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A robust synthesis and characterization of superparamagnetic CoFe₂O₄ nanoparticles as an efficient and reusable catalyst for green synthesis of some heterocyclic rings

Mahmoud Abd El Aleem Ali El-Remaily*, Ahmed M. Abu-Dief and Rafat M. El-Khatib

A robust synthesis for magnetic $CoFe_2O_4$ nanoparticles via a hydrothermal technique was investigated. The prepared magnetic nanoparticles were characterized using powder X-ray diffraction, scanning, transmission and high-resolution transmission electron microscopies, energy-dispersive X-ray and infrared spectroscopies, thermogravimetric analysis and vibrating sample magnetometry. Based on the obtained data, the prepared powder was composed of ultrafine particles in nanometer size range with highly homogeneous spherical shape and elemental composition. Moreover, the prepared magnetic $CoFe_2O_4$ nanoparticles were used as an efficient catalyst for green synthesis of tetrahydropyridines and pyrrole derivatives in excellent yields, with easy work-up and purification of products by non-chromatographic methods. The catalyst can be recovered for subsequent reactions and reused without any appreciable loss of activity. Copyright © 2016 John Wiley & Sons, Ltd.

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Keywords: magnetic CoFe₂O₄ nanoparticles; hydrothermal synthesis; TEM; tetrahydropyridines; pyrrole; non-chromatographic methods

Introduction

In recent years, being focused on green chemistry using environmentally benign reagents and conditions is one of the most fascinating developments in synthesis of widely used organic compounds.^[1-3] Also, magnetic nanoparticles (MNPs) have received a great deal of attention because of their potential biomedical applications in fields such as drug delivery,^[4,5] magnetic resonance imaging,^[6] biomolecular sensing,^[7] bioseparation^[8] and magneto-thermal therapy.^[9] Additionally, recent studies show that MNPs are excellent catalysts for organic reactions.^[10–13] Their magnetic properties make possible the complete recovery of a catalyst by means of an external magnetic field. These advantages become even more attractive if such reactions can be conducted in aqueous media. Tetrahydropyridines are widely distributed in naturally occurring alkaloids and synthetic drugs.^[14] A variety of structural features are exhibited by synthetically prepared piperidines, including many exhibiting significant biological properties. Many synthetic methods have been extensively studied for tetrahydropyridines because of their antihistamic,^[15] anti-HIV,^[16] antimicrobial,^[18] anticancer,^[17] antimalarial,^[19] antiinflammatory^[20] and anti-insecticidal^[21] activities. A few of them are also potent inhibitors for many biological systems.^[22] Boehm and Stoker in 1943 reported the first multicomponent reaction (MCR) between an amine, aldehyde and 1,3-dicarbonyl to synthesize functionalized piperidines.^[23] Apart from some Lewis and Bronsted acid catalysts,^[24] a few organocatalysts which include acid,^[25] picric acid,^[26] wet *p*-toluenesulfonic

bromodimethylsulfonium bromide,^[27] tetrabutylammonium tribromide,^[28] L-proline nitrate^[29] and thiourea oxide^[30] have been reported for this MCR. Mishra and co-workers have reported L-proline and trifluoroacetic acid as a dual catalytic system for this MCR.^[31] Shaterian and Azizi used imidazolium and guanidinium acidic ionic liquid for the synthesis of functionalized piperidines.^[32]

Pyrroles and their derivatives exhibit various important biological activities like antibacterial, antioxidant, cytotoxic, insecticidal, antiinflammatory, anticoagulant, antiallergic, antiarhythmic, hypotensive and anticonvulsant activities.^[33–39] The development of new MCRs and improving known multicomponent reactions are areas of considerable current interest. Designing organic reactions in aqueous media is another attractive area in green chemistry. Water is an abundant and environmentally benign solvent. This protocol offers flexibility in tuning molecular complexity and diversity. The reactions proceed to completion almost instantaneously, and pure product is obtained, without using any chromatographic techniques, simply by recrystallization from ethanol.

