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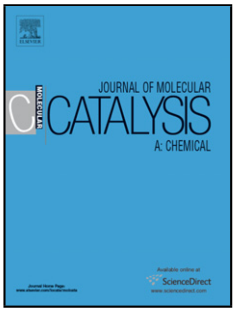

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PII: S1381-1169(13)00320-8
DOI: http://dx.doi.org/doi:10.1016/j.molcata.2013.08.028
Reference: MOLCAA 8849

To appear in: *Journal of Molecular Catalysis A: Chemical*

Received date: 18-7-2013
Revised date: 27-8-2013
Accepted date: 29-8-2013

Please cite this article as: J. Safari, Z. Zarnegar, A Magnetic nanoarticle-supported sulfuric acid as a highly efficient and reusable catalyst for rapid synthesis of amidoalkyl naphthols, *Journal of Molecular Catalysis A: Chemical* (2013), http://dx.doi.org/10.1016/j.molcata.2013.08.028

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A Magnetic nanoarticle-supported sulfuric acid as a highly efficient and reusable catalyst for rapid synthesis of amidoalkyl naphthols

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Abstract

Sulfuric acid functionalized magnetic Fe_3O_4 nanoparticles (MNPs-SO_3H) efficiently catalyze one-pot multicomponent condensation of β-naphthol with aromatic and aliphatic aldehydes and amide derivatives under solvent-free conditions to afford the corresponding amidoalkyl naphthols in excellent yields and in very short reaction times. High catalytic activity and ease of recovery using an external magnetic field are additional eco-friendly attributes of this catalytic system.

Keywords: Sulfuric acid functionalized Fe_3O_4 nanoparticles, Amidoalkyl naphthol, β-Naphthol, Multi-component reaction, Solvent-free.

1. Introduction

Sulfuric acid is an essential and efficient catalyst for the production of industrial important chemicals. Over 15 million tons of sulfuric acid are annually consumed as “an unrecyclable catalyst” which requires costly and inefficient separation of the catalyst from homogeneous reaction mixtures [1]. The use of recyclable strong solid acids in organic reactions are often considered to follow the principles of green chemistry, that is these catalyzed processes consume a minimum of energy and reagents or auxiliaries and minimize waste [2].

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Magnetic nanoparticles (MNPs) have recently appeared as an excellent type of catalyst support because of their good stability, easy synthesis and functionalization, high surface area and facile separation by magnetic forces, as well as low toxicity and price [3]. Also, surface functionalization of magnetic particles is an elegant way to bridge the gap between heterogeneous and homogeneous catalysis. These attractive features have made MNPs a promising alternative to porous/mesoporous catalyst supports. Thus, the development of silica-coated magnetite nanoparticles as attractive candidates in the search for supporting of catalysts is currently a subject of increasing interest in chemical process [4,5]. Sulfuric acid functionalized silica-coated magnetite 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 [6, 7].

The developing of one-pot multicomponent reactions (MCRs) and improving the known MCRs have attracted considerable attention in recent years [8, 9]. One of these MCRs is the preparation of amidoalkyl naphthol derivatives. 1-Amidoalkyl-2-naphthol derivatives are important class of compounds as they can be easily converted to biologically active compounds, 1-aminoalkyl-2-naphthols, by amide hydrolysis reaction [10, 11]. The synthesis of 1-amidoalkyl-2-naphthols can be carried out by multicomponent condensation of aldehydes, 2-naphthol and amide in the presence of various catalysts such as $SnCl_4$. $5H_2O$ [12], Nano-sulfated zirconia [13], Zirconium(IV) oxide chloride [14], dodecylphosphonic acid [15], $ZrO(OTf)_2$ [16], and $Bi(NO_3)_3$. $5H_2O$ [17]. However, some of these methods are not environmentally friendly and suffer from one or more disadvantages, such as prolonged reaction times, low yields, toxicity and recovery and reusability of the catalyst. Therefore, the development of clean processes and utilizing eco-

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friendly and green catalysts which can be simply recycled at the end of reactions have been under permanent attention. The demand for environmentally benign procedure with heterogeneous and reusable catalyst, promoted us to develop a safe alternate method for the preparation of amidoalkyl naphthols [18].

The aim of this protocol is to highlight the synergistic effects of the combined use of multicomponent reactions under solvent-free conditions and application of recyclable strong solid acid catalyst with inherent magnetic property for the development of new eco-compatible strategy for amidoalkyl naphthols synthesis. Therefore, we now wish to explore a straight forward convergent synthesis of 1-amidoalkyl-2-naphthols via the one-pot three-component reaction of β-naphthol, aldehydes derivatives, amides or urea under solvent free conditions using MNPs-SO_3H as an proficient, mild, harmless to the environment, non-toxic and magnetic powerful solid acid catalyst with good stability (Scheme 1). To the best of our knowledge, the use of magnetically solid acid catalyst for the synthesis of amidoalkyl naphthols previously has not been reported.

