FULL PAPER

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Application of $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^-$ as heterogeneous and recyclable nanocatalyst for synthesis of polyhydroquinoline derivatives

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Funding information Payame Noor University Research Council Four-component condensation reaction of aromatic aldehydes, dimedone, ethyl acetoacetate and ammonium acetate in the presence of a catalytic amount of ionic liquid on silica-coated Fe_3O_4 nanoparticles as a heterogeneous, recyclable and very efficient catalyst provided the corresponding polyhydroquinoline derivatives in good to excellent yields in ethanol under reflux condition. The $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^-$ catalyst was characterized using various techniques such as scanning electron microscopy, powder X-ray diffraction, thermogravimetric analysis, vibrating sample magnetometry and Fourier transform infrared spectroscopy. Furthermore, the recovery and reuse of the catalyst were demonstrated seven times without detectable loss in activity.

KEYWORDS

 $[Fe_{3}O_{4}@SiO_{2}@(CH_{2})_{3}Py]HSO_{4}^{-}, aldehydes, dimedone, ethyl acetoacetate, polyhydroquinoline$

1 | INTRODUCTION

Multicomponent reactions play an important role in modern synthetic organic chemistry because of the discovery of compounds in medicinal chemistry or combinatorial chemistry.^[1] The advantages of these multicomponent reactions include allowing compounds to be synthesized in a few steps, formation of new bonds in one pot with high atom economy, simplified purification, reduction of byproducts formed and ease of workup.^[2]

Polyhydroquinoline derivatives are important compounds in organic chemistry due to their various pharmaceutical properties and biological activities such as cardiovascular, hepatoprotective, bronchodilator, vasodilator, geroprotective, antitumour and antiartherosclerotic activities.^[3–8] Despite of a variety of applications for polyhydroquinoline derivatives, very few approaches have been established for the synthesis of these compounds. Substituted polyhydroquinolines are usually prepared by cyclization reactions (Hantzsch ring closure of aldehydes,

β-ketoester and ammonia).^[9] However, this method has some disadvantages like the harsh conditions of the reaction, tedious workup procedure, low yields, use of large quantities of volatile organic solvent and long eaction times. In recent years, more efficient catalysts have been reported for the synthesis of veast,^[10] polyhydroquinolines, such as baker's Ce(NH₄)₂(NO₃)₆,^[11] glycine,^[12] grinding,^[13] hafnium (IV) bis(perfluorooctanesulfonyl)imide complex in fluorous media, $^{[14]}$ Ni_{0.35}Cu_{0.25}Zn_{0.4}Fe₂O₄ magnetic nanoparticles (MNPs),^[15] Hy-Zeolite,^[16] Cu–*S*-(propyl)-2-aminobenzothioate,^[17] L-proline and derivatives,^[10] metal triflates,^[18] molecular iodine,^[19] Fe₃O₄-adenine-Ni,^[20] 4,4'-(butane-1,4-diyl)bis(1-sulfo-1,4-diazabicyclo[2.2.2] octane-1,4-diium)tetrachloride,^[21] PTSA,^[22] solar thermal energy,^[23] MCM-41@Serine@Cu(II),^[24] MNPs/DETA-SA,^[25] Ni-Cu-Mg Fe₃O₄ MNPs,^[26] ILOS@Fe/TSPP,^[27] alginic acid,^[28] Ni@IL-OMO,^[29] V-TiO₃^[30] and melamine trisulfonic acid.^[31] Furthermore, soluble metal catalysts often require a tedious catalyst separation step. The search

for alternative catalysts based on heterogeneous, cheap and environmentally benign metals is thus an increasingly important task.

These heterogeneous catalysts are recyclable, nontoxic, cleaner and involve easier workup methods. Recently, MNPs have shown great potential via recycling and recovery of the catalysts using an external magnetic field.^[32] Coating of MNPs prevents their aggregation in solution and enhances chemical stability.^[33] Also, the design of ionic liquid allows for the creation of additional functionalities into the ionic liquid structure with physical or chemical properties. The combination of functionalized ionic liquid and MNPs provides suitable heterogeneous systems.^[34]

In the work reported herein, we tried to synthesize a novel catalyst by immobilization of an ionic liquid on silica-coated MNPs as a support. Thus, we report the synthesis of polyhydroquinolines in the presence of the magnetic nanocatalyst.