Therefore, our work focuses on a new synthesis of stable and highly monodisperse cobalt ferrite nanoparticles. The magnetic features of the resulting modified nanoparticles have also been

Department of Chemistry, Faculty of Science, Sohag University, Sohag 82524, Egypt

^{*} Correspondence to: Mahmoud A. A. Ali El-Remaily, Department of Chemistry, Faculty of Science, Sohag University, Sohag 82524, Egypt. E-mail: msremaily@yahoo.com

determined and examined for their potential applications. Also, we report a simple and facile multi-component one-pot synthesis of tetrahydropyridines and pyrrole derivatives in high yields, using superparamagnetic $CoFe_2O_4$ nanoparticles (8 mol%) as a catalyst. Most of the above reported synthetic methods for the synthesis of tetrahydropyridines and pyrrole suffer from one or more drawbacks, such as hazardous reaction conditions, complex work-up and purification, strong acidic conditions, high temperature, use of toxic metal catalysts, poor yields, occurrence of side reactions and use of expensive reagents. Therefore, the development of a mild generalized method to overcome these shortcomings still remains an ongoing challenge for the synthesis of tetrahydropyridines and pyrrole derivatives for organic chemists.

Results and discussion

Structural characterization of prepared CoFe₂O₄ nanoparticles

Powder X-ray diffraction (PXRD) patterns of the prepared CoFe₂O₄ MNPs (Fig. 1) show the expected peaks for the cubic inverse spinel-type structure (Fd-3m space group) of CoFe₂O₄ (JCPDS PDF no. 221086). The crystallite size of the sample is about 16 nm, as determined by PXRD line-broadening analysis. A transmission electron microscopy (TEM) image (Fig. 2(a)) of the prepared nanoparticles shows uniform distribution of nearly spherical particles, with an average size of 15 nm (Fig. 2(b)) which is consistent with the value obtained from PXRD measurements. High-resolution TEM (HR-TEM) images displayed in Fig. 3 of the prepared nanoparticles show an interplanar spacing of 2.9 Å corresponding to (220) atomic planes. Selected area electron diffraction (SAED) pattern (Fig. 4) shows the polycrystalline nature of the samples and all the rings have been indexed as inverse spinel CoFe₂O₄ phase. Moreover, SAED and PXRD patterns are found to agree that the (311) plane shows the most intense reflection. CoFe₂O₄ nanoparticles were examined using scanning electron microscopy (SEM)-energy-dispersive X-ray spectroscopy (EDS), including quantitative point analysis. This study reveals a homogenous and uniform distribution of the prepared individual particles, and without any apparent preferential concentration in some areas, and the average molar ratio of Co:Fe elements is 1:2 (Fig. 5).



Figure 1. PXRD pattern for the prepared CoFe₂O₄ nanoparticles.



Figure 2. (a) TEM image for the prepared $CoFe_2O_4$ nanoparticles. (b) Calculated size distribution for the prepared $CoFe_2O_4$ nanoparticles.







Figure 4. SAED pattern for the investigated CoFe₂O₄ nanoparticles.

Fourier transform infrared (FT-IR) spectrum of prepared CoFe₂O₄ nanoparticles

The FT-IR spectrum of the prepared CoFe₂O₄ nanoparticles (Fig. S1) shows a characteristic vibration (around 3450 cm⁻¹) and deformation (at 1634 cm⁻¹) bands due to the adsorbed water molecules at the surface of the prepared nanoparticles. The band at 580 cm⁻¹ is characteristic for metal–oxide vibration band (cobalt ferrite) and



Figure 5. (a) SEM image of the prepared nanoparticles. (b) EDS spectrum of the prepared nanoparticles.

this confirms the spinel structure characteristic of the prepared cobalt ferrite nanoparticles.

