

Synthesis and characterization of pyridine-4-carboxylic acid functionalized Fe₃O₄ nanoparticles as a magnetic catalyst for synthesis of pyrano[3,2-*b*]pyranone derivatives under solvent-free conditions

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Abstract Pyridine-4-carboxylic acid (PYCA) functionalized Fe₃O₄ nanoparticles as an organic–inorganic hybrid heterogeneous catalyst was fabricated and characterized by FT-IR, XRD, TGA, TEM, SEM, and VSM techniques. The catalytic activity of the magnetic catalyst was probed through one-pot synthesis of pyrano[3,2-*b*]pyranone derivatives from three component reactions of aromatic aldehydes, kojic acid, and ethyl cyanoacetate under solvent-free conditions. Some advantages of this protocol are its environmentally benign method, simple procedure, high yields, and short reaction time. The catalyst was readily separated using an external magnet and reusable without significant loss of its catalytic efficiency.

Keywords Magnetic properties · Pyrano[3,2-*b*]pyranone · Arylaldehydes · Kojic acid · Ethyl cyanoacetate · Nanoparticles

Introduction

Nanomaterials have attracted a great deal of attention in organic synthesis owing to their high surface-to-volume ratio, which are responsible for the higher catalytic activity [1–3]. Surface functionalized iron oxide magnetic nanoparticles (MNPs) are novel functional materials, which have been widely used in biotechnology and catalysis [4–9]. Magnetic nanocatalysts can easily be separated and recycled from

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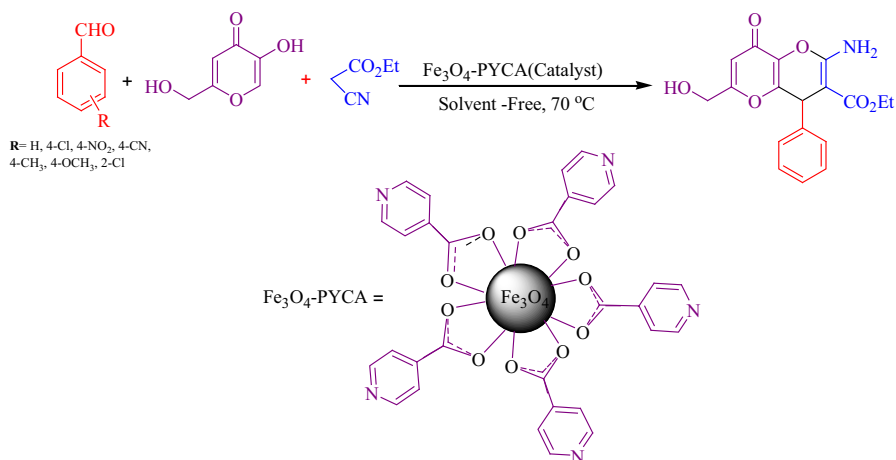
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the products by an external magnet. Good biocompatibility and biodegradability, as well as basic magnetic characteristics could be denoted for functional organic materials grafted to MNPs [10–12].

Multi-component reactions (MCRs) have proven to be valuable in organic and medicinal chemistry [13–16]. Such protocols can be used for drug design and drug discovery because of their simplicity, efficiency, and high selectivity [17, 18]. MCRs can reduce the number of steps and present advantages, such as low energy consumption and little to no waste production, leading to desired environmentally friendly processes. Synthesis of bioactive and complex molecules should be facile, fast, and efficient with minimal workup in this methodology [17–19]. The synthesis of 4*H*-pyran derivatives has attracted great interest because many of them have useful biological and pharmacological properties, e.g., as anticoagulant, spasmolytic, anticancer, and antianaphylactic agents [20–22]. Some 2-amino-4*H*-pyrans can also be used as photoactive materials [23]. Considering the importance of these compounds, many methods have been reported for their synthesis [24–30]. The reported methods for the synthesis of 2-amino-4*H*-pyran derivatives often involve multistep reactions, expensive catalysts [31], organic solvents, and microwave irradiation [32]. It is, therefore, important to find facile, efficient, and environmentally benign synthetic procedures for the preparation of these compounds. Previously, we reported the three-component reactions (3-CRs) of arylaldehydes, kojic acid, and ethyl cyanoacetate in the presence of a catalytic amount of K_2CO_3 in H_2O (5 ml) that led to pyrano[3,2-*b*]pyranones [33]. In continuation of our research, in this work, we synthesized a magnetic catalyst—pyridine-4-carboxylic acid (PYCA) functionalized Fe_3O_4 nanoparticles (Fe_3O_4 -PYCA)—and investigated its catalytic application for the three-component synthesis of pyrano[3,2-*b*]pyranone derivatives from arylaldehydes, kojic acid, and ethyl cyanoacetate under solvent-free conditions (Scheme 1).



