Supported Sulfonic Acid on Magnetic Nanoparticles

Used as a Reusable Catalyst for Rapid Synthesis of α-Aminophosphonates Mozhgan Afshari^{a,*}, Maryam Gorjizadeh^a, Mohammad Naseh^b

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Abstract

Sulfonic acid was anchored on the surface of silica coated cobalt ferrite core to obtain a new magnetically separable catalyst. The resultant composite was characterized by various techniques, including FT-IR, XRD, FESEM, EDX, TEM, TGA, and VSM. The immobilized sulfonic acid was shown to be an efficient heterogeneous catalyst for the synthesis of α -aminophosphonates under solvent free conditions at room temperature. The catalyst is readily recovered by simple magnetic decantation and can be recycled 7 times with no significant loss of catalytic activity.

Keywords

Cobalt ferrite, α -Aminophosphonates, Magnetic nanoparticles, Surface functionalization, Sulfonic acid

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Introdution

Recently magnetic nanoparticles (MNPs) widely have employed as a support for homogenous catalysts. A striking feature of the MNPs-supported catalysts is that they can be easily separated from the reaction mixture by external magnetic field and reused [1-3]. Additionally, the nanoparticle-based catalysts not only show superior catalytic activities to their corresponding bulk material but also a high degree of chemical stability, and they do not swell in organic solvents [4].

Among the different MNPs as the core magnetic supports, cobalt ferrite nanoparticles were chosen for use as magnetic supports since they have moderate saturation magnetization, inexpensive, high chemical stability and mechanical strength [5–7].

On the other hand, sulfonic acid catalysts have been widely used in various industries; however, it is often difficult to separate the final product after the reaction is completed. Thus magnetic nanoparticles can be as attractive candidates for supporting of sulfonic acid catalysts [8, 9]. Sulfonic acid functionalized magnetic nanoparticles as recyclable strong solid acid catalyst open up new avenue to introduce an amazing and efficient system for facilitating catalyst recovery in different organic reactions. This catalyst allows the combination of well known procedures for catalyst heterogenization with techniques for magnetic separation.

Although many procedure have been performed to immobilize acid moiety on magnetic nanoparticles, we mentioned only some reports have appeared in the literature about sulfonic acid supported on MNPs. Firstly the use of silica coated cobalt ferrite nanoparticles for the immobilization of sulfonic acid was reported by Jones et al. [8]. They evaluated acid catalysts in test reactions in terms of activity and recyclability and compared with commercially available

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heterogeneous acidic resins and homogeneous sulfonic acids. In another report, Sulfonic acid functionalized silica coated magnetite nanoparticles was prepared by chlorosulfonic acid and used as an efficient catalyst for the synthesis of a variety of tetraketone derivatives via the Knoevenagel condensation and Michael addition reactions [10]. In this study high conversions were obtained and the catalysts could be easily separated from the reaction solution by applying an external magnetic field and recycled several times. Esterification reaction of fatty alcohols was studied by another researcher group using an organosulfonic acid functionalized silica coated magnetic nanoparticles with dual functionality comprised of both hydrophobicity and acidity properties [11].

The developing of one-pot multicomponent reactions (MCRs) and improving the known MCRs have attracted considerable attention in recent years [12]. One of these MCRs is the preparation of α -aminophosphonates derivatives. α -Aminophosphonates as a kind of natural amino acid analogs occupy an important place and reveal diverse and interesting biological and biochemical properties [13–15]. One-pot syntheses of α -aminophosphonates have been carried out by multi component condensation of an aldehyde, an amine, and a phosphite in the presence of various catalysts such as Lewis acids [16–20], Brønsted acids [21, 22], solid acids [23,24], rare metal salts [25], or metal oxides [26] over recent decades. However, some of these methods are not environmentally friendly and suffer from one or more disadvantages, such as harsh conditions, long reaction times, and frequently low yields, toxicity and recovery and reusability of the catalyst. In view of these, the developments of clean processes and utilizing ecofriendly and green heterogeneous catalysts which can be simply recycled at the end of reactions are still relevant.