Thermogravimetric analysis (TGA) of prepared CoFe₂O₄ nanoparticles

The thermal stability of the prepared CoFe₂O₄ was investigated in nitrogen. The TGA/DTG curves are shown in Fig. S2. The TG/DTG curves for CoFe₂O₄ reveal a total mass loss of *ca* 6.22% from room temperature up to 680°C. The mass loss takes place in four stages. The first stage is with a total mass loss of *ca* 1.64% in the range 24.91–231.80°C (which reaches a maximum rate at 90°C), attributed to the vaporization of surface water molecules, while the other three steps are continuous with a total mass loss of *ca* 3.58% in the range 232–680°C (which reach their maximum rate at 310, 420 and 575°C), and may be due to the vaporization of trapped water molecules and decomposition of organic material.

Magnetic characteristics

The magnetic properties of as-prepared CoFe₂O₄ nanoparticles were investigated with a quantum vibrating sample magnetometer at 5 and 300 K ($T > T_B$) with a maximum applied field up to 100 kOe. The results are shown in Fig. 6 and summarized in Table 1.

The sample is found to be superparamagnetic from the complete reversibility of the *M*–*H* curve recorded at room temperature. The decrease in the density of magnetization with a decrease in the average diameter of the nanocrystallites can be attributed to surface effects and core–shell morphology.^[40] The magnetic properties of the superparamagnetic nanomaterials are very sensitive to the morphologies and structures $CoFe_2O_4$ nanoparticles. The coercivity behavior indicates that Co atoms in the Fe–O matrix increase magnetic anisotropy of the material.^[41] It is well known that the surface spin disorder enhancement caused by the decreasing of particles size and the coercivity would approach zero under a short thermal fluctuation (so-called superparamagnetism) if the crystal size is small enough.^[42]

CoFe₂O₄ nanoparticles as efficient catalyst

In this research, a general method for the synthesis of tetrahydropyridines was developed using superparamagnetic $CoFe_2O_4$ nanoparticles as catalyst using a simple and green process.

In order to study the catalytic effects of $CoFe_2O_4$ MNPs, catalytic behaviors of various types of catalysts such as $CoCl_2$, CoO powder, CoO MNPs, $FeCl_3$, Fe_3O_4 powder, Fe_3O_4 MNPs, $CoFe_2O_4$ powder and $CoFe_2O_4$ MNPs were compared in the reaction of aniline,





Figure 6. Magnetic field dependence of magnetization (M–H loops) measured for the prepared nanoparticles at (a) 5 K and (b) 300 K.

Table 1. N nanoparticles	lagnetic p	arameters	for	the	investigated	CoFe ₂ O ₄
Temperature (K)	Coercivity, <i>H</i> _c (kOe)	Rem magnetiza g	tion, J_{j}^{-1}	it M _r (en	Satura nu magnetiza (emu g	tion tion, <i>M</i> s g ⁻¹)
5 300	10.50 0.70	7) 2	0.12 4.28		84.4 75.2	-2 :8

benzaldehyde and ethyl acetoacetate (Table 2). The obtained results show that in the presence of $CoFe_2O_4$ MNPs the reaction proceeds to product in high yield; in the absence of catalyst, the reaction does not progress at all. Also the results in Table 2 indicate that the optimum amount of the catalyst is 8 mol% of $CoFe_2O_4$ MNPs. Notably, increasing this amount does not show any change in yield and time of reaction.

Subsequently to establish the best reaction conditions, we focused on the effect of various solvents with varying polarity. It is observed that water–ethanol (3:1) is the best choice for this reaction over any organic solvents such as $CHCl_3$, CH_3CN , DMF, CH_3NO_2 , $PhCH_3$ and MeOH (Table 3).

