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Sulfamic acid-functionalized magnetic Fe_3O_4 nanoparticles as an efficient and reusable catalyst for one-pot synthesis of α -amino nitriles in water

M.Z. Kassaee*, Hassan Masrouri, Farnaz Movahedi

Department of Chemistry, Tarbiat Modares University, P.O. Box 14155-4838, Tehran, Iran

A R T I C L E I N F O

ABSTRACT

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1. Introduction

Mounting interest is recently expressed for surface functionalization of nanocatalysts in which the nanoscale architecture of active centers plays a dominant role in determining their efficiency and selectivity [1-5]. Surface functionalized iron oxide magnetic nanoparticles (MNPs) are a kind of novel functional materials, which have been widely used in biotechnology and catalysis [6-13]. Good biocompatibility and biodegradability as well as basic magnetic characteristics could be denoted for functional organic materials grafted to MNPs. Magnetic nanocatalysts can easily be separated and recycled from the products by an external magnet. Moreover, their catalytic performance is enhanced, for the available surface area of the nonporous MNPs is external and the internal diffusion is practically avoided. The silane agents such as 3-aminopropyltriethyloxysilane (APTES), *p*-aminophenyl trimethoxysilane (APTS), and mercaptopropyltriethoxysilane (MPTES) are often considered as potential candidates for modifying the surface of MNPs directly. Such surface modification enhances the biocompatibility and provides rather high density surface functional endgroups which allow for connecting to other metals, polymers or biomolecules [14-17]. Existence of many hydroxyl groups on the MNPs surface leads to reaction with alkoxysilane reagents and formation of Si-O bonds which support terminal functional groups available for immobilization of other substances [18-20].

Grafting of chlorosulfuric acid on the amino-functionalized Fe_3O_4 nanoparticles afforded sulfamic acid-functionalized magnetic Fe_3O_4 nanoparticles (SA-MNPs) as a novel organic–inorganic hybrid heterogeneous catalyst, which was characterized by XRD, FT-IR, TGA, TEM, and elemental analysis. The catalytic activity of SA-MNPs was probed through one-pot synthesis of α -amino nitriles *via* three-component couplings of aldehydes (or ketones), amines and trimethylsilyl cyanide in water, at room temperature. The heterogeneous catalyst could be recovered easily and reused many times without significant loss of its catalytic activity.

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On the other hand, acid catalysts are used in a variety of organic transformations, including aldol condensations, hydrolyses, acylations, nucleophilic additions, etc. However, several drawbacks such as separation problems, reactor corrosion, waste neutralization and the incapability for reuse have depreciated the reactions catalyzed by soluble liquid acids [21]. Consequently, there has been considerable interest in the development of stable, reusable, and highly active solid acids [22-24] as environmentally benign replacements for their homogeneous counterparts. During the last few years, sulfamic acid (NH₂SO₃H, SA), a dry nonhygroscopic, nonvolatile, and odorless solid has been considered as an efficient heterogeneous catalyst substitute for conventional acidic catalysts [25-28]. Ketal formation or acetalization [29], esterification [25], nitrile formation [30], tetrahydropyranylation of alcohols [31] and transesterification of β -ketoesters [32] are among the reactions carried out in the presence of sulfamic acid.

In this study, we report immobilization of sulfamic acid groups on the synthesized magnetic Fe_3O_4 nanoparticles to achieve sulfamic acid-functionalized magnetic nanoparticles as a new heterogeneous catalyst for one-pot synthesis of α -amino nitriles *via* three-component couplings of aldehydes (or ketones), amines and trimethylsilyl cyanide in water, at room temperature.

2. Experimental

2.1. Chemicals and instruments

The reagents and solvents used in this work were obtained from Fluka or Merck and used without further purification. Nanostructures were characterized using a Holland Philips Xpert

^{*} Corresponding author. Tel.: +98 912 1000392; fax: +98 21 88006544. *E-mail address:* kassaeem@modares.ac.ir (M.Z. Kassaee).

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X-ray powder diffraction (XRD) diffractometer (CuK, radiation, $\lambda = 0.154056$ nm), at a scanning speed of 2°/min from 10° to 100° (2 θ). The particle size and morphology were investigated by a JEOL JEM-2010 transmission electron microscope (TEM) on an accelerating voltage of 200 kV. FT-IR measurements were performed using KBr disc on a Thermo IR-100 infrared spectrometer (Nicolet). Elemental analyses for C, H and N were performed using a Heraeus CHN–O–Rapid analyzer. The thermogravimetric analysis (TGA) curves are recorded using a PL-STA 1500 device manufactured by Thermal Sciences. The ¹H- and ¹³C-spectra were measured at 500.1, and 125.7 MHz, respectively, on a Bruker DRX 500-Avance FT-NMR instrument with CDCl₃ as a solvent.