Scheme 1 Synthesis of pyrano[3,2-*b*]pyranone derivatives using pyridine-4-carboxylic acid functionalized Fe_3O_4 nanoparticles (Fe_3O_4 -PYCA) as a nanomagnetic catalyst

Experimental

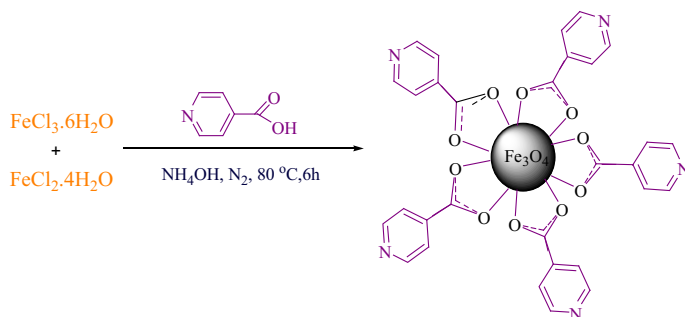
Chemicals and materials

Melting points were measured on an Electrothermal 9100 apparatus. The X-ray powder diffraction (XRD) of the catalyst was carried out on a Philips PW 1830 X-ray diffractometer with CuK α source ($\lambda = 1.5418 \text{ \AA}$) in a range of Bragg's angle (10–80°) at room temperature. Scanning electron microscope (SEM) analyses were taken using VEGA//TESCAN KYKY-EM 3200 microscope (acceleration voltage 26 kV). Transmission electron microscopy (TEM) experiments were conducted on a Philips EM 208 electron microscope. Thermogravimetric analysis (TGA) was recorded on a Stanton Red craft STA-780 (London, UK). NMR spectra were recorded with a Bruker DRX-400 AVANCE instrument (400.1 MHz for ^1H , 100.6 MHz for ^{13}C). The spectra were measured in DMSO- d_6 as solvent. IR spectra were recorded on an FT-IR Bruker vector 22 spectrophotometer. Magnetic measurements were performed using vibration sample magnetometer (VSM, MDK, and Model 7400) analysis.

General procedure

Preparation of pyridine-4-carboxylic acid functionalized Fe₃O₄ nanoparticles (Fe₃O₄-PYCA)

FeCl₃·6H₂O (4.865 g, 0.018 mol) and FeCl₂·4H₂O (1.789 g, 0.0089 mol) were added to 100 ml deionized water and sonicated until the salts dissolved completely. Then, 0.010 mol (0.123 g) of PYCA and NH₄OH (10 ml) solution were added to the above mixture until the pH was raised to 11, at which point a black suspension was formed. This suspension was then refluxed at 100 °C for 6 h, with vigorous stirring. Fe₃O₄-PYCA nanoparticles (about 1.5 g) was separated from the aqueous solution by magnetic decantation, washed with distilled water several times, and then dried in an oven overnight (Scheme 2). Synthesis was done under N₂ atmosphere.



Scheme 2 Preparation of Fe₃O₄-PYCA nanoparticles

*General procedure for the synthesis of pyrano[3,2-*b*]pyranone derivatives under solvent-free conditions*

A mixture of aromatic aldehydes (1 mmol), kojic acid (1 mmol, 0.14 g), and ethyl cyanoacetate (1 mmol, 0.11 g), with Fe₃O₄-PYCA nanoparticles (8 mol%) as a catalyst, was stirred under solvent-free conditions for 45–55 min at 70 °C. After completion of the reaction, which was monitored by TLC, the reaction mixture was cooled to room temperature. Then, the reaction mixture was dissolved in dichloromethane (10 ml), and subsequently, the Fe₃O₄-PYCA nanoparticle catalyst was separated by an external magnet for 5 min. The solution containing the product was evaporated, the residue solid was recrystallized using hexane/ethyl acetate (9:1), and the product obtained was a white powder. Finally, the isolated catalyst was washed several times with dried CH₂Cl₂, and dried under vacuum at 60 °C to give the pure Fe₃O₄-PYCA nanoparticle catalyst.