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The demand for environmentally benign procedure with heterogeneous and reusable catalyst, promoted us to develop a safe alternate method for the preparation of α -aminophosphonates. In pursuit of this goal we wish to explore a straight forward synthesis of α -aminophosphonate via the one pot three component reaction under solvent free conditions using a new sulfonic acid moiety grafted on the surface of silica coated cobalt ferrite (CoFe₂O₄@SiO₂-RSR-SO₃H) as an efficient magnetic powerful solid acid catalyst with good stability (Scheme 1).

Experimental

General

All the chemicals were of analytical grade and used without further purification. . X-ray diffraction (XRD) patterns of the synthesized samples were taken with a Philips X-ray diffractometer (model PW1840) using Cu K α radiation ($\lambda = 1.54056$ Å). FT-IR spectra were obtained using BOMEM MB-Series 1998 FT-IR spectrometer. The FESEM images were obtained using a Hitachi Japan S4160 scanning electron microscope. The TEM images were recorded using a Leo 912 AB transmission electron microscope operated at a 100 keV. The magnetic properties of the fabricated CoFe₂O₄@SiO₂-RSR-SO₃H composite as well as other samples were studied using vibrating sample magnetometer (VSM) of Meghnatis Daghigh Kavir Company, Iran. NMR spectra were recorded in CDCl₃ on a Bruker Advanced DPX 400 MHz spectrometer.

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Synthesis of sulfonic acid supported on silica coated cobalt ferrite

Cobalt ferrite MNPs were prepared using the method reported by Maaz et al. [27]. Coating of $CoFe_2O_4$ nanoparticles with a layer of silica was achieved through Stöber method [28-30]. A one pot procedure was used to synthesize sulfonic acid supported on $CoFe_2O_4@SiO_2$ as follow. At first, a mixture of 3-meraptopropyltrimehoxy silane (5.9 ml, 32 mmol) and 1, 3-propane sultone (3.25 ml, 32 mmol) was heated at 110 °C for 24 h with continuous stirring under N₂ atmosphere. The product of this step was dissolved in 25 mL of toluene followed by addition of $CoFe_2O_4@SiO_2$ (1.1 g) and the mixture was refluxed for 24 h. finally the produced sulfonic acid silica coated magnetic nanoparticles ($CoFe_2O_4@SiO_2$ -RSR-SO₃H) were magnetically separated and washed twice with toluene and ether. A schematic representation of $CoFe_2O_4@SiO_2-RSR-SO_3H$ synthesis is shown in Scheme 2.

Measuring of Sulfonic acid loadings

Sulfonic acid loadings of the catalyst (mmol of sulfonic acid per g of $CoFe_2O_4@SiO_2-RSR-SO_3H$) were determined by the back titration method [31]. 0.5 g of the sample was soaked overnight in 50 ml of distilled water containing 5ml of 0.1 N NaOH to exchange sodium ions with the protons in the nano catalyst. Back-titration was accomplished by titrating the remaining NaOH in solution with 0.1 MHCl solutions.

General procedure of Catalytic a-aminophosphonates synthesis

To a mixture of an aldehyde (1 mmol), aniline (1 mmol), triethyl phosphate (1.2 mmol) was added 0.05 g CoFe₂O₄@SiO₂-RSR-SO₃Hcatalyst and the mixture was stirred for an appropriate time at room temperature. After completion of the reaction (monitored by TLC), CH₃Cl was

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added to dilute the reaction mixture and the organic layer was simply decanted by means of an external magnet. The isolated solution was purified on a silica-gel plate to obtain pure product. The products were identified by FT-IR and ¹H NMR matches with the literature.

Results and discussion

Characterization of CoFe₂O₄@SiO₂-RSR-SO₃H

As described in the experimental section, the catalyst was prepared by straightforward one pot procedure and characterized by various techniques. The FT-IR spectrum of $CoFe_2O_4(a)$, $CoFe_2O_4@SiO_2(b)$ and $CoFe_2O_4@SiO_2-RSR-SO_3H(c)$, shows the characteristic peaks of Fe-O at 589 cm⁻¹ and an intense broad peak at 1000–1250 cm⁻¹ in Fig. 1b and 1c corresponded to the Si–O stretch in the amorphous silica shell [32] (Fig. 1). The O–H stretch and vibration of surface hydroxyl groups and physisorbed water were present as broad peaks at 3000–3700 cm⁻¹ and a sharper peak at 1640 cm⁻¹, respectively. The presence of the anchored alkyl groups in $CoFe_2O_4@SiO_2-RSR-SO_3H$ is confirmed by the aliphatic weak C- H stretching vibrations appearing at 2943 cm⁻¹. Evidence of the surface functionalization was difficult to observe due to the low loadings of SO₃H and overlapping of peaks corresponding to Si–O–Si, Fe–O–Si, and symmetric SO₂ stretching [8, 33].