2.2. Preparation of the magnetic Fe_3O_4 nanoparticles (MNPs)

Naked Fe₃O₄ nanoparticles were prepared by chemical coprecipitation of Fe³⁺ and Fe²⁺ ions with a molar ratio of 2:1 [33]. Typically, FeCl₃·6H₂O (5.838 g, 0.0216 mol) and FeCl₂·4H₂O (2.147 g, 0.0108 mol) were dissolved in 100 mL deionized water at 85 °C under N₂ atmosphere and vigorous mechanical stirring (500 rpm). Then, 10 mL of 25% NH₄OH was quickly injected into the reaction mixture in one portion. The addition of the base to the Fe²⁺/Fe³⁺ salt solution resulted in the formation of the black precipitate of MNPs immediately. The reaction continued for another 25 min and the mixture was cooled to room temperature. The black precipitate was washed with doubly distilled water and 0.02 M solution of NaCl through magnetic decantation. Practically, the NaCl solution helped delete the excess amount of ammonia providing a better and faster decantation of suspended Fe₃O₄ nanoparticles in water, when an external magnet was used. The average diameter of obtained MNPs was estimated around 14 nm by transmission electron microscopy (TEM).

2.3. Preparation of MNPs coated by (3-aminopropyl)triethoxysilane

The obtained MNPs powder (1.5 g) was dispersed in 250 mL ethanol/water (volume ratio, 1:1) solution by sonication for 30 min, and then APTES (99%, 2.5 mL) was added to the mixture. After mechanical agitation under N₂ atmosphere at 40 °C for 4 h, the suspended substance was separated with centrifugation (RCF = 13,200 × g for 30 min). The settled product was re-dispersed in ethanol by sonication and then was isolated with magnetic decantation for 5 times. The precipitated product (APTES–MNPs) was dried at room temperature under vacuum.

2.4. Preparation of sulfamic acid-functionalized magnetic Fe₃O₄ nanoparticles (SA-MNPs)

The APTES–MNPs (500 mg) were dispersed in dry CH_2Cl_2 (3 mL) by ultrasonic bath for 10 min. Subsequently, chlorosulfuric acid (0.8 mL) was added dropwise over a period of 30 min at room temperature. Hydrogen chloride gas evolved from the reaction vessel immediately. Then, the as prepared functionalized MNPs nanoparticles were separated by magnetic decantation and washed three times with dry CH_2Cl_2 to remove the unattached substrates.

2.5. General procedure for the synthesis of α -amino nitriles

To a 10 mL round-bottomed flask were added aldehyde (or ketone) (1.0 mmol), amine (1.0 mmol), TMSCN (1.1 mmol), H_2O (3 mL) and SA-MNPs (20 mg) sequentially. The suspension was stirred vigorously at room temperature followed by appropriate times of stirring. The progress of the reaction was monitored by TLC (eluent:EtOAc/n-hexane, 30:70). After the reaction was completed, the catalyst was separated by an external magnet and reused as



Scheme 1. Preparation steps for fabricating sulfamic acid-functionalized magnetic Fe₃O₄ nanoparticles.



Fig. 1. XRD patterns of (a) MNPs, (b) APTES-MNPs and (c) SA-MNPs.

such for the next experiment. Consequently the crude product was extracted from the aqueous phase by EtOAc (3×5 mL), and then the organic layer was washed with saturated brine and dried over anhydrous MgSO₄. Finally the solvent was removed and the desired α -amino nitrile obtained through a column of silica gel.

3. Results and discussion

3.1. Characterization of the prepared SA-MNPs

Scheme 1 presents the synthetic strategy for SA-MNPs; naked magnetic Fe_3O_4 nanoparticles were prepared through chemical coprecipitation method, and subsequently were coated with 3-aminopropyltriethoxysilane (APTES) to achieve amino-functionalized magnetic nanoparticles. Ultimately, the reaction of amino groups with chlorosulfuric acid led to sulfamic acid-functionalized magnetic Fe_3O_4 nanoparticles (SA-MNPs). Elemental analysis showed the S content to be 8.93%. Typically a loading at ca. 0.32 mmol/g was obtained. Furthermore, when the prepared SA-MNPs catalyst was placed in an aqueous NaCl solution (1 M, 25 mL) the pH dropped instantaneously to \approx 1.97, indicating an ion exchange between sulfamic acid protons and sodium ions, and an ion exchange capacity was found to be 0.31 mmol/g of sulfamic acid groups which is in good agreement with the results obtained from TGA and back-titration.

