the pure Cu(II)-OHPC-Fe₃O₄ nanoparticle catalyst.

Selected spectra for two known products are given below:



Scheme 4. Preparation of Cu(II)-OHPC-Fe₃O₄ nanoparticles.

7-Hydroxy-4-methylcoumarin (Table 2, entry 1): ¹H NMR (400 MHz; DMSO-d6): $\delta_{H} = 2.32$ (brs, 3H), 6.11 (s, 1H), 6.70 (d, J = 2.4 Hz, 1H), 6.78–6.82 (dd, J = 8.8 Hz, J = 2.4 Hz, 1H), 7.56 (d, J = 8.8 Hz, 1H), 10.51 (brs, 1H) ppm.; ¹³C-NMR (100 MHz, DMSO- d_6): $\delta_C = 18.1$, 102.2, 110.1, 112.1, 113.2, 127.0, 154.1, 155.7, 160.0, 161.2 ppm.

5,7-dihydroxy-4-methylcoumarin (Table 2, entry 4): ¹H NMR (400 MHz; DMSO-*d*₆): $\delta_{\rm H}$ = 10.34 (s, 1H), 7.39–7.36 (d, *J* = 8.75 Hz, 1H), 6.83–6.79 (d, *J* = 8.5 Hz, 1H), 6.06 (s, 1H), 2.31 (s, 3H), 2.11 (s, 3H) ppm.; ¹³C NMR (100 MHz, DMSO-*d*₆): $\delta_{\rm C}$ = 11.2, 18.6, 110.3, 111.1, 112.1, 112.4, 123.5, 153.2, 154.1, 159.3, 160.8 ppm.

4. Conclusion

The preparation of 5-oxo-4,5-dihydro-pyrrole-3-carboxylic acid functionalized Fe_3O_4 nanoparticles (Cu(II)-OHPC-Fe₃O₄) as efficient, novel and reusable heterogeneous nanocatalysts are reported. The nano magnetic catalyst was characterized by XRD, ICP-AES, SEM, TEM, FT-IR, TGA, VSM and EDX techniques and employed for Pechmann reactions between different substituted phenols and ethyl acetoacetate to synthesize various coumarin derivatives. Cu(II)-OHPC-Fe₃O₄ nano magnetic catalyst has an average particle size of 26 nm. The nanocatalyst was recovered by filtration and reused for several cycles. Advantages for the prepared nanocatalyst include high specific surface area, good accessibility, high chemical and thermal stability, reducing the leaching of theses nanocatalyst into the bio environment, having organic groups for easier modification and less accumulation of them than other nanocatalysts.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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