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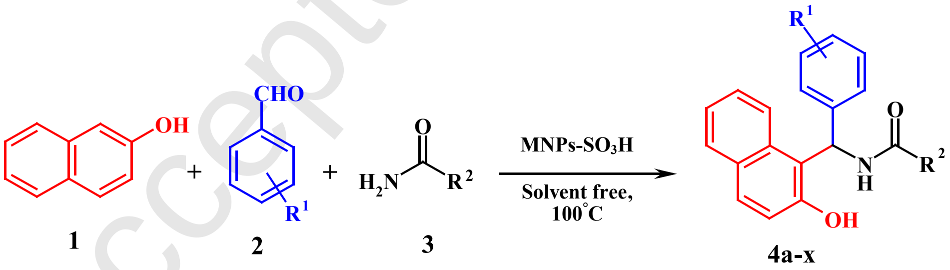

Scheme 1. Synthesis of amidoalkyl naphthols.

2. Experimental

Chemical reagents in high purity were purchased from the Merck and Sigma Chemical Company. All materials were of commercial reagent grade. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker DRX-400 spectrometer at 400 and 100 MHz respectively. FT-IR spectra were obtained with potassium bromide pellets in the range 400-4000 cm^{-1} with a Perkin–Elmer

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550 spectrometer. The element analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer carried out on Perkin–Elmer 240c analyzer. The thermogravimetric analysis (TGA) curves are recorded using a PL-STA 1500 device manufactured by Thermal Sciences. Nanostructures were characterized using a Holland Philips Xpert X-ray powder diffraction (XRD) diffractometer (CuK, radiation, λ= 0.154056 nm), at a scanning speed of 2°/min from 10° to 100° (2θ). Scanning electron microscope (SEM) was performed on a FEI Quanta 200 SEM operated at a 20 kV accelerating voltage. The samples for SEM were prepared by spreading a small drop containing nanoparticles onto a silicon wafer and being dried almost completely in air at room temperature for 2 h, and then were transferred onto SEM conductive tapes. The transferred sample was coated with a thin layer of gold before measurement.

2.1. Preparation of the magnetic Fe_3O_4 nanoparticles (MNPs)

Fe_3O_4-MNPs were prepared using simple chemical coprecipitation described in the literature [19]. Typically, 20 mmol of $FeCl_3.6H_2O$ and 10 mmol of $FeCl_2.4H_2O$ were dissolved in 75 ml of distilled water in a three-necked bottom (250 mL) under Ar atmosphere for 1 h. Thereafter, under rapid mechanical stirring, 10 ml of NaOH (10 M) was added into the solution within 30 min with vigorous mechanical stirring and ultrasound treatment under continuous Ar atmosphere bubbling. After being rapidly stirred for 1 h, the resultant black dispersion was heated to 85 $^{\circ}$C for 1 h. The black precipitate formed was isolated by magnetic decantation, exhaustively washed with double-distilled water until neutrality, and further washed twice with ethanol and dried at 60 $^{\circ}$C in vacuum. To obtain the well-dispersed Fe_3O_4 nanoparticles, the prepared magnetic nanoparticles were added to 100 mL citric acid solution (0.3 M) and heated at 80 $^{\circ}$C for 1 h. The obtained citric acid modified magnetic nanoparticles (CMP) were precipitated with acetone to

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remove the excessive citrate groups adsorbed on the nanoparticles, collected with a magnet, and vacuum-dried at 30 °C.

2.2. Silica coated magnetic nanoparticles ($Fe_3O_4@SiO_2$ MNPs)

The $Fe_3O_4@SiO_2$ core–shell nanoparticles were prepared according to the modified by the Stöber method [20]. The details were as follows: 0.50 g of the obtained CMP above were homogeneously dispersed in a mixture of 50 ml of ethanol, 9 ml of deioned water, and 1.0 ml of 28 wt% concentrated ammonia aqueous solution ($NH_3 \cdot 3H_2O$), followed by the addition of 0.50 mL of tetraethyl orthosilicate (TEOS). After vigorous stirring at room temperature for 16 h, the core–shell magnetic nanoparticles ($Fe_3O_4@SiO_2$ MNPs) were isolated by magnetic decantation to remove the unbounded silica particles and dried at room temperature at vacuum after being washed with de-ionized water, ethanol and acetone.

