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This catalyst was easily prepared and showed excellent level of reusability.

Short Communication

Synthesis and characterization of sulfonated-phenylacetic acid coated Fe₃O₄ nanoparticles as a novel acid magnetic catalyst for Biginelli reaction

Farzad Zamani *, Elham Izadi

Department of Chemistry, Shahreza Branch, Islamic Azad University, Shahreza 31186145, Isfahan, Iran Laboratory of Applied Chemistry, Central Laboratory Complex, Isfahan Science and Technology Town, Isfahan University of Technology, Isfahan 8415683111, Iran

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ABSTRACT

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1. Introduction

Organic shell/inorganic core composite particles have received a lot of attention in a wide range of industrial fields due to their functional properties, high dispersibility and stability after a certain thickness of polymer coating [1]. The core/shell nanostructure is an ideal composite system that combines the advantages of both the core and the shell to offer enhanced physical and chemical properties. In recent years, magnetic nanoparticles (MNPs) (e.g. Fe₃O₄) have been extensively investigated as inorganic cores for the synthesis of organic/inorganic core–shell composite particles, due to their potential applications in many industrial and biological fields [2]. Fe₃O₄ nanoparticles are naturally hydrophilic because of the existence of plentiful hydroxyl groups on the particle surface. Since, they are prone to aggregate and their dispersion in an organic media is difficult, the surface coating or modification of iron oxide nanoparticles is very important in many applications.

Over the last decade, magnetic organic–inorganic nanocomposites have become interesting as magnetic catalysts in both academic and industrial fields. The use of these magnetic nanoparticle catalysts can address the isolation and recycling problem encountered in many heterogeneous and homogenous catalytic reactions. Most importantly, the magnetic-supported catalysts show not only high catalytic activity but also a high degree of chemical stability and they do not swell in organic solvents [3–5]. They can also be recovered with an external magnetic field and their catalytic efficiency remains after many repeated reactions [6].

In this paper, we wish to report the synthesis and characterization of sulfonated-phenylacetic acid coated on

Fe₃O₄ nanoparticles by a simple method. This catalyst was effectively employed as a novel acid magnetic catalyst

for the one-pot synthesis of different 3,4-dihydropyrimidin-2(1H)-ones under mild and solvent-free conditions.

Dihydropyrimidinones (DHPMs) and their derivatives attracted considerable interest due to their wide spectra of biological activities [7–9]. The direct synthesis involves the condensation between $\alpha_{,}\beta_{-}$ ketoesters, aldehydes and ureas or thioureas in the presence of either Lewis or mineral acids, which was originally reported by P. Biginelli in 1893 [10]. However, this method suffers from low yields of products, strong acidic condition and difficult isolation. Over the last decade, numerous catalytic methods have been employed in order to improve the main drawbacks of the Biginelli reaction [11–20].

In continuing our efforts towards the development of efficient and environmentally benign heterogeneous catalysts [21–23], herein, sulfonated-phenylacetic acid coated Fe_3O_4 nanocomposite (Fe_3O_4 / PAA-SO₃H) was prepared as a highly efficient acid magnetic catalyst by a simple method. The main goal of this catalytic synthesis was to introduce a novel and efficient magnetic nanocomposite to expand the use of these types of composites for organic reactions. In order to investigate the catalytic activity of this magnetic catalyst, one-pot synthesis of different 3,4-dihydropyrimidin-2(1H)-ones via three-component reaction was chosen as important synthetic compounds.

2. Experimental

2.1. Catalyst preparation

The procedure for preparing sulfonated-phenylacetic acid coated $\rm Fe_3O_4$ nanocomposite includes two steps which were described as follows.





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^{*} Corresponding author at: Department of Chemistry, Shahreza Branch, Islamic Azad University, Shahreza 31186145, Isfahan, Iran. Tel.: +98 311 3865355; fax: +98 311 3869714.

E-mail address: fzamani@iaush.ac.ir (F. Zamani).