The X-ray diffraction patterns of MNPs, APTES–MNPs and SA-MNPs are shown in Fig. 1. The position and relative intensities of all peaks confirm well with standard XRD pattern of Fe₃O₄ (JCPDS card No. 85-1436) indicating retention of the crystalline cubic spinel structure during functionalization of MNPs. A weak broad band (2θ = 18–27°) appeared in the APTES–MNPs and the SA-MNPs which could be assigned to the amorphous silane shell formed around the magnetic cores [34]. The average MNPs core diameter was calculated to be 14 nm from the XRD results by Scherrer's equation, $D = k\lambda/\beta \cos \theta$, where *k* is a constant (generally considered as 0.94), λ is the wavelength of Cu Ka (1.54Å), β is the corrected diffraction line full-width at half-maximum (FWHM), and θ is Bragg's angle [35].

The thermogravimetric analysis (TGA) curves of the MNPs, APTES–MNPs and SA-MNPs show the mass loss of the organic materials as they decompose upon heating (Fig. 2). The initial weight loss from the MNPs up to 126 °C is due to the removal of physically adsorbed solvent and surface hydroxyl groups. The weight loss of about 2.2% between 260 and 355 °C may be associated to the thermal crystal phase transformation from Fe₃O₄ to γ -Fe₂O₃ [36]. The



Fig. 2. TGA curve of (a) MNPs, (b) APTES–MNPs and (c) SA-MNPs.

weight loss of APTES-modified magnetite NPs appears about 2.8% at 270–430 °C which is contributed to the thermal decomposition of the 3-aminopropyl groups. For SA-MNPs, there is a well-defined mass weight loss of 4.9% between 250 and 465 °C related to the breakdown of the SA moieties. On the basis of these results, the well grafting of APTES and SA groups on the MNPs is verified.

Fig. 3 shows Fourier transform infrared (FT-IR) spectra for magnetic Fe₃O₄ nanoparticles (MNPs), APTES-MNPs, and SA-MNPs. The FT-IR bands at low wavenumbers (\leq 700 cm⁻¹) come from vibrations of Fe-O bonds of iron oxide, in which for the bulk Fe₃O₄ samples appear at 570 and 375 cm^{-1} but for Fe₃O₄ nanoparticles at 624 and 572 cm⁻¹ as a blue shift, due to the size reduction [37,38]. The FT-IR spectra of APTES-MNPs and SA-MNPs show Fe-O vibrations in the same vicinity. The introduction of APTES to the surface of MNPs is confirmed by the bands at 1126 and 1001 cm^{-1} assigned to the Si–O stretching vibrations. The broad band at 3392 cm⁻¹ is referred to the N-H stretching vibration [39]. The presence of the anchored propyl group is confirmed by C-H stretching vibrations that appear at 2918 and 2846 cm⁻¹. Reaction of APTES-MNPs with chlorosulfuric acid produces SA-MNPs in which the presence of sulfonyl moiety is asserted with 1217 and 1124 cm⁻¹ bands in FT-IR spectra.

TEM micrographs provide more accurate information on the particle size and morphology of MNPs and SA-MNPs (Fig. 4).



Fig. 3. The comparative FT-IR spectra for (a) MNPs, (b) APTES-MNPs and (c) SA-MNPs.

60nm a b

Fig. 4. TEM images of (a) MNPs and (b) SA-MNPs.

Table 1

The naked Fe₃O₄ nanoparticles show slight agglomeration, which could be related to the absence of surfactants and the lack of any repulsive force between the MNPs. For both the pristine and SA-functionalized nanoparticles, the average diameter of the core is around 14 nm with an approximate spherical shape, which is in accord with the XRD pattern. There is no detectable outer shell within the sensitivity limit of TEM (Fig. 4b). A reasonable explanation might be that silanization with APTES results in to the formation of a monolayer Si–O network which is too thin to be recognized.