 $CoFe_2O_4$ MNPs were used as an efficient catalyst for the synthesis of highly functionalized tetrahydropyridines via five-component reaction of aromatic aldehyde, amine and ethyl acetoacetate in water–ethanol (3:1) as solvent (Scheme 1 and Table 4). The present

Table 2.	Optimization of model read	ction using various c	atalysts ^a
Entry	Catalyst (mol%)	Time (min)	Yield (9

Entry	Catalyst (mol%)	Time (min)	Yield (%) ⁶
1	Without catalyst	240	0
2	CoCl ₂ ·6H ₂ O (10)	180	23
3	FeCl ₃ ·6H ₂ O (10)	180	30
4	CoO powder (10)	180	32
5	CoO MNPs (10)	180	52
6	Fe ₃ O ₄ powder (10)	180	57
7	Fe ₃ O ₄ MNPs (10)	180	74
8	CoFe ₂ O ₄ powder (10)	180	68
9	CoFe ₂ O ₄ MNPs (2)	60	70
10	CoFe ₂ O ₄ MNPs (4)	60	78
11	CoFe ₂ O ₄ MNPs (6)	60	86
12	CoFe ₂ O ₄ MNPs (7)	60	90
13	CoFe ₂ O ₄ MNPs (8)	60	94
14	CoFe ₂ O ₄ MNPs (9)	60	94
15	CoFe ₂ O ₄ MNPs (10)	60	93

^aReaction conditions: **1** (2 mmol), **2a** (2 mmol), **3** (1 mmol) and catalyst (0.08 mmol) in a mixture of water and ethanol (3:1 ratio) refluxed at 120°C.

^bIsolated yield based on **4a**.

Table 3. Optimization of model reaction using various solvents					
Entry	Solvent	Time (min)	Yield (%) ^a		
1	CHCl₃	180	64		
2	CH₃CN	180	71		
3	DMF	180	82		
4	CH ₃ NO ₂	180	80		
5	PhCH₃	180	69		
6	MeOH	120	88		
7	H ₂ O-EtOH (3:1)	60	94		
^a lsolated yield.					



Scheme 1. Synthesis of tetrahydropyridine derivatives 4a-p.

approach offers several advantages such as high yields, environmental benignity, simple work-up, excellent yield of products, short reaction times as well as recoverability and reusability of the catalyst.

We turned our attention to a study of the mechanistic aspect of this one-pot, five-component reaction. A plausible reaction mechanism (Scheme 2) is suggested. The catalyst may activate the ethyl acetoacetate and benzaldehyde to react with aniline and give the β -enaminone 1 and imine 2. The reaction between β -enaminone 1 and imine 2 is an intermolecular Mannich reaction in the presence of CoFe₂O₄ MNPs to produce intermediate 3. Subsequently, the reaction of activated aldehyde with intermediate 3 proceeds

to afford the intermediate **5** with elimination of water. Next, tautomerization of **5** generates intermediate **6**, which immediately undergoes intramolecular Mannich-type reaction to give intermediate **7**. Eventually, the intermediate **7** tautomerizes to generate the desired tetrahydropyridine **4a** due to conjugation with the ester group (Scheme 2).

Hence, we investigated the effects of various reaction parameters on the catalytic activity in order to optimize the protocol for formation of 1*H*-pyrrole derivatives (Scheme 3). We chose the reaction of aniline (2 mmol) with ethyl pyruvate (2 mmol) as a model reaction under microwave irradiation; the results are summarized in Table 5. It is noted that in the absence of $CoFe_2O_4$ MNP catalyst, there is no detectable amount of the desired product formed (Table 5, entry 1). The results show clearly that the catalyst is effective for this transformation. Various catalyst concentrations were also tested and use of a higher amount of catalyst does not improve the yield (Table 5, entry13). When comparing with other catalysts, the $CoFe_2O_4$ MNPs give the best result (Table 5, entry13). When comparing with other catalysts, the $CoFe_2O_4$ MNPs give the best result (Table 5, entry13).

Then, the reactions were conducted in the presence of various solvents such as $CHCl_3$, CH_3CN , DMF, CH_3NO_2 , $PhCH_3$ and MeOH (Table 6). A good yield of 96% is obtained in water–ethanol (1:3) (Table 6, entry 7).