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In the first step, phenylacetic acid coated Fe₃O₄ nanocomposite was synthesized by the method as reported previously [24]. FeCl₃.6H₂O (13 g) and FeCl₂.4H₂O (4.8 g) were dissolved in 100 mL deionized water and stirred at 40 °C for 15 min under nitrogen atmosphere. Then, 8 mL phenylacetic acid (PAA) was added to the above mixture and PH was adjusted to 11 with NH₄OH solution (25 wt.%). The suspension was then refluxed at 100 °C for 6 h under nitrogen atmosphere with vigorous stirring. Finally, the obtained nanocomposite was separated from the aqueous solution by magnetic decantation, washed several times with distilled water and then dried in a vacuum oven overnight to yield Fe₃O₄/PAA.

In the second step, the Fe₃O₄/PAA was sulfonated using various amounts of chlorosulfonic acid (10.5, 12.5, 14.5, 16.5, 18.5 and 20.5 mmol). The Fe₃O₄/PAA composite (1 g) was dispersed in 10 mL of acetonitrile in a three-neck flask glass reactor. Chlorosulfonic acid was added drop-wise into the mixture at room temperature. Upon completion of the addition, the mixture was stirred for 6 h under N₂ atmosphere at room temperature. The resulted magnetic nanocomposite was separated from the suspension by an external magnet, washed several times with acetonitrile and anhydrous ethanol and dried at 60 °C to give Fe₃O₄/PAA-SO₃H.

The content of acid sites of Fe₃O₄/PAA-SO₃H nanocomposite was estimated by back titration using HCl (0.337 N). 10 mL of NaOH (0.130 N) was added to 0.1 g of these composites and stirred for 30 min. The catalysts were separated and washed with deionized water. The excess amount of NaOH was titrated with HCl (0.337 N) in the presence of phenolphthalein as indicator. The acid site contents were 2.14, 2.58, 2.93, 3.32, 3.71 and 3.76 mmol g⁻¹ for 10.5, 12.5, 14.5, 16.5, 18.5 and 20.5 mmol of used chlorosulfonic acid, respectively.

2.2. Catalyst characterization

The crystalline structures of the samples were evaluated by X-ray diffraction (XRD) analysis on a Bruker D8 Advance diffractometer with CuK_{α} radiation at 40 kV and 20 mA. Fourier transform infrared (FT-IR) spectra were recorded with a Perkin Elmer 65 spectrometer in the range of 400–4000 cm⁻¹. Transmission electron microscopy (TEM) analysis was performed on a Phillips CM10 microscope at an accelerating voltage of 200 kV. Magnetization measurements were carried out on a BHV-55 vibrating sample magnetometer (VSM). Thermal stability of the catalyst was investigated by Thermogravimetric analysis (TGA, TSTA Type 503) at a heating rate of 10 °C/min under nitrogen atmosphere.

2.3. General procedure for Biginelli reaction catalyzed by Fe₃O₄/PAA-SO₃H

In a typical procedure, a mixture of aldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (or thiourea) (1.2 mmol) and Fe_3O_4 /PAA-SO_3H (0.06 g) was placed in a round-bottom flask. The suspension was stirred at room temperature. Completion of the reaction was monitored by Thin Layer Chromatography (TLC). After completion of the reaction, the catalyst was separated from the solid crude product using an external magnet. The precipitated solid was then collected and recrystallized from ethanol to afford the pure product. The product was identified with ¹H NMR, ¹³C NMR and FT-IR spectroscopy techniques.

3. Results and discussion

3.1. Catalyst characterization

Crystalline phases of the Fe₃O₄/PAA-SO₃H nanocomposite before calcination and after calcination (at 600 °C for 3 h) were identified by XRD and the resultant patterns were shown in Fig. 1. The XRD patterns indicate that for both products (Fig. 1a,b) the diffraction peaks at 20 of 30.1°, 35.4°, 43.1°, 53.4°, 56.9° and 62.5° correspond to the

Fig. 1. X-ray powder diffraction patterns of $Fe_3O_4/PAA-SO_3H$ nanocomposite, (a) uncalcined and (b) calcined form (at 600 °C for 3 h).

spinel structure of Fe₃O₄ [25], which can be assigned to the diffractions of the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) faces of the crystals, respectively. In addition, the XRD patterns represent similar diffraction peaks which indicate that the coating agent does not significantly affect the crystal structure of the magnetite nanoparticles. The XRD results indicate that the Fe₃O₄ particles were successfully coated with the phenylacetic acid.