All of the desired products were characterized by comparison of their physical data with those of known compounds. Selected spectra for two known products are given below:

*Ethyl 2-amino-6-(hydroxymethyl)-8-oxo-4-phenyl-4,8-dihydropyrano[3,2-*b*]pyran-3-carboxylate* (Table 2, entry 1) White powder; mp = 193–194 °C. IR (KBr): ν_{\max} = 3460, 3383 (NH₂), 3266 (OH), 1672 (C=O), 1621 (C=C), 1208 (C_{sp2}-O), 1024 (C_{sp3}-O) cm⁻¹; ¹H NMR (400.13 MHz, DMSO-*d*₆): δ = 1.00 (t, 3H, ³J_{HH} = 7.2 Hz, CH₃), 3.93 (q, 2H, ³J_{HH} = 7.2 Hz, OCH₂-CH₃), 4.20 (2 dd, 2H, ²J_{HH} = 15.6 Hz, ³J_{HH} = 5.6 Hz, CH₂OH), 4.80 (s, 1H, CH), 5.69 (t, 1H, ³J_{HH} = 6.0 Hz, OH), 6.32 (s, 1H, CH), 7.21–7.25 (m, 3H, 3 Ar-H), 7.30–7.34 (m, 2H, 2 Ar-H), 7.84 (s, 2H, NH₂) ppm; ¹³C NMR (100.6 MHz, DMSO *d*₆): δ = 14.5 (CH₃), 40.3 (CH), 59.4, 59.6 (2 OCH₂), 75.5 (Cq), 111.8 (CH), 127.6 (CH), 128.0 (2 CH), 129.0 (2 CH), 136.4, 143.5, 152.2, 160.2, 168.0 (5 Cq), 168.6 (C=O, ester), 170.1 (C=O, pyrone) ppm.

*Ethyl 2-amino-4-(4-cyanophenyl)-6-(hydroxymethyl)-8-oxo-4,8-dihydropyrano[3,2-*b*]pyran-3-carboxylate* (Table 2, entry 4) White powder; mp = 194–196 °C. IR (KBr): ν_{\max} = 3355, 3262 (NH₂, OH), 2227 (CN), 1671 (C=O), 1631 (C=C), 1210 (C_{sp2}-O), 1033 (C_{sp3}-O) cm⁻¹; ¹H NMR (400.13 MHz, DMSO-*d*₆): δ = 0.97 (t, 3H, ³J_{HH} = 7.2 Hz, CH₃), 3.88–3.96 (m, 2H, OCH₂CH₃), 4.19 (2 dd, 2H, ²J_{HH} = 16.0 Hz, ³J_{HH} = 6.0 Hz, CH₂OH), 4.93 (s, 1H, CH), 5.69 (t, 1H, ³J_{HH} = 6.0 Hz, OH), 6.32 (s, 1H, CH), 7.46 (d, 2H, ³J_{HH} = 8.4 Hz, 2 Ar-H), 7.80 (d, 2H, ³J_{HH} = 8.4 Hz, 2 Ar-H), 7.93 (s, 2H, NH₂) ppm.; ¹³C NMR (100.6 MHz, DMSO *d*₆): δ = 14.5 (CH₃), 40.5 (CH), 59.5, 59.6 (2 OCH₂), 74.6 (Cq), 110.5 (CH), 111.1 (CH), 119.9 (CN), 129.3 (2 CH), 133.0 (2 CH), 136.5, 149.0, 150.8, 160.1, 167.8 (5 Cq), 168.7 (C=O, ester), 170.0 (C=O, pyrone) ppm.