Figure 2 illustrates the XRD pattern of $CoFe_2O_4$, $CoFe_2O_4@SiO_2$ and $CoFe_2O_4@SiO_2$ -RSR-SO₃H, The peaks are compatible with pure $CoFe_2O_4$ phase (JCPDS PDF #221086), indicating the retention of cubic reverse spinel structure of $CoFe_2O_4$ during coating and functionalization. The XRD pattern of Si-MNPs and $CoFe_2O_4@SiO_2$ -RSR-SO₃H (Fig. 2b and 2c) shows an

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obvious diffusion peak at $2\theta = 20-28^{\circ}$ that appeared because due to the existence of amorphous silica in the shell of CoFe₂O₄.

In order to investigate the crystalline nature and morphological features of the catalyst, scanning electron microscopy (SEM). SEM image (Fig.3) of the catalyst shows that $CoFe_2O_4@SiO_2-RSR-SO_3H$ nanoparticles are nearly spherical and the average size of these nanoparticles is in the range of 30 nm. In these cases, the TEM image (Fig.4) provide more accurate information on the particle size and morphology of MNPs, therefore, these image was investigated. TEM observations clearly reveal the core–shell structure of the nanoparticles.

In order to further confirm the composition of the as-fabricated $CoFe_2O_4@SiO_2-RSR-SO_3H$ composite, energy dispersive X-ray (EDX) analysis was conducted. The EDX spectrum, which is displayed in Fig. 5, clearly reveals the presence of all the expected main elements (O, Si, Fe, Co, and S) comprising this composite.

The magnetic properties of $CoFe_2O_4$, $CoFe_2O_4@SiO_2$ and $CoFe_2O_4@SiO_2$ -RSR-SO₃H were studied by a vibrating sample magnetometer (VSM) at 300 K with a peak field of 10 kOe and their hysteresis curves are presented in Fig. 4. It could be seen from the loops in Fig. 4 that saturation magnetization (M_S) of $CoFe_2O_4$, $CoFe_2O_4@SiO_2$ and $CoFe_2O_4@SiO_2$ -RSR-SO₃H are 59.42, 38.93 and 31.16 emu g⁻¹ respectively. The decrease in mass saturation magnetization may be ascribed to the contribution of the non-magnetic silica shell and functionalized groups [34]. However, the as- fabricated nanocomposite, can still be efficiently and easily separated from solution with the help of an external magnetic force.

Thermogravimetric analysis (TGA) of CoFe₂O₄@SiO₂-RSR-SO₃H catalyst was performed to prove its thermal stability. There are two weight loss steps in TGA curve of CoFe₂O₄@SiO₂-

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RSR-SO₃H catalyst (Fig. 7).The first mass loss of 4.19 % (between 30 to 192 °C) may be due to removal of surface adsorbed water of the catalyst. The loss of weight at temperatures higher than 192 °C could be mainly attributed to the evaporation and subsequent decomposition of RSR-SO₃H groups. The TGA analysis of the as-prepared catalyst showed that the sulfonic acid moiety loading approximately 0.48 mmol/g. It is worth mentioning that this value of loading show agreement with the values calculated by back-titration (0.50 mmol/g). In addition, elemental analysis showed 3.25 % S (= 0.51 mmol/g SO₃H) that confirmed catalyst loading obtained from TGA and back-titration.

a-Aminophosphonates synthesis

At the outset, the three-component reaction of benzaldehyde, aniline, and thriethylphosphite was investigated in various conditions at room temperature. Initially, we have focused our attention on the effect of the solvent on model reaction; we have studied the effect of different solvents such as CH₃CN, CH₂Cl₂, and EtOH in the presence of CoFe₂O₄@SiO₂-RSR-SO₃H as catalyst. But solvent -free approach showed better results (see Table 1). Secondly, to investigate the effect of SO₃H moiety on this catalysis reaction, we have also examined CoFe₂O₄@SiO₂ in similar reaction in the separate experiment. As seen in Table 1, CoFe₂O₄@SiO₂ showed the weak catalytic activity for the α -aminophosphonates synthesis.

