# Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid core–shell composite as a novel nanomagnetic solid acid: synthesis, characterization and application as an efficient and reusable catalyst for one-pot synthesis of 3,4-dihydropyrimidinones/thiones under solvent-free conditions

# Ali Reza Kiasat • Jamal Davarpanah

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Abstract A simple and convenient method was used to prepare  $Fe_3O_4@Silica$ sulfuric acid core-shell composite using Fe<sub>3</sub>O<sub>4</sub> spheres as the core and silica sulfuric acid nanoparticles as the shell. Magnetite nanoparticles were synthesized by the co-precipitation of FeCl<sub>2</sub> and FeCl<sub>3</sub> in ammonia solution. To improve the chemical stability of magnetite nanoparticles, its surface engineering was successfully performed by the suitable deposition of silica onto nano-particles' surface by the ammonia-catalyzed hydrolysis of tetraethoxysilane. Next, the SiO<sub>2</sub> spheres served as a support for the immobilization of SO<sub>3</sub>H groups by simple mixing of the core-shell composite and chlorosulfonic acid in CH<sub>2</sub>Cl<sub>2</sub>. The resulting solid acid nanoparticles were characterized by infrared spectroscopy, scanning electron microscope, thermogravimetric analysis, and vibrating sample magnetometer. The catalytic activity of this solid acid nanocomposite was probed through one-pot synthesis of 3,4-dihydropyrimidinones via three-component couplings of aldehydes, β-diketone, and urea or thiourea under solvent-free conditions. In this reaction, Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid shows a highly catalytic nature, easy to handle procedure, short reaction time, recycle exploitation, and excellent isolated yields. The nanomagnetic catalyst could be readily separated from the solution via application of an external magnet, allowing straightforward recovery and reuse.

**Keywords**  $Fe_3O_4@Silica sulfuric acid \cdot Nanomagnetic solid acid \cdot 3,4-Dihydropyrimidinones \cdot Solvent-free$ 

#### Introduction

Due to their high specific surface area, superparamagnetic properties and biocompatibility, magnetic nanoparticles can effectively improve the loading and

A. R. Kiasat (🖂) · J. Davarpanah

Chemistry Department, College of Science, Shahid Chamran University, 61357-4-3169 Ahvaz, Iran e-mail: akiasat@scu.ac.ir

the catalytic efficiency of immobilized catalysts [1, 2]. In this field, iron oxides, magnetite (Fe<sub>3</sub>O<sub>4</sub>), and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) are by far the most used magnetic nanoparticles, because they are much less toxic than their metallic counterparts, and they have high saturation magnetization and superparamagnetic behavior, among which magnetite is a very promising choice due to its already proven biocompatibility [3]. However, an unavoidable problem associated with the application of "naked" magnetite nanoparticles as catalyst support is its instability over longer periods of time due to high initial chemical activity, easy oxidation in air, loss of magnetism, dispersion, and agglomeration. In this regard, considerable attention has recently been paid to the preparation of the Fe<sub>3</sub>O<sub>4</sub>-based nanoparticles with a coreshell structure [3–6]. The silane agents are often considered as potential candidates for directly modifying the surface of magnetite [7]. Such surface modification enhances the biocompatibility and provides quite high density surface functional end groups which allow for connecting to catalysts [8].

Sulfuric acid is one of the most popular acid catalysts for practical chemical processes and is widely used in the production of industrially important chemicals. Such homogeneous acids generally require special processing in the form of neutralization, which involves energy-inefficient catalyst separation from products and results in the formation of a large amount of sulfate wastes [9]. Consequently, the development of solid acid catalysts, especially of the magnetic type, is expected to have a major impact in industrial applications as well as for scientific aspects.

During the last few years, sulfonic acid-functionalized hydroxyapatite-encapsulated  $Fe_2O_3$  magnetic nanoparticles [10], sulfamic acid-functionalized magnetic  $Fe_3O_4$  nanoparticles [11], and nano-*n*-propylsulfonated  $Fe_2O_3$  nanoparticles [12] have been successfully considered as heterogeneous magnetic solid acids in organic transformation.