Results and discussion

Characterization of the prepared Fe₃O₄-PYCA nanoparticles

X-ray diffraction (XRD) analysis

Phase investigation of the supported catalyst was performed by XRD and result presented in Fig. 1. The result shown in Fig. 1 was fitted for six observed peaks with the following Miller indices: (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0). The XRD pattern indicates that Fe₃O₄-PYCA nanoparticles is broadened owing to very small crystallite size, indicating that the PYCA have been successfully supported on Fe₃O₄ nanoparticle. The average MNPs core diameter was calculated to be about 11 nm from the XRD results by Scherer's equation, $D = k \lambda / \beta \cos \theta$, where k is a constant (generally considered as 0.94), λ is the wavelength of Cu K α (1.54 Å), β is the corrected diffraction line full-width at half-maximum (FWHM), and θ is Bragg's angle [34, 35].

Fourier transform infrared (FT-IR)

In The FT-IR data of Fe₃O₄-PYCA nanoparticles, the distinctive absorption bands of 1629, 1130, 2923, and 2853 cm⁻¹ are attributed to the C=O, C-O and C-H stretching of pyridine-4-carboxylate unit. The characteristic absorbing peaks of Fe₃O₄ appear at 633 and 583 cm⁻¹, which can be ascribed to the vibrations of Fe-O group. Therefore, the data obtained from FT-IR spectroscopy can confirm the existence of the nanomagnetic particle and heterocyclic moiety in the structure of Fe₃O₄-PYCA nanoparticles (Fig. 2).

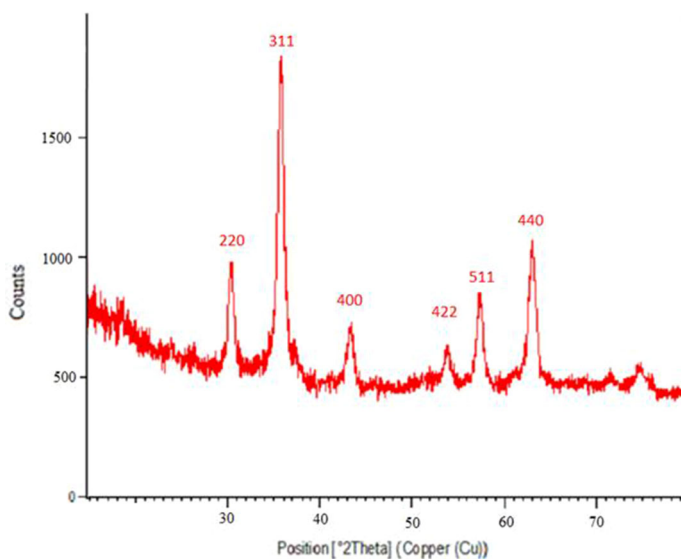


Fig. 1 XRD powder pattern of Fe₃O₄-PYCA nanoparticles

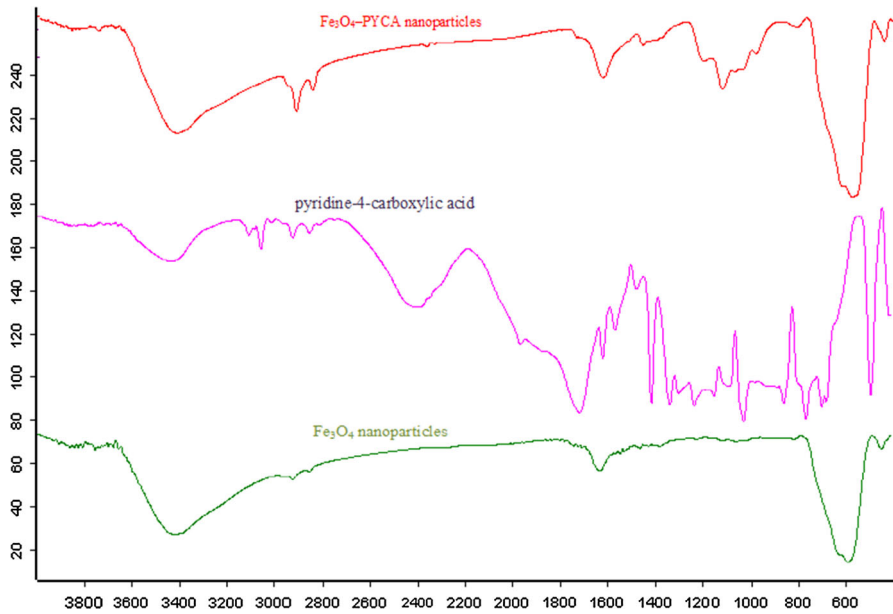


Fig. 2 FT-IR spectra for Fe_3O_4 nanoparticles, pyridine-4-carboxylic acid, and Fe_3O_4 -PYCA nanoparticles

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) and differential thermal analysis (DTG) were performed at the range of 25–900 °C, to determine the loading of organic groups coated on the surface of the magnetite (Fig. 3). The amount of adsorbed pyridine-4-carboxylic acid calculated by Eq. (1) is 0.4 mmol g^{-1} .