Then, this condensation reaction with various aldehydes, amines, and triethylphosphite in the presence of $CoFe_2O_4@SiO_2$ -RSR-SO₃H as the catalyst was explored under the optimized reaction conditions described above, and the results are presented in Table 2.

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It can easily be seen that this one-pot, three component condensation completed within 10–40 min, and the products were isolated in good to excellent yields. For aromatic aldehydes carrying either electron-donation or electron withdrawing substituents could afford good yields of α -aminophosphonates. The lower yields obtained for furfural and 2-amino pyridine are probably due to the lower reactivity of the heterocyclic substrates.

A plausible mechanism for the one-pot, three-component condensation reaction of aldehydes, amines and triethyl phosphite is believed to involve formation of an activated imine by supported sulfonic acid so that addition of the phosphite is facilitated to give a phosphonium intermediate, which then undergoes reaction with the water to give the α -aminophosphonate and ethanol as shown in Scheme 3 [35].

A comparison of the efficacy of $CoFe_2O_4@SiO_2$ -RSR-SO₃H catalyst with some of those reported in the literature is presented in Table 3.

Catalyst recycling

The nanocatalyst reusability was also investigated. For this purpose, the same model reaction was again studied under the optimized conditions. After the completion of the first reaction, the product was diluted with CH₃Cl and the solution was removed by magnetic decantation. The left used catalyst was washed with methanol and CHCl₃ and dried at 60 °C for 30 min prior to the next run. A new reaction was then conducted with fresh reactants under the same reaction conditions. The results showed the yield of α -aminophosphonates dropped from 92 % to 83% after seven runs (see Table 4). Elemental analysis of the recovered catalyst demonstrated no change in amount of S content after recycle it for seven times. Thus, the slight decrease in the

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activity could be attributed to mainly unavoidable loss of the catalyst during the process of collection.

Conclusions

Sulfonic acid supported on silica coated $CoFe_2O_4$ magnetic nanoparticles is successfully achieved by a one pot synthetic procedure which is confirmed with XRD, FT-IR, TGA, VSM, TEM, FESEM and EDX techniques. The immobilized sulfonic acid was shown environmentally safe heterogeneous solid acid catalyst for synthesis of α -aminophosphonates under solvent- free conditions at room temperature. This method offers several advantages including short reaction time, good to excellent product yields, simple work-up, ease of separation of the magnetic catalyst, as well as the ability to tolerate a wide variety of substitutions in the reagents. Moreover catalyst could be recovered from the reaction mixture by compartmentation with the aid of an external magnet and could be reused seven times with no significant loss of catalytic activity.

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Entry	Catalyst	Solvent	Time (min)	Yield ^b (%)
1	CoFe ₂ O ₄ @SiO ₂ -RSR-SO ₃ H	CH ₃ CN	25	86
2	CoFe ₂ O ₄ @SiO ₂ -RSR-SO ₃ H	CH ₂ Cl ₂ ,	30	88
3	CoFe ₂ O ₄ @SiO ₂ -RSR-SO ₃ H	EtOH	30	70
4	CoFe ₂ O ₄ @SiO ₂ -RSR-SO ₃ H	Neat	10	92
5	CoFe ₂ O ₄ @SiO ₂	Neat	120	30

Table 1. Effect of various catalysts and solvents on the synthesis of α -aminophosphonates

^a All reaction conditions: benzaldehyde(1 mmol), aniline (1 mmol), P(OEt)₃ (1.2 mmol), Catalyst

(0.05 g) at room temperature

^b Isolated yield

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Table 2. Synthesis of diversified α -aminophosphonates in the presence of CoFe₂O₄@SiO₂-RSR-SO₃H ^a