Fig. 2 depicts the FT-IR spectrum of Fe₃O₄/PAA-SO₃H nanocomposite. The adsorption peak at 592 cm^{-1} is the characteristic absorption of Fe-O bond which confirms the presence of Fe_3O_4 nanoparticles. The absorption peaks at 3000–3100 cm^{-1} and 1688–1850 cm^{-1} correspond to C-H of the benzene ring. The absorption peaks at 1461 and 1605 cm^{-1} correspond to the C–C bonds in the benzene ring, and the absorption peaks at 700 and 755 cm^{-1} are caused by the bending vibration of the C–H on the benzene ring [26]. It is also clear that the strong C=O band of carboxyl group, which is generally present at 1650 cm^{-1} , was absent in the spectrum of Fe₃O₄/PAA-SO₃H. Instead, two characteristic bands appeared at 1569 and 1512 cm⁻¹, which were ascribed to COO_{as}^{-} and COO_{s}^{-} stretch of carboxyl group [24]. This result can be indicated that the bonding pattern of the carboxylic acids on the surface of Fe₃O₄ nanoparticles was a combination of molecules bonded symmetrically and molecules bonded at an angle to the surface [24]. The bands at 2800–3000 cm⁻¹ were attributed to the asymmetric and symmetric CH₂ stretching vibrations. In addition, two bands at 1381 cm⁻¹ and 1245 cm⁻¹ can be seen which are related to grafted sulfonic acid groups on rings [27]. Based on the above observations, it can be concluded that the Fe₃O₄ nanoparticles





and sulfonated-phenylacetic acid exist in the composite particles. Furthermore, it has been reported that the wave number separation between the COO_{as} and COO_{s} IR bands can be used to distinguish the type of the interaction between the carboxylate head and the metal atom [28]. Since the wave number separation between the COO_{as} and COO_{s} bands in the spectrum of Fe₃O₄/PAA-SO₃H is 57 cm⁻¹ (1569–1512 = 57 cm⁻¹), it can be concluded that the interaction between the COO⁻ group and the Fe atom was covalent and bidentate [24].

The morphology of the nanocomposite was observed on transmission electron microscopy. Fig. 3 displays the TEM micrograph of $Fe_3O_4/PAA-SO_3H$ nanocomposite. As can be seen, the nanocomposite has spherical morphology with the average particle size of about 15 nm (Fig. 3). This observation from the TEM image indicates that the synthesized nanocomposite has nearly single crystalline character.

The magnetic properties of the Fe_3O_4 /PAA-SO₃H nanocomposite before calcination and after calcination (at 600 °C for 3 h) were measured via vibrating sample magnetometer (VSM) at room temperature (Fig. 4). The hysteresis loops show the superparamagnetic behavior for the uncalcined and calcined in which the remanence and the coercivity are close to zero [29]. It can be also seen that the saturation magnetization (Ms) values of the samples are 58.7 emu/g and 68.9 emu/g for the uncalcined and calcined products, respectively. By comparison of two samples, the calcined composite has higher magnetization values and it is possibly related to the removal and reduction of non-magnetic layers on the magnetic nanoparticle which results a greater magnetization [24]. From the results of the magnetic properties and TEM analysis, the presence of sulfonatedphenylacetic acid around the Fe₃O₄ nanoparticles can be further proved.

In order to investigate thermal stability of the Fe₃O₄/PAA-SO₃H, the TG curve of the nanocomposite was represented in Fig. 5. It can be observed that the magnetic catalyst shows two weight loss steps in the temperature range of TG analysis (Fig. 5). The first weight loss at <150 °C is due to the desorption of physically adsorbed water and the second step at about 250 °C to nearly 450 °C is attributed to the decomposition of coating layer in the nanocomposite. According to the TG analysis, the Fe₃O₄/PAA-SO₃H has a good thermal stability which is possibly due to the strong interaction between PAA and Fe₃O₄.