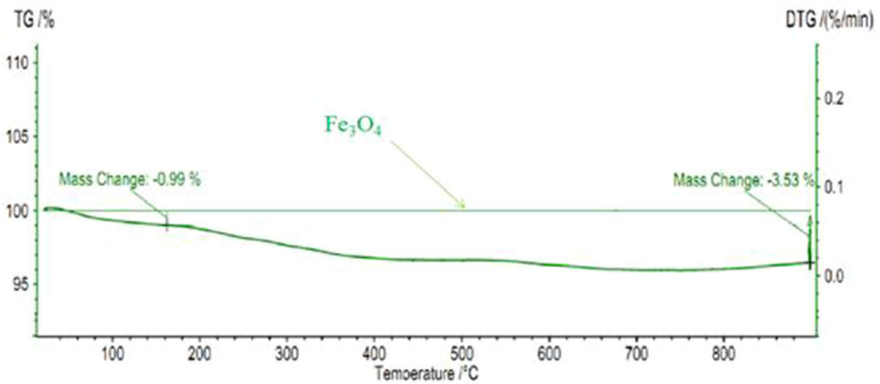


Fig. 3 TGA thermograms of Fe_3O_4 -PYCA nanoparticles

$$\begin{aligned} & \text{mmol pyridine-4-carboxylic acid} \\ & = (\text{weight loss}/100 \times \text{Mw pyridine-4-carboxylic acid}) \\ & \times 1000 = 0.4 \text{ mmol} \end{aligned} \quad (1)$$

TEM analysis

Morphology of synthesized Fe_3O_4 -PYCA nanoparticles were investigated by TEM, and are shown in Fig. 4 to be spherical. Average particle size is estimated to be about 13 nm from the TEM micrographs, which is in very good agreement with the crystallite size estimated from XRD at 11.5 nm. This is an indication of the nearly single-crystalline character of Fe_3O_4 -PYCA nanoparticles.