2 | MATERIALS AND METHODS

2.1 | General

The reagents and solvents used in this work were obtained from commercial companies and were used without further purification. Analytical TLC was performed using Merck silica gel GF₂₅₄ plates. All products are known and were characterized by comparison of their spectral (NMR) and physical data with those of authentic samples. X-ray diffraction (XRD) patterns were recorded with a Philips X'pert powder X-ray diffractometer (Co K_{q} radiation = 0.1540 nm), scanning at 2 min⁻¹ from 10° to 100°. Scanning electron microscopy (SEM) images were recorded with a TESCAN MIRA3. Thermogravimetric analysis (TGA) was conducted with a Shimadzu DTG-60 instrument. NMR spectra were recorded with a Bruker FX 400Q NMR spectrometer. The supermagnetic properties of the nanocatalyst were measured with a vibrating sample magnetometry (VSM) instrument (MDKFD) operating at room temperature.

2.2 | General procedure for preparation of novel $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^-$

Fe₃O₄ nanoparticles were synthesized according to reported literature.^[35] FeCl₃·6H₂O (0.216 mol, 5.84 g) and FeCl₂·4H₂O (0.0108 mol, 2.17 g) were dissolved into 100 ml of deionized water at 80 °C followed by addition of 10 ml of aqueous NH₃ (25%) under vigorous stirring and nitrogen protection. The obtained MNPs were separated from solution using a powerful magnet and rinsed three times with 200 ml of deionized water. Finally, the SAJJADIFAR AND AZMOUDEHFARD

In a 250 ml flask, Fe_3O_4 nanoparticles (2 g) were dispersed in 50 ml of distilled water and 20 ml of ethanol for 20 min. Then, poly(ethylene glycol) 400 (PEG) (3.36 g), 10 ml of aqueous NH₃ (25%) and tetraethyl orthosilicate (TEOS; 2 ml) were added to the mixture for 38 h. The obtained brown MNPs were separated from solution using a powerful magnet and rinsed with ethanol. Finally, the products were dried at room temperature for 48 h to afford Fe_3O_4 @SiO₂.

In a 250 ml flask, $Fe_3O_4@SiO_2$ (1.5 g) was dispersed in 50 ml of toluene for 30 min. (3-Chloropropyl) trimethoxysilane (2.5 ml) was added to $Fe_3O_4@SiO_2$ under vigorous stirring and nitrogen protection at 40 °C for 8 h. The obtained MNPs were separated from solution using a powerful magnet and rinsed with ethanol. Finally, the products were dried at 50 °C for 48 h to afford $Fe_3O_4@SiO_2@(CH_2)_3$ -Cl.

In a 250 ml flask, $Fe_3O_4@SiO_2@(CH_2)_3-Cl$ (5 g) dispersed in 50 ml of toluene and pyridine (2 ml) were added under reflux conditions for 12 h. The obtained MNPs were separated from solution using a powerful magnet and rinsed with CH_2Cl_2 . Finally the products were dried to afford $[Fe_3O_4@SiO_2@(CH_2)_3Py]Cl^-$. Then $[Fe_3O_4@SiO_2@(CH_2)_3Py]Cl^-$ (5 g) was dispersed in 10 ml of CH_2Cl_2 , and H_2SO_4 (1 ml) was added dropwise and stirred under reflux conditions for 24 h. The obtained MNPs were separated from solution using a powerful magnet and rinsed with ethanol. Finally the products were dried to afford $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^-$.

2.3 | General procedure for preparation of polyhydroquinolines

A mixture of aldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1 mmol), ammonium acetate (1.2 mmol) and $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^-$ (25 mg) in ethanol (5 ml) was stirred under reflux condition for the appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated via an external magnetic. The reaction mixture was dissolved in ethyl acetate and poured into water. The resulting precipitate was filtered and was purified by recrystallization from ethanol to afford the desired compound in pure form.

3 | **RESULTS AND DISCUSSION**

3.1 | Characterization

 Fe_3O_4 nanoparticles were coated using TEOS. The successfully generated $Fe_3O_4@SiO_2$ nanostructure was



SCHEME 1 Preparation of $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^-$ and its application for the synthesis of polyhydroquinoline derivatives

modified using (3-chloropropyl)trimethoxysilane and pyridine. This was followed by sulfonation with H_2SO_4 to afford [Fe₃O₄@SiO₂@(CH₂)₃Py]HSO₄⁻ with a core-shell nanostructure as a novel ionic liquid magnetic nanocatalyst (Scheme 1). The catalytic activity of [Fe₃O₄@SiO₂@(CH₂)₃Py]HSO₄⁻ was investigated for the synthesis of polyhydroquinoline derivatives.

The synthesized $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^-$ catalyst was characterized using SEM, powder XRD, TGA, VSM and Fourier transform infrared (FT-IR) spectroscopy. SEM images were applied to verify the nanostructure of $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^-$. The nanostructure morphology exhibited a spherical shape and the average particle size of the catalyst was about 14–21 nm (Figure 1).