3.2. Evaluation of the catalytic activity of SA-MNPs through the synthesis of α -amino nitriles

 α -Amino nitriles are significantly important intermediates for the synthesis of a wide variety of amino acids, amides, diamines, nitrogen-containing heterocycles and other biologically active molecules. Therefore, we investigated catalytic activity of SA-MNPs as a heterogeneous catalyst in one-pot synthesis of α -amino nitriles through three-component reaction of aldehydes (or ketones), amines, and trimethyl cyanide (Scheme 2). For this purpose, the reaction of benzaldehyde, aniline and TMSCN as a simple model reaction was probed to establish the feasibility of the strategy and optimize the reaction conditions. Various catalysts including nano metal oxides, sulfamic acid, and SA-MNPs were evaluated for this model reaction, and the results are summarized in Table 1. Metal oxide nanoparticles such as nano-Fe₃O₄, ZnO, TiO₂ and ZrO₂ rendered higher yields in CH₃CN than water, for somewhat the later seemed to poison the nano catalyst. Among the used catalysts SA-MNPs rendered the highest yield. Indeed, Fe₃O₄ nanoparticles as well as sulfamic acid (NH₂SO₃H) would catalyze the reaction per Optimization of the SA-MNPs catalyzed model reaction for synthesis of α -amino nitriles.^a

Entry	Catalyst	Solvent	Time (min)	Yield (%) ^b
1	Nano-Fe ₃ O ₄ (10 mol%)	CH₃CN	90	75
2	Nano-Fe ₃ O ₄ (10 mol%)	H_2O	90	68
3	Nano-ZnO (10 mol%)	CH ₃ CN	60	86
4	Nano-ZnO (10 mol%)	H_2O	120	64
5	Nano-TiO ₂ (10 mol%)	CH ₃ CN	60	90
6	Nano-TiO ₂ (10 mol%)	H_2O	120	71
7	Nano-ZrO ₂ (10 mol%)	CH ₃ CN	45	85
8	Nano-ZrO ₂ (10 mol%)	H_2O	120	58
9	NH ₂ SO ₃ H (10 mol%)	CH ₃ CN	30	81
10	NH ₂ SO ₃ H (10 mol%)	-	20	90
11	NH ₂ SO ₃ H (10 mol%)	H_2O	90	62
12	SA-MNPs (20 mg)	CH ₃ CN	30	93
13	SA-MNPs (20 mg)	Toluene	120	42
14	SA-MNPS (20 mg)	-	90	95
15	SA-MNPs (20 mg)	EtOH	30	86
16	SA-MNPs (20 mg)	H_2O	10	97
17	SA-MNPs (10 mg)	H_2O	20	72
18	SA-MNPs (50 mg)	H ₂ O	10	98
19	No catalyst	H ₂ O	240	18

^a Reaction conditions: Benzaldehyde (1 mmol), aniline (1 mmol), trimethylsilyl cyanide (1.2 mmol), catalyst, solvent (3 mL), room temperature.
 ^b Isolated yields.

se, with 75 and 81% yield, respectively. Yet, their combination in the form of SA-MNPs boosts the yield to 98%.

To appraise the effects of media, we carried out the condensation of benzaldehyde, aniline and TMSCN in various organic solvents by using SA-MNPs (20 mg per 1 mmol of reactants) as the catalyst (Table 1, entries 12–16). It should be noted that SA-MNPs



Table 2

One-pot synthesis of α -amino nitriles by the Strecker reaction of aldehydes, amines, and TMSCN in the presence of SA-MNPs in water.^a

			SA-MNPs (20 mg) HN ^R			
$R-CHO + R'-NH_2 + TMSCN$			CN -	H ₂ O,	rt R	CN
1	2				3	CIV
	R' = Ph		2a			
	R' = 4-C1-C	$_{6}H_{4}$	2b			
	R' = 4-Me-0	C_6H_4	2c			
	R' = Benzv		2d			
	R' = n-Buty	1	2e			
Entry	R	Amin	ie	Product	Time (min)	Yield (%) ^b
1	Ph	2a		3a	10	97
2	4-Cl-C ₆ H ₄	2a		3b	10	95
3	3-Cl-C ₆ H ₄	2a		3c	15	91
4	4-Me-C ₆ H ₄	2a		3d	15	92
5	2-Me-C ₆ H ₄	2a		3e	25	88
6	4-MeO-C ₆ H ₄	2a		3f	10	93
7	2-Furyl	2a		3g	20	92
8	2-Thienyl	2a		3h	30	85
9	$4-Br-C_6H_4$	2a		3i	15	95
10	i-Pr	2a		3ј	30	90
11	n-Pr	2a		3k	30	88
12	Ph	2b		31	10	98
13	4-Cl-C ₆ H ₄	2b		3m	10	93
14	Cinnamyl	2b		3n	45	90
15	Ph	2c		30	30	95
16	4-MeO-C ₆ H ₄	2c		Зp	30	96
17	Ph	2d		3q	15	93
18	4-Me-C ₆ H ₄	2d		3r	15	91
19	2-Furyl	2d		3s	20	87
20	Ph	2e		3t	45	96
21	A-Br-C-H	20		211	45	0/

^a Reaction conditions: Aldehydes (1 mmol), amines (1 mmol), TMSCN (1.2 mmol), SA-MNPs (20 mg), water (3 mL), room temperature.