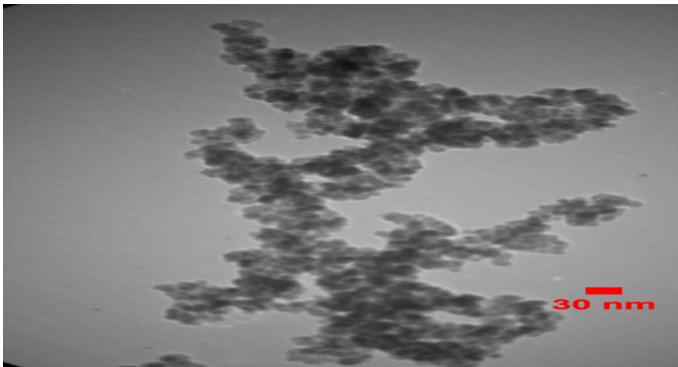


Fig. 4 TEM micrographs of Fe_3O_4 -PYCA nanoparticles

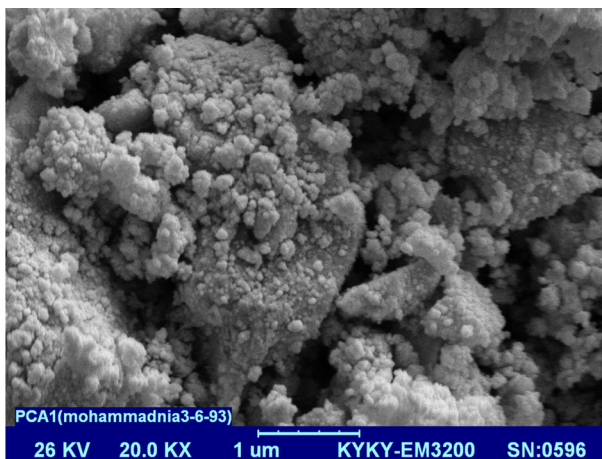


Fig. 5 The SEM images of Fe_3O_4 -PYCA nanoparticles

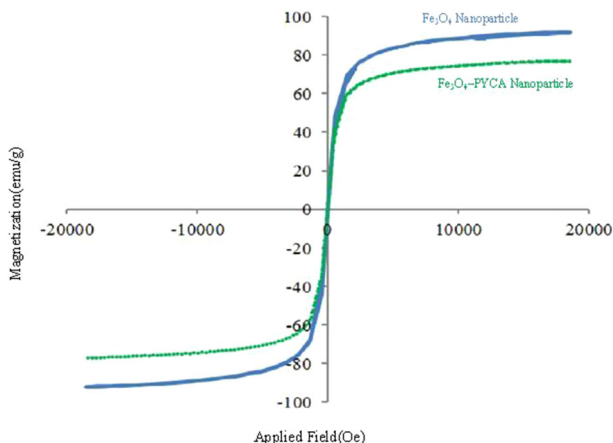


Fig. 6 Room temperature magnetization curves of Fe_3O_4 nanoparticle and Fe_3O_4 -PYCA nanoparticle

Scanning electron microscope (SEM)

Scanning electron microscopy (SEM) is a primary tool for determining the size distribution, particle shape, surface morphology, and fundamental physical properties. Fig. 5 shows the SEM image of the Fe_3O_4 -PYCA nanoparticle.

Vibrating sample magnetometer (VSM)

The room temperature magnetization curves proved that the Fe_3O_4 -PYCA nanoparticle is super paramagnetic. Saturation magnetization of MNPs was 92.13 emu/g and saturation magnetization of Fe_3O_4 -PYCA nanoparticles was 76.89 emu/g. Compared with the uncoated Fe_3O_4 nanoparticle, the saturation magnetization of the Fe_3O_4 -PYCA nanoparticle obviously decreased because the

Table 1 Optimization conditions for preparation ethyl 2-amino-6-(hydroxymethyl)-8-oxo-4-phenyl-4,8-dihydropyrano[3,2-*b*]pyran-3-carboxylate from benzaldehyde (1 mmol), kojic acid (1 mmol), and ethyl cyanoacetate (1 mmol) in the presence of different amounts of Fe_3O_4 -PYCA nanoparticle as catalyst in different temperatures under solvent-free conditions

Entry	Amount of catalyst (mol%)	Temperature ($^{\circ}\text{C}$)	Time (min)	Yield (%) ^a
1	4	25	120	–
2	8	25	120	Trace
3	12	25	120	37
4	4	50	100	50
5	8	50	70	60
6	12	50	65	75
7	4	70	55	82
8	8	70	50	95
9	12	70	50	96

^a Yields refer to isolated pure product

Table 2 Three-component synthesis of pyrano[3,2-*b*]pyranone derivatives using aromatic aldehydes (1 mmol), kojic acid (1 mmol), and ethyl cyanoacetate (1 mmol) in the presence of Fe₃O₄-PYCA nanoparticles (8 mol%) as catalyst under solvent-free conditions at 70 °C