On the other hand, 3,4-dihydropyrimidinones (DHPM) and their derivatives are very well known for their wide range of biological activities [13] as calcium channel blockers [14], antihypertensive agents, and neuropeptide Y antagonists [15]. By considering all the above-mentioned points and in continuation of our interest in using solid acid catalysts in organic synthesis [16–18], here, SO<sub>3</sub>H-functionalized silica-coated magnetite nanoparticles with a core–shell structure, Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid, were successfully prepared and their performance as a magnetic powerful solid acid catalyst for the synthesis of DHPM/thiones under solvent-free conditions was investigated.

#### Experimental

General

Chemical materials were purchased from Fluka and Merck and used without further purification. MNPs were synthesized by co-precipitation of FeCl<sub>3</sub>.6H<sub>2</sub>O and FeCl<sub>2</sub>.4H<sub>2</sub>O in ammonia solution, according to the reported procedure [19]. Products were characterized by comparison of their physical data, IR and <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra with known samples.

The TGA curve of the Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid was recorded on a BAHR SPA 503 at heating rates of 10 °C min<sup>-1</sup> under air atmosphere, over the temperature range of 25–1,000 °C. The particle morphology was examined by SEM.

Preparation of silica-coated magnetic nanoparticles, Fe<sub>3</sub>O<sub>4</sub>@Silica

Silica-coating of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles was carried out in a water–ethanol solution with ammonia-catalyzed reaction of tetraethylortosilane. Then, 2.0 g of the synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles were diluted with 120 mL water and 450 mL ethanol. This suspension was dispersed under ultrasonification for 25 min. In the presence of a constant nitrogen flux and at room temperature, ammonium hydroxide 25 % solution (10 mL) was added to the suspension. Then, under continuous mechanical stirring, 2.0 mL TEOS was slowly added to this dispersion, and, after stirring for 12 h, silica was formed on the surface of the magnetite nanoparticles through hydrolysis and condensation of TEOS. The coated particles were finally separated from the liquid by a magnetic decantation and washed several times with deionized water. They were then dried under vacuum at 60 °C overnight.

Preparation of  $SO_3H$  functionalized silica-coated magnetite nanoparticles,  $Fe_3O_4@Silica$  sulfuric acid

A 500-mL suction flask was equipped with a constant pressure dropping funnel. The gas outlet was connected to a vacuum system through an adsorbing solution of alkali trap.  $Fe_3O_4@Silica~(2.5~g)$  was added to the flask and dispersed by ultrasonics for 10 min in CH<sub>2</sub>Cl<sub>2</sub> (75 mL). Chlorosulfonic acid (1.75 g, ca. 1 mL, 15 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added dropwise over a period of 30 min at room temperature. After completion of the addition, the mixture was shaken for 90 min, while the residual HCl was eliminated by suction. Then, the Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid was separated from the reaction mixture by a magnetic field and washed several times with dried CH<sub>2</sub>Cl<sub>2</sub>. Finally, Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid was dried under vacuum at 60 °C.

pH-analysis of Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid

To an aqueous solution of NaCl (1 M, 25 mL) with an initial pH 5.9, the  $Fe_3O_4@Silica$  sulfuric acid (100 mg) was added and the resulting mixture was stirred for 24 h after which the pH of the solution decreased to 2.10. This is equal to a loading of 1.98 mmol  $SO_3H/g$  of acidic catalyst. Additionally, this result was confirmed by back-titration analysis of the catalyst.

Typical procedure for the preparation of 3,4-dihydropyrimidin-2(1H)-ones/ thiones

A mixture of aromatic aldehyde (1.0 mmol),  $\beta$ -diketone (1.0 mmol), urea or thiourea (2 mmol) and Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid (0.05 g) was heated at 80 °C for the times shown in Table 1. After complete consumption of aromatic aldehyde as

judged by TLC (using *n*-hexane-ethylacetate as eluent), the mixture was washed with distilled water to separate the excess of urea or thiourea. The crude product was dissolved in hot ethanol and the magnetic catalyst was concentrated on the sidewall of the reaction vessel using an external magnet. The hot solution was separated by decantation and was allowed to reach room temperature.