^b Isolated yields.

showed good catalytic activity in a variety of organic solvents such as acetonitrile and ethanol, where over than 80% conversion was obtained. Nevertheless, the reaction in water is very clean and this is the solvent of choice, environmentally appreciable.

To investigate the effect of the catalyst concentration, systematic studies are carried out in the presence of different amounts of the catalyst (0, 5, 20, 50 mg) in water, affording α -amino nitriles with 18%, 72%, 97%, and 98% isolated yields, respectively. Thus, the best yield is found in the presence of just 20 mg SA-MNPs, and the use of higher amounts of catalyst (50 mg) does not improve the result to an appreciable extent (Table 1, entry 18).

The reaction can tolerate a wide range of aliphatic and aromatic aldehydes carrying either electron-donating or electronwithdrawing substituents in the ortho, meta and para positions. Acid sensitive aldehydes such as furfuraldehyde worked well without the formation of any side products and gave the α -amino nitrile derivative in 92% yield (Table 2, entry 7). Aliphatic amines such as benzylamine and butylamine as well as aromatic amines gave good yields (Table 2). Inspired by the results obtained with aldehydes (products 3a-3u), we then investigated whether these simple protocols were also valid for the Strecker reaction with ketones. Thus, various aliphatic and aromatic ketones, regardless of differences in the electronic characters, smoothly reacted with aniline and TMSCN to give the corresponding products in good to high yields, after short reaction times (products 5a-5l). Cyclopentanone and cyclohexanone both rapidly underwent the condensation within 15 min in excellent yields (Table 3, entries 1 and 2). Sterically hindered ketones, such as benzophenone, also reacted with aniline and TMSCN to give the corresponding products in good yields, although

Table 3

One-pot synthesis of α -amino nitriles using various ketones, amines, and TMSCN in the presence of SA-MNPs as a catalyst in water.^a



^a Reaction conditions: Ketones (1 mmol), amines (1 mmol), trimethylsilyl cyanide (1,2 mmol), SA-MNPs (20 mg), H₂O (3 mL), room temperature.

^b Isolated yields.

Table 4Reusability of the SA-MNPs catalyst.^a

Entry	Yield (%)	Recovery of SA-MNPs (%)
Refresh	97	99
1	96	99
2	96	98
3	94	98
4	91	98

^a *Reaction conditions*: Benzaldehyde (1 mmol), aniline (1 mmol), trimethylsilyl cyanide (1.2 mmol), SA-MNPs (20 mg), H₂O, room temperature.

the reactions proceeded relatively slowly (Table 3, entry 8). All products were characterized on the basis of their spectroscopic data such as FT-IR, 1 H and 13 C NMR spectra.

The catalytic activity and the ability to recycle and reuse SA-MNPs were studied in this system (Table 4). The catalyst was separated by an external magnet and was reused as such for subsequent experiments under similar reaction conditions. Yields of the product decreased only slightly after four times reuse of catalyst.

A comparison for the efficiency of the catalytic activity of SA-MNPs with several pervious methods is presented in Table 5. The results show that this method is superior to some of the earlier methods in terms of yields and reaction times.

Table 5				
Comparison of	catalytic activity	of SA-MNPs with	i several kn	own catalysts.

Entry	Catalyst	Conditions	Yield (%)	Ref.
1	InI ₃	Water, 0.5 h	95	[40]
2	Silica-based scandium (III)	CH ₂ Cl ₂ , 14 h	94	[41]
3	Silica sulfuric acid	CH ₂ Cl ₂ , 0.5 h	88	[42]
4	Montmorillonite	CH ₂ Cl ₂ , 3.5 h	90	[43]
5	TlCl ₃ ·4H ₂ O	Neat, 15 min	94	[44]
6	LiBF ₄	Neat, 12 min	90	[45]
7	Silica-bonded S-sulfonic acid	EtOH, 30 min	94	[46]
8	SA-MNPs	Water, 10 min	98	This work

^a *Reaction conditions*: Benzaldehyde (1 mmol), aniline (1 mmol), trimethylsilyl cyanide (1.2 mmol).

4. Conclusion

Covalent functionalization of sulfamic acid onto the magnetic Fe_3O_4 nanoparticles is successfully achieved by a multiple synthetic procedure which is confirmed with XRD, FT-IR, TGA, and TEM. The most interesting features of the present work include durability as well as efficient catalytic activity for one-pot synthesis of α -amino nitriles *via* three-component coupling reactions of aldehydes (or ketones), amines and trimethylsilyl cyanide in water, at room temperature. 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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