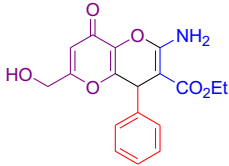
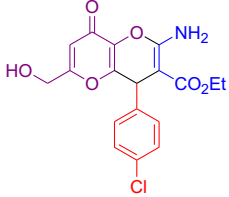
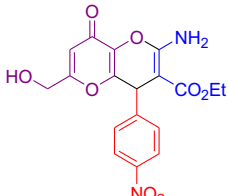
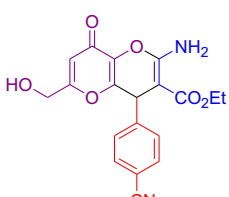
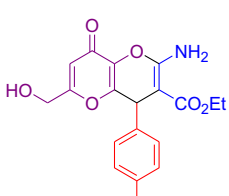
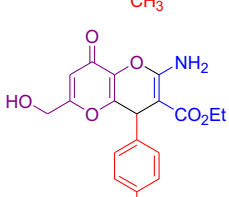
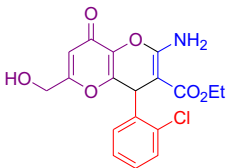
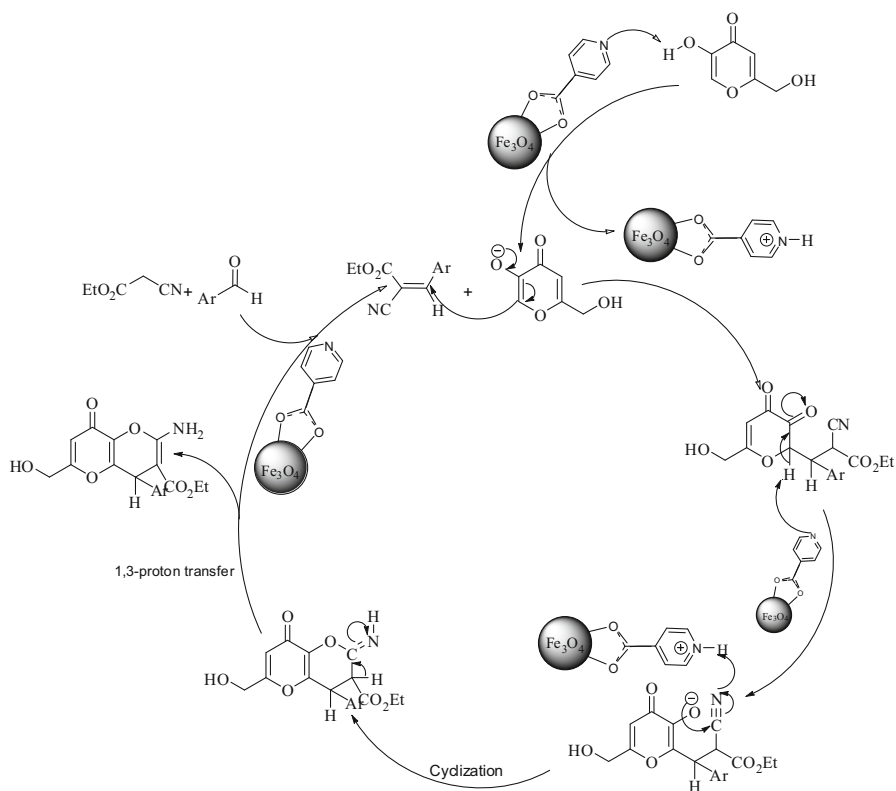
Entry	Aldehyde	Product	Time (min)	Yield (%)	Melting point (°C)	
					Found	Reported (references)
1	C ₆ H ₅		50	92	193–194	194–196 [33]
2	4-ClC ₆ H ₄		47	95	196–198	195–197 [33]
3	4-NO ₂ C ₆ H ₄		45	96	201–203	203–205 [33]
4	4-CN C ₆ H ₄		46	95	194–196	196–198 [33]
5	4-MeC ₆ H ₄		53	89	189–190	187–189 [33]
6	4-OMeC ₆ H ₄		55	85	83–84	79–81 [33]

Table 2 continued

Entry	Aldehyde	Product	Time (min)	Yield (%)	Melting point (°C)	
					Found	Reported (references)
7	2-ClC ₆ H ₄		47	93	194–196	197–199 [33]

^a Yields refer to the isolated pure products



Scheme 3 The suggested mechanism for the formation of the pyrano[3,2-*b*]pyranone derivatives

diamagnetic contribution of the organic group resulted in a low mass fraction of the Fe₃O₄ magnetic substance. Even with this reduction in the saturation magnetization, the solid could still be efficiently separated from solution with a permanent magnet (Fig. 6).



Fig. 7 Image showing that Fe_3O_4 -PYCA nanoparticles can be separated by an applied magnetic field. A reaction mixture in the absence (*right*) or presence of a magnetic field (*left*)