# **Results and discussion**

Investigation around the approach of  $Fe_3O_4@Silica$  sulfuric acid preparation and its structural and morphological analysis

 $SO_3H$ -functionalized silica-coated magnetite nanoparticles have the advantages of both magnetic separation techniques and nano-sized materials, which can be easily recovered or manipulated with an external magnetic field. As the acidic groups are usually immobilized on the surface of the magnetic nanoparticles, easy access of reactants to this active site can also be achieved. In the present study, Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles were prepared by a coprecipitation method from ferrous and ferric ion solutions in basic media. The magnetic nanoparticles prepared by this method had significant numbers of hydroxyl groups on the surface from contact with the aqueous phase. The MNPs are easily coated with amorphous silica using the conventional sol–gel method. The sol–gel process is based on the hydrolysis of TEOS, and subsequent condensation of hydrolyzed TEOS on surface iron hydroxyls. Next, the SiO<sub>2</sub> spheres served as a support for the immobilization of SO<sub>3</sub>H groups by simple mixing of the core–shell composite and chlorosulfonic acid in CH<sub>2</sub>Cl<sub>2</sub>. The schematic diagram for the synthetic procedure is shown in Scheme 1.

Entry Solvent		T (°C)	Catayst (g)	Time (min)	Yield (%) <sup>a</sup>	
1	Ethanol	Reflux	0.05	180	80	
2	Acetonitrile	Reflux	0.05	180	78	
3	Water	Reflux	0.05	300	35	
4	Toluene	Reflux	0.05	300	35	
5	Solvent-free	130	0.05	30	Mix <sup>b</sup>	
6	Solvent-free	120	0.05	30	Mix	
7	Solvent-free	100	0.05	30	Mix	
8	Solvent-free	90	0.05	35	78	
9	Solvent-free	80	0.1	35	81	
10	Solvent-free	80	0.05	35	92	
11	Solvent-free	80	0.02	45	62	
12	Solvent-free	80	_	180	20	

Table 1 Solvent-free reaction of benzaldehyde, ethylacetoacetate, and urea under different conditions

<sup>a</sup> Isolated yield

<sup>b</sup> Mixture of products

Due to the paramagnetic nature of the nanoparticle core, the nuclear magnetic resonance technique could not be used to confirm  $Fe_3O_4$ @Silica sulfuric acid synthesis. Instead, titration and FT-IR were used to characterize the core–shell composite structure. Sulfonic acid loading was calculated based on titration of the proton-exchanged brine solutions and showed the loading of 1.98 mmol SO<sub>3</sub>H/g of catalyst.

The FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub> nanoparticles, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, and Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid are shown in Fig. 1. The FT-IR analysis of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid exhibits two basic characteristic peaks at ~3,300 cm<sup>-1</sup> (O–H stretching) and 580 cm<sup>-1</sup> (Fe–O vibration) [20]. The bands at 1,092 cm<sup>-1</sup>, 800 cm<sup>-1</sup>, and 447 cm<sup>-1</sup> come from the Si–O–Si group. The peak at ~900 cm<sup>-1</sup> in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> is attributed to  $\upsilon$  ( $\equiv$ Si–OH) of free silanol groups [21]. The presence of sa ulfonyl group in Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid is confirmed by 1,217 and 1,124 cm<sup>-1</sup> bands, which were covered by a stronger absorption of Si–O bonds at 1,092 cm<sup>-1</sup>, and the peak of the Si–OH group at 900 cm<sup>-1</sup> disappears for Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid [11]. A wide peak at 3,393 cm<sup>-1</sup> is due to the stretching of OH groups in the SO<sub>3</sub>H.

Figure 2 shows the TGA curves of  $Fe_3O_4@SiO_2$  and  $Fe_3O_4@Silica$  sulfuric acid powders. For two curves, the weight loss below 200 °C might be due to the evaporation of the H<sub>2</sub>O molecules adsorbed onto the surface and the release of the structural water resulted from the bonded hydroxyl groups [22]. Curve (a) indicates that the silica-coated MNPs are thermally stable, and no obvious weight loss was observed below 1,000 °C, while in curve (b), the mass loss of  $Fe_3O_4@Silica$  sulfuric acid at 650–710 °C is attributed to the SO<sub>3</sub>H groups.