To explain the role of microwaves, reactions were compared under reflux conditions (method A) and with microwave irradiation (method B) in H₂O–EtOH (1:3) in the presence of 8 mol% of CoFe₂O₄ MNPs (Table 7). When the reaction is carried out under reflux conditions the reaction proceeds with long times and yields of products are comparatively low, while the same reaction carried under microwave irradiation gives excellent yields of products in short reaction times. Moreover the structures of compounds **5a** and **5c** were confirmed via X-ray crystallographic analysis^[41,42] (Figures 7 and 8) and their close packing structures are shown in Figs 9 and 10.

A plausible reaction mechanism (Scheme 4) is suggested in which the catalyst may activate ethyl pyruvate to react with aniline and give the ethyl 2-anilinoacrylate **3a** and imine **3b**. The reaction between the ethyl 2-anilinoacrylate **3a** and imine **3b** is an intermolecular Mannich reaction in the presence of $CoFe_2O_4$ MNPs to produce intermediate **4**. The final product **5** is afforded from intermediate **4** with elimination of EtOH (Scheme 4).

Recycling of the catalyst is an important process from various aspects such as environmental concerns, costs of the catalyst and its toxicity. Therefore, we studied the recycling of the $CoFe_2O_4$ MNP catalyst for synthesis of tetrahydropyridines and pyrrole derivatives under optimized conditions (Fig. 11). The catalyst was recovered using a magnetic field and was washed with ethanol, dried at 50°C under vacuum to remove residual solvents and reused for subsequent reactions at least five times without observation of appreciable loss in its catalytic activity.

Experimental

Materials

All reagents were of analytical grade and used without further purification. $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ (Sigma-Aldrich) were used as cobalt and iron precursors while NaOH (pellets, 98%, Alfa Aesar) acted as precipitant. All solutions were prepared with doubly distilled water.

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Table 4. Synthesis of tetrahydropyridine derivatives 4a-p									
Product	R	R ₁	Time (min)	Yield (%)	Product	R	R ₁	Time (min)	Yield (%)
4a	Ph	Ph	60	94	4i	4-MePh	Ph	100	89
4b	4-MeOPh	Ph	60	93	4j	Ph	4-ClPh	60	92
4c	2-MeOPh	Ph	70	90	4k	4-MeOPh	4-ClPh	90	89
4d	4-CIPh	Ph	60	94	41	2-MeOPh	4-ClPh	90	85
4e	2-CIPh	Ph	90	91	4m	4-ClPh	4-ClPh	100	90
4f	4-BrPh	Ph	80	92	4n	4-FPh	4-ClPh	90	90
4g	4-FPh	Ph	80	93	4o	4-NO ₂ Ph	4-ClPh	100	92
4h	4-NO ₂ Ph	Ph	70	92	4p	4-MePh	4-ClPh	120	88



 \bigcirc = CoFe₂O₄ MNPs

 $\ensuremath{\textit{Scheme}}$ 2. Possible mechanism for the synthesis of tetrahydropyridine derivatives.



Scheme 3. Synthesis of 1*H*-pyrrole derivatives 5a-j.

Synthesis of CoFe ₂ O ₄ nanop	particles
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To prepare $CoFe_2O_4$ MNPs, in an appropriate ratio, stoichiometric molar amounts of $Co(NO_3)_2$ · $6H_2O$ and $Fe(NO_3)_3$ · $9H_2O$ were each dissolved in 15 ml of distilled water to form a clear solution and mixed together. The mixture was stirred with a magnetic stirrer until the reactants were dissolved completely. During the stirring process, 10 ml of PEG-400 was added dropwise to the solution mixture