3.2. Catalytic activity

Having synthesized and characterized the Fe₃O₄/PAA-SO₃H, its role as a catalyst was evaluated for the synthesis of dihydropyrimidinones in Biginelli reaction. A reaction model among benzaldehyde, ethyl acetoacetate and urea as the substrates in Biginelli reaction was

Fig. 3. TEM micrograph of Fe₃O₄/PAA-SO₃H nanoparticles.

50 nm



Fig. 4. Room temperature magnetization curves of Fe $_3O_4$ /PAA-SO $_3H$ nanocomposite, (a) calcined and (b) uncalcined form (at 600 °C for 3 h).

investigated over the catalyst with the best content of acid sites (reported in the Experimental section, 3.71 mmol/g) at room temperature. In order to optimize the reaction conditions and obtain best catalytic activity, this reaction was conducted in different reaction parameters such as solvent and amount of catalyst.

As far as the effect of solvent is concerned, the model reaction was carried out in several solvents as well as solvent-free condition to investigate the efficiency of the catalyst (Table 1). As can be seen, the best yield was obtained when the reaction was performed under solventfree condition (48%). Moreover, the effect of catalyst amount on the Biginelli reaction was also carried out by different amounts of the catalyst (Table 1). It was observed that while the amount of catalyst increased from 0.03 to 0.06 g, the product yield raised significantly from 48% to 90%, which is probably due to the availability of more acid sites. Since then, the percentage of yield remained almost stable between 0.06 g and 0.07 g. In addition, the major by-product in the lower yields was the α -benzylidene- β -keto ester derivative which was produced through Knoevenagel condensation of benzaldehyde and ethyl acetoacetate. According to the results, 0.06 g was chosen as the optimum amount of catalyst, due to the best yield and selectivity, for the further steps.



Fig. 5. TG curve of Fe₃O₄/PAA-SO₃H nanocomposite.

Table I	Table	1
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Effects of different solvents and amounts of catalyst on the	e Biginelli reaction in the	presence of Fe ₃ O ₄ /PAA-SO ₃ H. ⁴
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Solvent	Catalyst (g)	Amount of acid sites (mmol) ^b	Benzaldehyde conversion (%) c	Ethyl acetoacetate conversion (%) $^{\rm c}$	By-product yield (%) ^d	Yield (%) ^e
Water	0.03	0.1113	18	15	<5	12
Acetonitrile	0.03	0.1113	39	33	8	32
Ethanol	0.03	0.1113	35	30	6	28
Toluene	0.03	0.1113	25	22	12	10
Solvent-free	0.03	0.1113	51	50	Trace	48
Solvent-free	0.04	0.1484	69	65	Trace	63
Solvent-free	0.05	0.1855	87	85	Trace	81
Solvent-free	0.06	0.2226	95	94	Trace	90
Solvent-free	0.07	0.2597	97	93	Trace	91

^a Reaction conditions: benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.2 mmol), reaction time = 120 min, room temperature.

^b Amount of acid sites in the used catalyst (determined by back titration using HCl (0.337 N)).

^c Determined by GC analysis.

^d The major by-product was α -benzylidene- β -keto ester derivative (determined by GC analysis).

^e Isolated vield.

In the view of industrial purposes, reusability of the catalyst was tested by carrying out repeated runs of the reaction on the same batch of the catalyst in the case of the model reaction. In order to regenerate the catalyst, after each cycle, it was separated by a magnet and washed several times with deionized water and ethanol. Then, it was dried in oven at 60 °C and used in the Biginelli reaction. The yields of the model reaction observed in the first to sixth reuses were 90%, 90%, 88%, 88%, 88% and 87% respectively, demonstrating high recyclability of the Fe₃O₄/PAA-SO₃H magnetic catalyst. Moreover, after recycling for six times, Fe₃O₄/PAA-SO₃H exhibited a little decrease in acid concentration from 3.71 mol/g (fresh) to 3.56 mmol/g (used).

Biginelli reactions of various aldehydes with ethyl acetoacetate and urea (or thiourea) in the presence of $Fe_3O_4/PAA-SO_3H$ were investigated (Table 3). In all cases, the three-component reaction proceeded smoothly to give the corresponding 3,4-dihydropyrimidin-2(1H)-ones/thiones in moderate to good yields. The reaction with aromatic aldehydes carrying electron-withdrawing or electron-donating groups gave the corresponding products in good yields and high purity. Thiourea also provided the Biginelli products in reasonable yields (Table 3, entries 6–10).