Entry	Aldehyde	R ¹ (Amine)	Time (min)	Yield ^b (%)
2	R=H	Н	10	92
3	R=H	2-Br	25	95
4	R=H	4-F	30	86
5	R=H	4-OMe	25	89
6	R=2-Br	Н	25	94
7	R=2-Br	4-Br	25	90
8	R= 3-OMe	Н	20	92
9	R= 3-OMe	4-Br	25	90
10	R= 3-OMe	4-F	25	90
11	R=4-OMe	4-Br	20	91
12	R=4-OMe	4-F	15	89
13	R=4-OMe	2-Br	15	92
14	$R=4-NO_2$	Н	10	95
15	R=2-Br	4-F	20	95
16	R=2-Br	4-OMe	20	95
17	R=4-OMe	Н	15	93
18	$R=4-NO_2$	2-amino	30	76

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		pyridine		
19	furfural	Н	30	85
20	furfural	2-amino pyridine	40	70

^a All reaction condition: aldehydes (1 mmol), amine (1 mmol), P(OEt)₃ (1.2 mmol) and 0.05 g of

CoFe₂O₄@SiO₂-RSR-SO₃H at room temperature

^b Isolated yields

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Table 3. Comparison of $CoFe_2O_4@SiO_2$ -RSR-SO_3H with other catalysts reported in the literature for the one-pot three component coupling reaction of benzaldehyde, aniline, and triethyl phosphite^a

Entry	Catalyst	Time	Yield ^b	Ref.
·	·	(min)	(%)	
1	H_2SO_4	45	63	[36]
2	SiO ₂ @Al ₂ O ₃	60	93	[37]
3	Fe ₃ O ₄ @SiO ₂ - poly(amidoamine)- SO ₃ H	25	91	[36]
4	CoFe ₂ O ₄ @SiO ₂ -Imid/H ₃ PW ₁₂ O ₄₀	15	95	[7]
5	Fe ₃ O ₄ @(CH ₂) ₃ NSO ₃ H	60	78	[38]
6	Fe ₃ O ₄ @SiO ₂ -2mimid-SO ₃ H	20	94	[39]
7	CoFe ₂ O ₄ @SiO ₂ -RSR-SO ₃ H	10	92	This work

^a Reaction conditions: solvent-free and room temperature

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Table 4. Catalyst recycling experiments for α -aminophosphonates synthesis

Cycle	1st	2st	3st	4st	5st	6st	7st
Yeild %	92	90	90	88	86	85	83

^a All reaction condition: aldehydes (1 mmol), amine (1 mmol), P(OEt)₃ (1.2 mmol) and 0.05 g of

CoFe₂O₄@SiO₂-RSR-SO3H at room temperature

^b Isolated yields

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Fig.1. FT-IR spectra of (a) $CoFe_2O_4$, (b) $CoFe_2O_4@SiO_2$ and (c) $CoFe_2O_4@SiO_2$ -RSR-SO₃H

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Fig. 2. XRD pattern of (a) CoFe₂O₄, (b) CoFe₂O₄@SiO₂ and (c) CoFe₂O₄@SiO₂-RSR- SO₃H

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Fig. 3. FESEM image of the CoFe₂O₄@SiO₂-RSR- SO₃H catalyst

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Fig. 4. TEM image of the CoFe₂O₄@SiO₂-RSR- SO₃H catalyst

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Fig. 5. EDX spectrum of CoFe₂O₄@SiO₂-RSR- SO₃H catalyst

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Fig. 6. Hysteresis loops of (a) CoFe₂O₄, (b) CoFe₂O₄@SiO₂ and (c) CoFe₂O₄@SiO₂-RSR- SO₃H

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Fig. 7. TGA of CoFe₂O₄@SiO₂-RSR- SO₃H

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Scheme 1. CoFe₂O₄@SiO₂-RSR-HSO₃ catalyzed synthesis of α -aminophosphonates

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Scheme 2. Schematic representation of the formation of $CoFe_2O_4@SiO_2$ -RSR- SO₃H catalyst

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Scheme 3. Proposed mechanism for the synthesis of α -aminophosphonates catalyzed by CoFe₂O₄@SiO₂-RSR-HSO₃

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