Scanning electron microscopy is a useful tool for determining the size distribution, particle shape, and porosity. It has been a primary tool for



Fe<sub>3</sub>O<sub>4</sub> @ Silica sulfuric acid

Fe<sub>3</sub>O<sub>4</sub> @ Silica

Scheme 1 Schematic diagram for the synthesis of Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid



Fig. 1 FT-IR spectra of a Fe<sub>3</sub>O<sub>4</sub>, b Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, and c Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid



Fig. 2 TGA curves of a Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and b Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid powders

characterizing the surface morphology and fundamental physical properties of the surface [21]. According to Fig. 3, both kinds of nanoparticles are apparently similar in size and shape and have nano-dimensions ranging from 90 to 170 nm. The particles are rather uniform in their morphology.

The magnetic properties of the uncoated magnetic iron oxide (Fe<sub>3</sub>O<sub>4</sub>), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, and Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid were measured by vibrating sample

magnetometer, VSM, at room temperature (Fig. 4). In Fig. 4, the hysteresis loops that are characteristic of superparamagnetic behavior can be clearly observed for all the nanoparticles. Superparamagnetism is the responsiveness to an applied magnetic field without retaining any magnetism after removal of the applied magnetic field. From M versus H curves, the saturation magnetization value (Ms) of uncoated MNPs was found to be 66 emu g<sup>-1</sup>. For Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid, the magnetization obtained at the same field were 38 and 17 emu g<sup>-1</sup>, respectively, lower than that of uncoated Fe<sub>3</sub>O<sub>4</sub>. This is mainly attributed to the existence of nonmagnetic materials on the surface of the nanoparticles.

Application of Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid as nanomagnetic solid acid catalyst for one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones

To evaluate the catalytic activity of  $Fe_3O_4@Silica$  sulfuric acid as a nanomagnetic heterogeneous solid acid catalyst in the synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones (DHPMs) through multicomponent reaction (Scheme 2), a model three-component coupling reaction of benzaldehyde (1 mmol), ethylacetoacetate (1 mmol), and urea (2 mmol) was examined to determine whether the use of



Fig. 3 SEM images of a Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and b Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid

 $Fe_3O_4$ @Silica sulfuric was efficient and to investigate the optimized conditions (Table 1).

Subsequently, with optimal conditions in hand, 1:1:2 molar ratios of aldehyde, ethylacetoacetate, and urea and 0.05 g of  $Fe_3O_4@Silica$  sulfuric acid at 80 °C under solvent-free conditions, the generality and synthetic scope of this coupling protocol were demonstrated by synthesizing a series of 3,4-dihydropyrimidin-2(1H)-ones (Table 2).

As shown in Table 2, aromatic aldehydes, having electron-releasing as well as electron-withdrawing groups, were uniformly transformed into the corresponding 3,4-dihydropyrimidin-2(1H)-ones in high yields within 25–55 min. Substituents on the aromatic ring had no obvious effect on yield or reaction time under the above optimal conditions.

The reusability of the catalyst in the reaction of benzaldehyde, ethylacetoacetate, and urea under solvent-free conditions at 80 °C was evaluated. In this procedure,



**Fig. 4** VSM magnetization curves of the *a*  $\text{Fe}_3\text{O}_4$ , *b*  $\text{Fe}_3\text{O}_4$ @SiO<sub>2</sub>, and *c*  $\text{Fe}_3\text{O}_4$ @Silica sulfuric acid nanoparticles



Scheme 2 Synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones through multicomponent reaction promoted by  $Fe_3O_4@Silica$  sulfuric acid