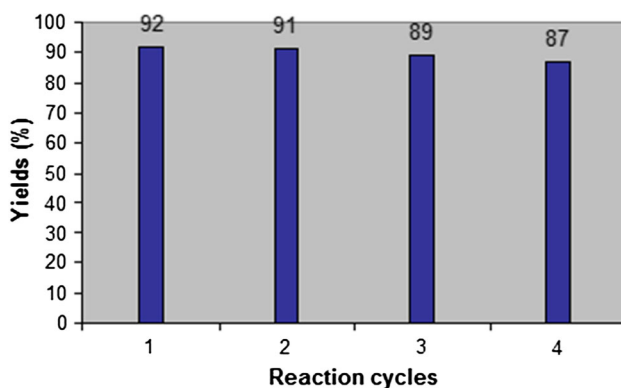


Fig. 8 The recycling of the Fe_3O_4 -PYCA nanoparticles as catalyst

Catalytic application of Fe_3O_4 -PYCA nanoparticles

First, to find optimization conditions, the reaction of benzaldehyde, kojic acid, and ethyl cyanoacetate in the presence of the Fe_3O_4 -PYCA nanoparticles as catalyst was selected as model reaction. The reaction was carried out with different amounts of Fe_3O_4 -PYCA nanoparticles as catalyst (4, 8, 12 mol%) in different temperatures (25, 50, 70 °C). The obtained results in Table 1 showed that optimal conditions were 8 mol% of Fe_3O_4 -PYCA nanoparticles at 70 °C (Table 1, entry 8).

Next, various aromatic aldehydes were used in the reactions that led to the corresponding products in high to excellent yields (Table 2). As shown in Table 2, reactions with aromatic aldehydes, including electron-donating or electron-withdrawing substituents, afforded the desired products in high to excellent yields.

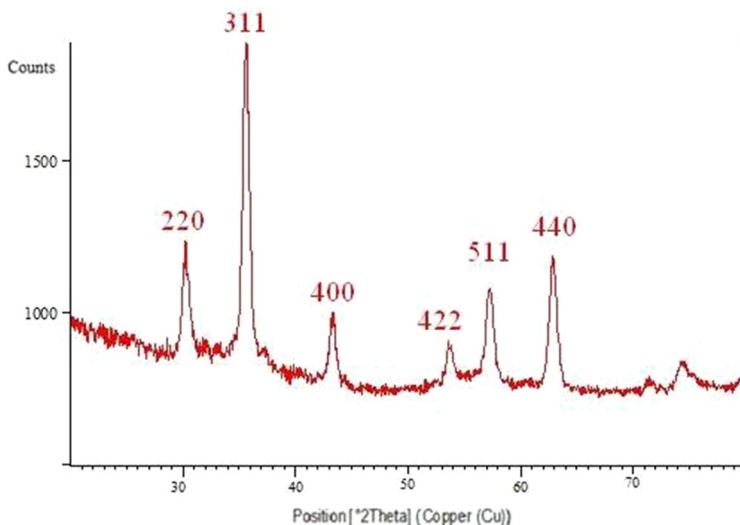


Fig. 9 XRD powder pattern of Fe_3O_4 -PYCA nanoparticles after recycling four times

The suggested mechanism for the formation of the products, according to the literature survey [33], is shown in Scheme 3.

We also investigated recycling of the Fe_3O_4 -PYCA nanoparticles as catalyst under solvent-free at 70 °C conditions using the model reaction of benzaldehyde, kojic acid, and ethyl cyanoacetate. The recovered catalyst was reused for four runs without any loss of its activities (Fig. 7, 8). However, the XRD spectrum of recycled Fe_3O_4 -PYCA (after recycling four times) was provided and compared with fresh catalyst (Fig. 9). Analysis of these two spectra showed no difference.

The results show that the reactions in the presence of Fe_3O_4 -PYCA nanoparticles were carried out in short times (45–55 min) and with high yield relative to the reported inorganic catalyst (K_2CO_3) by us [alimi] [33].

Conclusions

We synthesized Fe_3O_4 -PYCA nanoparticles as an organic–inorganic hybrid heterogeneous catalyst and characterized them by FT-IR, XRD, TGA, TEM, SEM, and VSM techniques. Size evaluation via various techniques revealed the size of Fe_3O_4 -PYCA nanoparticles to be around 11–13 nm with nearly single-crystalline character. The most interesting features of the present work include durability as well as efficient catalytic activity for synthesis of pyrano[3,2-*b*]pyranone derivatives via the reaction of aromatic aldehydes, kojic acid, and ethyl cyanoacetate under solvent-free conditions at 70 °C. The attractive features of this protocol are its simple procedure, inexpensive workup, ease of handling, high yields of products, and use of reusable nanomagnetic catalyst.

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