FIGURE 1 SEM image of [Fe₃O₄@SiO₂@(CH₂)₃Py]HSO₄⁻

To investigate the presence of organic structure on the Fe_3O_4 MNPs, TGA was performed. The TGA curve of $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^-$ shows a mass loss of the organic functional groups as it decomposes upon heating. The TGA curve shows a small amount of weight



FIGURE 2 TGA of [Fe₃O₄@SiO₂@(CH₂)₃Py]HSO₄⁻



FIGURE 3 Powder XRD pattern of [Fe₃O₄@SiO₂@(CH₂)₃Py] HSO₄⁻

loss below 100 °C corresponding to removal of adsorbed solvents. The mass loss of about 30% of organic functional groups has been reported to desorb at temperatures above 200 °C. A weight loss at about 500 °C is related to the phase changes of Fe_3O_4 MNPs (Figure 2).

Powder XRD is an effective technique used to identify the magnetite crystal phase in the $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^-$ nanocatalyst. The XRD diffraction pattern of $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^$ shows several peaks at $2\theta = 30.2^\circ$, 35.6° , 43.3° , 54.1° , 57.4° and 63.1° , which are assigned to the (220), (311), (400), (422), (511) and (440) crystallographic faces of magnetite. This pattern is in good agreement with the stan-



FIGURE 4 VSM analysis of [Fe₃O₄@SiO₂@(CH₂)₃Py]HSO₄⁻



dard Fe₃O₄ XRD pattern^[36] (Figure 3). The crystallite size was determined from Scherrer's equation, $D = k\lambda/\beta \cos \theta$, and it was found to be about 20 nm.

The magnetic property of the nanocatalyst was investigated using VSM. The magnetization curve for the $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^-$ nanoparticles is shown in Figure 4. From the VSM analysis, the saturation magnetization of $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^-$ is about 15.12 emu g⁻¹, which is much lower than that of bare Fe_3O_4 nanoparticles (about 39.1 emu g⁻¹) reported in the literature^[17].

Figure 5 shows the FT-IR spectra of Fe_3O_4 nanoparticles, $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2@(CH_2)_3$ -Cl, $[Fe_3O_4@SiO_2@(CH_2)_3Py]Cl^-$ and $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^-$ nanoparticles. The FT-IR spectrum of Fe_3O_4 nanoparticles (Figure 5a) shows a strong band at 3383 cm⁻¹, which corresponds to OH bonds linked to the surface of iron atoms. Bands of stretching vibration of Fe&bond;O bonds appear at

FABLE 1	Influence	of solvent	in	synthesis	of
oolyhydroqu	unoline ^a				

Entry	Solvent	Time (min)	Yield (%) ^b
1	H ₂ O	90	41
2	PEG	90	84
3	MeCN	90	46
4	EtOAc	90	32
5	EtOH	90	98
6	Solvent-free	90	71

^aConditions of reaction: benzaldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1 mmol), ammonium acetate (1.2 mmol), catalyst (25 mg), solvent (5 ml) and 80 °C.

^bIsolated yield.

TABLE 2	Influence of temperature and amount of catalyst in
synthesis of	polyhydroquinoline ^a

Entry	Amount of catalyst (mg)	Temperature (°C)	Time (min)	Yield (%) ^b
1	10	Reflux	90	54
2	15	Reflux	90	69
3	20	Reflux	90	80
4	25	Reflux	90	98
5	30	Reflux	85	99
6	25	60	100	64
7	25	40	100	29

^aConditions of reaction: benzaldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1 mmol), ammonium acetate (1.2 mmol), catalyst and EtOH (5 ml).

^bIsolated yield.

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TABLE 3 Synthesis of polyhydroquinolines in presence of [Fe₃O₄@SiO₂@(CH₂)₃Py]HSO₄^{-a}

Entry	Aldehyde	Product	Time (min)	Yield (%) ^b	M.p. (°C)
1	CHO	O O OEt	90	98	203-204 ^[37]
2	CHO Cl	O CI O O O O O O Et	80	95	245-246 ^[38]
3	CHO OMe	OMe O O O O O O O O Et	100	91	257–259 ^[37]
4	CHO OH	OH O O O O O O O Et	140	90	230-231 ^[37]
5	CHO OEt	OEt O OEt O OEt OEt	105	93	175–178
6	CHO Br	Br O O O C O C O Et	85	95	252–253 ^[37]
7	СНО	OEt O O O O O O O O O O O O O O O O O O	180	83	303-306
8	СНО	OH O O O O O O O Et	125	90	230-232 ^[39]
9			115	90	198–199 ^[40]

(Continues)

TABLE 3 (Continued)



^aConditions of reaction: benzaldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1 mmol), ammonium acetate (1.2 mmol), catalyst (25 mg), EtOH (5 ml) and reflux condition.

^bIsolated yield.