Table 2

Solvent-free Biginelli reactions over Fe₃O₄/PAA-SO₃H.^a

R	Х	Product ^b	Time (min)	Yield (%) ^c
Н	0	4a	120	90
4-OMe	0	4b	150	85
4-NO ₂	0	4c	115	92
2-Cl	0	4d	130	86
2-OH	0	4e	150	82
Н	S	4f	130	82
4-OMe	S	4g	185	79
4-NO ₂	S	4h	125	85
2-Cl	S	4i	155	81
2-OH	S	4j	185	75
	R H 4-OMe 4-NO ₂ 2-Cl 2-OH H 4-OMe 4-NO ₂ 2-Cl 2-OH	R X H O 4-OMe O 4-NO2 O 2-Cl O 2-OH O H S 4-OMe S 4-OMe S 2-OH S 2-Cl S 2-Cl S 2-OH S	R X Product ^b H O 4a 4-OMe O 4b 4-NO2 O 4c 2-CI O 4d 2-OH O 4d 4-OMe S 4f 4-OMe S 4g 4-NO2 S 4h 2-OH S 4j	RXProductbTime (min)H04a120 $4-OMe$ 04b150 $4-NO_2$ 04c115 $2-Cl$ 04d130 $2-OH$ 04e150HS4f130 $4-OMe$ S4g185 $4-OMe$ S4h125 $2-Cl$ S4i155 $2-OH$ S4j185

^a Reaction conditions: benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea or thiourea (1.2 mmol), catalyst (0.06 g, Fe₃O₄/PAA-SO₃H), room temperature.

^b Products were characterized by FT-IR, ¹H NMR and ¹³C NMR spectroscopies.

^c Isolated yield.

A comparative study was performed for the use of $Fe_3O_4/PAA-SO_3H$ with some of the reported catalysts for the Biginelli reaction (Table 2). The reaction with different catalysts required high reaction temperature compared with $Fe_3O_4/PAA-SO_3H$ at room temperature. Moreover, in most methods, the reaction was performed in solvent such as dioxane, acetonitrile, ethanol and toluene. Thus, $Fe_3O_4/PAA-SO_3H$ promoted the reaction more effectively under mild conditions than the other catalysts and it could be considered as one of the best choice for selecting an environmentally benign and user-friendly catalyst.

4. Conclusion

A novel magnetic organic–inorganic nanocomposite (Fe_3O_4 / PAA-SO_3H) was prepared by a very simple and inexpensive method. This new acid magnetic catalyst can practically replace soluble acids in view of the following advantages: a) high catalytic activity under mild reaction conditions; b) easy separation of the catalyst after reaction by an external magnet; and c) reusability of the catalyst for several times without any significant loss in the yield of the reaction. Moreover, we have developed a facile, convenient and environmentally benign

Table 3

Biginelli reaction with benzaldehyde, ethyl acetoacetate and urea with different catalysts.

Entry	Catalyst	Time (min)	Yield (%)	Temperature (°C)	Solvent	Ref.
1	Trichloroisocyanuric acid	720	94	Reflux	Ethanol	[20]
2	40% PW/SiO ₂	60	95	80	Acetonitrile	[19]
3	Imidazol-1-yl-acetic acid	35	92	Reflux	Water	[15]
4	Tetra-butyl ammonium bromide	40	96	100	KOH	[18]
5	Bentonite/PS-SO ₃ H	30	89	120	Solvent-free	[11]
6	PS-PEG-SO ₃ H	600	86	80	Dioxane	[14]
7	SiO ₂ -KAl(SO ₄) ₂ .12H ₂ O	240	92	80	Solvent-free	[13]
8	MPMCM-41	360	92	Reflux	Toluene	[16]
9	$Cu(OTf)_2$	60	65	100	Ethanol	[17]
10	Fe ₃ O ₄ /PAA-SO ₃ H	120	90	Room temperature	Solvent-free	This work

one-pot synthesis of different 3,4-dihydropyrimidin-2(1H)-ones under mild conditions using $Fe_3O_4/PAA-SO_3H$ in very good yields.

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