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2.3. General procedure for the synthesis of sulfuric acid functionalized Fe_3O_4 nanoparticles (MNPs-SO_3H)

A 500 ml suction flask was equipped with a pressure equalizing dropping funnel containing chlorosulfunic acid and gas inlet tube for conducting HCl gas over adsorbing the solution water. A flask was charged with $Fe_3O_4@SiO_2$ MNPs (500 mg) and dispersed in dry CH_2Cl_2 by ultrasonic bath for 10 min. Subsequently, chlorosulfunic acid (0.4 mL in dry CH_2Cl_2) was added drop-wise manner to a cooled (ice-bath) solution of $Fe_3O_4@SiO_2$ over a 30 min period, which HCl gas evolved from the reaction vessel immediately. After the addition was completed, the mixture was shaken for 30 min and brown solid (MNPs-SO_3H) collected using an external magnet and washed with methanol before being dried in an oven at 60 °C.

2.4. General synthesis for the preparation of amidoalkyl naphthols

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A mixture of β-naphthol (2 mmol), aldehyde (2 mmol), amide/urea (2.4 mmol) and MNPs-SO_3H (0.02 g) were taken in round bottom flask and stirred and heated at 100 °C. After the TLC indicates the disappearance of starting materials, the reaction was cooled to room temperature. The resultant solid was then washed with hot water to remove excess amide and the catalyst was separated by an external magnet and reused as such for the next experiment. Then acetone was added to it stirred well and filtered off. The filtrate was evaporated to remove solvent and the crystalline material left was taken up in ethanol for recrystallization. The synthesized amidoalkyl naphthols were characterized by IR, ^1H NMR, ^{13}C NMR and elemental analysis and comparison of their physical data with the literatures.

2.5. Spectral data for new compounds

2.5.1. N-[(3-hydroxy-4-methoxyphenyl)-(2-hydroxynapthalen-1-yl)-methyl]acetamide ***(4l)***. IR (KBr) (υ_{max}/cm^{-1}): 3400 (NH stretch), 3300-3050 (OH stretch), 1643 (C=O stretch), 1605, 1450 (C=C stretch), 1547 (NH bend), 753 (CH bend); ^1H NMR (400 MHz, DMSO-d_6): δ_H 9.90 (s, H, OH), 8.75 (s, H, OH), 8.35 (d, *J*=8 Hz, 1H), 7.73 (d, *J*=7.8 Hz, 1H), 7.02-7.72 (m, 4H, Ar–H), 6.950-6-973 (m, 5H, Ar–H), 3.63 (s, 3H, OCH_3), 1.90 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 169.4, 160.4, 146.7, 145.5, 140.4, 138.8, 134.1, 130.4, 127.4, 126.7, 125.5, 124.2, 119.3, 115.2, 55.6, 49.2, 23.1 ppm; Anal. Calcd. for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15; O, 18.97%. Found: C, 71.18; H, 5.66; N, 4.13; O, 18.94%.

2.5.2. N-[(2,3-dimethoxyphenyl)-(2-hydroxynapthalen-1-yl)-methyl]acetamide ***(4m)***. IR (KBr) (υ_{max}/cm^{-1}): 3398 (NH stretch), 3300-3000 (OH stretch), 1645 (C=O stretch), 1600, 1455 (C=C stretch), 1547 (NH bend), 750 (CH bend); ^1H NMR (400 MHz, DMSO-d_6): δ_H 10.49 (s, 1H, OH), 8.84 (d, *J*=8 Hz, 1H), 8.02 (d, *J*=7.8 Hz, 1H), 7.96-8.54 (m, 4H, Ar–H), 6.54-7.69 (m, 5H, Ar–H), 4.27 (s, 3H, OCH_3), 3.30 (s, 3H, OCH_3), 1.47 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz,

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DMSO-d_6): δ_C 169.3, 160.7, 155.2, 148.7, 136.3, 134.7, 130.2, 128.4, 127.5, 126.8, 124.2, 123.1, 119.5, 116.5, 113.3, 62.8, 57.5, 45.2, 23.2 ppm; Anal. Calcd. for $C_{21}H_{21}NO_4$: C, 71.78; H, 6.02; N, 3.99; O, 18.21%. Found: C, 71.74; H, 5.97; N, 3.95; O, 18.19%.