Table 2A solvent-freereaction for synthesis of 3,4 -dihydropyrimidin-2(1H)-ones/	Entry	R <sup>b</sup>	X <sup>b</sup>	$R_2^b$	Time (min)	Yield (%) <sup>a</sup>
thiones in presence of Fe <sub>3</sub> O <sub>4</sub> @Silica sulfuric acid	1	Н	0	OEt	35	92
	2	Н	S	OEt	50	86
	3	$4-O_2N$	0	OEt	25	92
	4	$4-O_2N$	S	OEt	25	87
	5	$4-O_2N$	0	Me	25	94
	6	$4-O_2N$	S	Me	25	92
	7	4-Cl	0	OEt	30	88
	8	4-Cl	S	OEt	35	84
	9	4-Cl	0	Me	30	90
	10	4-Cl	S	Me	35	86
	11	4-CH <sub>3</sub> O	0	OEt	50	86
	12	4-CH <sub>3</sub> O	0	Me	45	88
	13	4-CN	0	OEt	25	90
	14	4-CN	0	Me	25	92
	15	2-HO	0	OEt	45	83
	16	2-HO	S	OEt	45	81
	17	2-HO	0	Me	45	85
	18	4-H <sub>3</sub> C	0	OEt	55	82
	19	4-H <sub>3</sub> C	S	OEt	55	80
9 <b>-</b> 1 - 1 - 1 - 1	20	Н	0	Me	35	92
" Isolated yield	21	Н	S	Me	35	90

<sup>b</sup> According to scheme 2



Fig. 5 Recyclabilitry of Fe<sub>3</sub>O<sub>4</sub>@Silica sulfuric acid

after completion of each reaction, hot ethanol was added and the catalyst was separated by an external magnet. The recovered catalyst was washed with ethanol, dried, and reused four times (Fig. 5). The pH change during the reaction process was also considered for fresh and recovered catalyst, and the pH decrease was not observed after the reaction process. Based on titration of the proton-exchanged brine solutions, fresh and recovered catalysts showed the loading of 1.98 mmol SO<sub>3</sub>H/g.

Entry	Catalyst	Catalyst loading (g or wt%)	Time (h)	Yield (%)	Ref
1	Fe3O4@Silica sulfuric acid	0.05 g	0.6	92	This work
2	Montmorillonite KSF	15 %	48	77	[23]
3	Sulfated zirconia	15.15 %	4	94	[24]
4	PS-PEG-SO <sub>3</sub> H	0.3 g	10	80	[15]
5	ZrOCl <sub>2</sub> .8H <sub>2</sub> O	10 mol%	2	56	[25]
6	Silica-sulfuric acid	35 %	6	91	[13]
7	H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	11 %	5	80	[26]
8	Zeolite [HY(Si/Al = 2.43, $H_{56}(SiO_2)_{136}(AlO_2)_{56}]$	15 %	12	80	[27]
9	Bentonite/PS-SO <sub>3</sub> H	0.1 g	0.5	89	[28]

Table 3 Comparison of the efficacy of  $Fe_3O_4@Silica$  sulfuric acid catalyst with some of those reported in the literature

To evaluate the generality and synthetic scope of this coupling protocol, this three-component condensation reaction also proceeded with acetyl acetone and thiourea (Table 2).

In order to show the merits of the presented protocol in DHPMs synthesis, we have compared the results of the  $Fe_3O_4@silica$  sulfuric acid catalyst with some of those reported in the literature. The model reaction of benzaldehyde, ethyl acetoacetate, and urea was considered as a representative example (Table 3). As can be seen, in addition to having the general advantages attributed to the inherent magnetic property of nanocatalysts,  $Fe_3O_4@silica$  sulfuric acid is an equal or more efficient catalyst for this three-component reaction.

## Conclusion

 $Fe_3O_4$ @Silica sulfuric acid core-shell composite was successfully achieved by a multiple synthetic procedure which was confirmed with FT-IR, TGA, SEM, and VSM. The most interesting features of the present work include durability as well as efficient catalytic activity for one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones via three-component coupling reactions, under solvent-free conditions at 80 °C. This method offers several advantages including high yield, short reaction time, simple work-up procedure, ease of separation, and recyclability of the magnetic catalyst, as well as the ability to tolerate a wide variety of substitutions in the reagents.

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