Table 5.	Optimization of model reaction using various catalysts ^a				
Entry	Catalyst (mol%)	Time (min)	Yield (%) ^b		
1	Without catalyst	45	Trace		
2	CoCl ₂ ·6H ₂ O (10)	30	30		
3	FeCl ₃ ·6H ₂ O (10)	30	37		
4	CoO powder (10)	30	34		
5	CoO MNPs (10)	30	51		
6	Fe ₃ O ₄ powder (10)	30	63		
7	Fe ₃ O ₄ MNPs (10)	30	82		
8	CoFe ₂ O ₄ powder (10)	30	66		
9	CoFe ₂ O ₄ MNPs (2)	10	72		
10	CoFe ₂ O ₄ MNPs (4)	10	81		
11	CoFe ₂ O ₄ MNPs (6)	10	89		
12	CoFe ₂ O ₄ MNPs (7)	10	92		
13	CoFe ₂ O ₄ MNPs (8)	10	96		
14	CoFe ₂ O ₄ MNPs (9)	10	96		
15	CoFe ₂ O ₄ MNPs (10)	10	96		
^a Reaction conditions: 1a (2 mmol), 2 (2 mmol) and catalyst (0.08 mmol)					

^aReaction conditions: **1a** (2 mmol), **2** (2 mmol) and catalyst (0.08 mmol) in a mixture of water and ethanol (1:3 ratio). ^bIsolated yield based on **5a**.

Table 6.	Optimization of model reaction using various solvents					
Entry	Solvent	Solvent Time (min) Yield (%				
1	CHCl ₃	30	70			
2	CH₃CN	30	78			
3	DMF	30	87			
4	CH ₃ NO ₂	30	82			
5	PhCH ₃	30	78			
6	MeOH	30	83			
7	H ₂ O-EtOH (1:3)	10	96			
^a lsolated yield.						

to serve as a surfactant that covers MNPs and prevents agglomeration. The obtained solution was stirred for an additional 1 h to ensure mixing of PEG with the reactants. After that, the pH of the solution was adjusted to 12. This can be achieved by adding 2 M NaOH drop-by-drop with stirring. After continuous stirring at 500 rpm for 2 h, a homogeneous solution containing hydroxide precipitates of the reactants was obtained. The obtained solutions up to total volume of 80 ml were put in to autoclaves. Finally, the

Table 7. Synthesis of 1H-pyrrole derivatives 5a-j

Product	R	Method A		Method B	
		Time (h)	Yield (%) ^a	Time (min)	Yield (%) ^a
5a	Н	4	89	10	96
5b	4-Br	2	87	10	95
5c	4-Cl	3	86	10	94
5d	4-NO ₂	3	87	15	89
5e	4-OH	5	72	15	88
5f	4-OMe	2	83	10	93
5g	$4-CH_3$	4	85	15	94
5h	naphthyl	5	75	15	87
5i	$2-CH_3$	5	80	15	90
5j	$3-CH_3$	6	77	15	86
^a lsolated yield.					



Figure 9. Close packing structure of compound 5a.



Figure 10. Close packing structure of compound 5c.





Figure 8. X-ray crystal structure of compound 5c.

Scheme 4. Possible mechanism for the synthesis 1*H*-pyrrole derivatives.



Figure 11. Recyclability of $CoFe_2O_4$ MNPs in the model reaction for (a) synthesis of tetrahydropyridine **4a** and (b) synthesis of 1*H*-pyrrole derivative **5a**.



Figure 7. X-ray crystal structure of compound 5a.

autoclaves were left in an oven at 180°C for 24 h and then were allowed to cool to room temperature gradually. The products were centrifuged and washed several times with deionized water, acetone and absolute ethanol. Then the samples were put again in an oven at 90°C to dry for 3 h. The solid-phase samples obtained were ground in a mortar to powder them. Obtained powders were used further for all of the measurements.