444 and 579 cm⁻¹ in all the FT-IR spectra. The presence of (3-chloropropyl)trimethoxysilane is confirmed by a characteristic peak at 1070–1100 cm⁻¹ which is ascribed to the Fe&bond;O&bond;Si stretching vibration and C&bond;H stretching vibration band appears at 2973 cm⁻¹.

3.2 | Catalytic studies

After characterization of the catalyst, to find the optimal conditions, $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^-$ as a nanocatalyst was examined in the synthesis of polyhydroquinoline derivatives. In this respect, the cyclocondensation of benzaldehyde, dimedone, ethyl acetoacetate and ammonium acetate was investigated as

a model reaction under various conditions. The effects of solvent, catalyst amount and temperature were examined. Initially, we used solvents such as H_2O , PEG, MeCN, EtOAc and EtOH. EtOH was the most effective solvent for this reaction, and the polyhydroquinoline was obtained in 98% yield (Table 1, entry 6).

In the next stage, the effects of temperature and amount of catalyst in the progress of the reaction were examined. According to Table 2, the best result was obtained under reflux conditions. Meanwhile, the amount of catalyst showed a significant effect on the product yield. Best results were obtained in the presence of 25 mg of catalyst (Table 2, entry 4).

To generalize this methodology, we synthesized a series of polyhydroquinolines in the presence of $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^-$ as homogeneous



SCHEME 2 Plausible reaction mechanism of $[Fe_3O_4@SiO_2@(CH_2)_3Py]$ HSO_4^- -catalysed polyhydroquinoline synthesis



FIGURE 6 Recycling experiment of [Fe₃O₄@SiO₂@(CH₂)₃Py]HSO₄⁻ in condensation of benzaldehyde, dimedon, ethyl acetoacetate and ammonium acetate

catalyst under reflux conditions. Many types of aldehydes having electron-donating and electron-withdrawing moieties were used to obtain the corresponding polyhydroquinolines (Table 3).

In Scheme 2, a plausible reaction mechanism involving the [Fe₃O₄@SiO₂@(CH₂)₃Py]HSO₄⁻ catalyst is presented. The first step is protonation of the carbonyl group in aldehyde. The role of the catalyst comes in the Knoevenageltype condensation of aldehydes with active methylene compounds and in the Michael-type addition of intermediates to give final product.

The recyclability of the catalyst was examined for the reaction of benzaldehyde with dimedon, ethyl acetoacetate and ammonium acetate as a model reaction in ethanol using 25 mg of [Fe₃O₄@SiO₂@(CH₂)₃Py] HSO₄⁻ catalyst. Upon completion of the reaction, [Fe₃O₄@SiO₂@(CH₂)₃Py]HSO₄⁻ was conveniently removed from the product using an external magnet, and the remaining solution was decanted. The recovered catalyst was washed using ethanol to remove residual product

TABLE 4 Comparison results for [Fe₃O₄@SiO₂@(CH₂)₃Py] HSO₄⁻ with those for other catalysts

Entry	Catalyst	Time (min)	Yield (%) ^a	Ref.
1	Pd-SBTU@Fe ₃ O ₄	90	98	[41]
2	GSA@MNPs	240	90	[42]
3	Cu-SPATB/Fe ₃ O ₄	150	89	[17]
4	Fe ₃ O ₄ -SA-PPCA	120	97	[43]
5	Cu (II)/L-His@Fe ₃ O ₄	95	92	[44]
6	Boehmite-SSA	215	94	[45]
7	Ga(OTf) ₃	300	89	[46]
8	[Fe ₃ O ₄ @SiO ₂ @(CH ₂) ₃ Py] HSO ₄ ⁻	90	98	This work

and then dried under vacuum and recycled in further reactions. As shown in Figure 6, the catalyst was used for over seven runs without any significant loss of activity.

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the benefits of our То show procedure in comparison with other reported catalysts, we summarize several reported catalysts for the preparation of polyhydroquinolines in Table 4. Synthesis polyhydroquinolines the of in presence of $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^-$ showed higher yield and good reaction time compared to other catalysts reported in the literature.

| CONCLUSIONS 4

An effective $[Fe_3O_4@SiO_2@(CH_2)_3Py]HSO_4^-$ catalysis was formulated for the synthesis of polyhydroquinolines with benzaldehyde, dimedon, ethyl acetoacetate and ammonium acetate. The Fe₃O₄ MNPs were prepared and further ionic liquid was immobilized on their surface. This catalyst was characterized using TGA, XRD, SEM and VSM techniques. This catalyst can be recovered and reused seven times. All products were obtained in good yields and high purity. The high yields, operational ease, practicality and applicability to a number of substrates render this method as a valuable substitute to other previously utilized approaches.

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