General procedure for piperidine derivatives (4a-p)

To a 50 ml round-bottom flask were added aromatic aldehyde (2 mmol), aromatic amine (2 mmol) and ethyl acetoacetate (1 mmol) in the presence of 8 mol% of $CoFe_2O_4$ nanoparticles in water and ethanol (3:1 ratio) as a solvent. Then the reaction mixture was refluxed at 120°C for the stipulated period of time (60–120 min). The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated magnetically. The reaction mixture was allowed to stand overnight. The solid material was filtered off, washed with water, dried and recrystallized from ethanol to furnish pure piperidine derivatives. All products have been reported previously.^[24–32,40]

General procedure for 1H-pyrrole derivatives (5a-j)

Method A

To a 50 ml round-bottom flask were added aromatic amine (2 mmol) and ethyl pyruvate (2 mmol) in the presence of 8 mol% of CoFe₂O₄ nanoparticles in water and ethanol (1:3 ratio) as a solvent. Then the reaction mixture was refluxed at 120°C for the stipulated period of time (2–6 h). The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated magnetically. The reaction mixture was allowed to stand overnight. The solid material was filtered off, washed with water, dried and recrystallized from ethanol to furnish pure 1*H*-pyrrole derivatives. Some products have been reported previously.^[44–46]

Method B

To a 50 ml round-bottom flask were added aromatic amine (2 mmol) and ethyl pyruvate (2 mmol) in the presence of 8 mol% of CoFe₂O₄ nanoparticles in water and ethanol (1:3 ratio) as a solvent. Then the reaction mixture was subjected to microwave irradiation for the stipulated period of time (10–15 min). The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated magnetically. The solid material was obtained quickly and filtered off, washed with water, dried and recrystallized from ethanol to furnish pure 1*H*-pyrrole derivatives. Some products have been reported previously.^[43,44,46]

Instrumentation

The pH of the solutions of the prepared nanoparticles was determined with a single electrode pH meter (Denver Instrument Co., USA). The structures of as-prepared samples were characterized using PXRD. The X-ray patterns at 2 θ from 5° to 80° with a step of 0.05° and a counting time of 2.5 s per step were collected with a Philips X'Pert PRO MPD (PANalytical, The Netherlands) using graphite-monochromatized Cu K α radiation (λ = 1.54184 Å), operating at 45 kV and 40 mA. The samples were gently ground in an agate mortar to minimize the preferred orientation. The instrument resolution (programmable divergent slits) was determined using LaB6 standard reference material (SRM 660a) provided by National Institute of Standards and Technology (NIST), commonly used for calibrating line position and line shape in powder diffractometers. The morphology of samples was studied using field-emission SEM, performed with a JSM-6100 microscope (JEOL, Japan) at an acceleration voltage of 30 kV. The chemical composition of the synthesized nanostructures was also analyzed using an energy-dispersive X-ray analysis unit attached to the SEM instrument. TEM, HR-TEM and SAED studies were performed with a JEOL JEM-2100F transmission electron microscope operated at an accelerating voltage of 200 kV, equipped with a field emission gun and an ultrahigh-resolution pole-piece that provided a point-resolution better than 0.19 nm. The samples for TEM were dispersed in ethanol, sonicated and sprayed on a carbon-coated copper grid and then allowed to air-dry. Finally, a Gatan SOLARUS 950 was used before observation.

All melting points were recorded with a Melt-Temp II melting point apparatus. IR spectra were measured as KBr pellets with a Shimadzu DR-8001 spectrometer. ^[1]H NMR spectra were recorded with a Bruker DRX 400 MHz using tetramethylsilane as an internal reference and DMSO-*d*₆ and CDCl₃ as solvents. All compounds were checked for their purity on TLC plates.

Conclusions

A robust synthesis of $CoFe_2O_4$ highly stable magnetic nanocatalyst has been presented using a combined hydrothermal and coprecipitation process. It is used as an efficient and environmentally friendly nanocatalyst with average particle size of 15 nm for organic reactions. Additionally, the magnetic properties make possible the complete recovery of the catalyst by means of an external magnetic field, and it could be reused up to five times without any significant loss of the initial catalytic activity. These advantages become even more attractive if such reactions can be conducted in aqueous media.

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Supporting information

Additional supporting information may be found in the online version of this article at the publisher's web site.

Figure S1: FT-IR spectra for the prepared CoFe₂O₄ nanoparticles. **Figure S2:** TG/DTG curves for the prepared CoFe₂O₄ nanoparticles.