2.5.3. N-[(2-fluorophenyl)-(2-hydroxynapthalen-1-yl)-methyl]acetamide ***(4n)***. IR (KBr) (υ_{max}/cm^{-1}): 3392 (NH stretch), 3300-2900 (OH stretch), 1639 (C=O stretch), 1600, 1452 (C=C stretch), 1538 (NH bend), 752 (CH bend); ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 9.91 (s, 1H, OH), 8.69 (d, *J*=8.2 Hz, 1H), 8.02 (d, *J*=7.8 Hz, 1H), 7.57-7.83 (m, 4H, Ar–H), 7.71-6.97 (m, 6H, Ar–H), 2.14 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 170.2, 167.6, 160.8, 137.1, 134.5, 133.8, 131.4, 127.3, 126.5, 125.2, 124.5, 119.7, 116.6, 48.7, 24.1 ppm; Anal. Calcd. for $C_{19}H_{16}FNO_2$: C, 73.77; H, 5.21; F, 6.14; N, 4.53; O, 10.34%. Found: C, 73.72; H, 5.17; F, 6.09; N, 4.48; O, 10.30%.

2.5.4. N-((2-Hydroxynaphthalen-1-yl)-(naphthalen-1-yl)methyl)acetamide **(4o).** IR (KBr) (υ_{max}/cm^{-1}): 3415 (NH stretch), 3300-2310 (OH stretch), 1638 (C=O stretch), 1605, 1437 (C=C stretch), 1523 (NH bend), 748 (CH bend); ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 9.41 (s, 1H, OH), 8.52 (d, *J*=8.5 Hz, 1H), 8.12 (d, *J*=8.1 Hz, 1H), 7.81-7.85 (m, 7H, Ar–H), 7.28-7.34 (m, 6H, Ar–H), 2.88 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 169.3, 161.4, 139.6, 137.5, 137, 134.1, 130.8, 126.8, 125.6, 124.7, 124.1, 119.4, 48.1, 23.5 ppm; Anal. Calcd. for $C_{23}H_{19}NO_2$: C, 80.92; H, 5.61; N, 4.10; O, 9.37%. Found: C, 80.85; H, 5.57; N, 4.02; O, 9.33%.

3. Results and discussion

The magnetite nanoparticles were prepared by coprecipitation of iron(II) and iron(III) ions in basic solution. To improve the chemical stability of Fe_3O_4 nanoparticles, their surface engineering was successfully performed by the suitable deposition of silica onto nanoparticles surface by the ammonia-catalyzed hydrolysis of tetraethylorthosilicate (TEOS). Then, the

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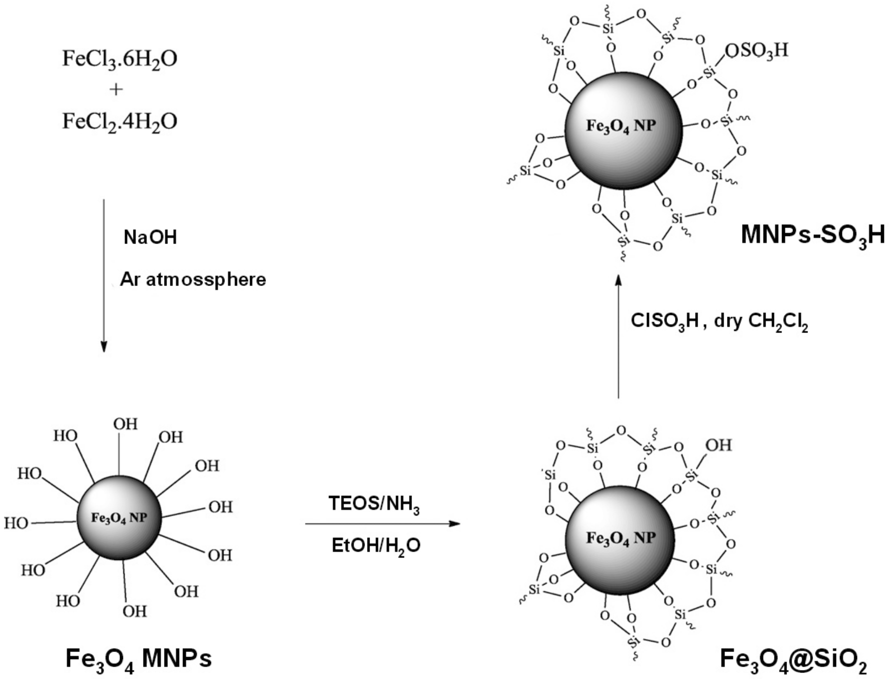
$Fe_3O_4@SiO_2$ served as support for the immobilization of SO_3H groups by simple mixing of core–shell nanocomposite and chlorosulfonic acid in CH_2Cl_2 (MNPs-SO_3H) (Scheme 2). The number of H^+ sites of MNPs-SO_3H was determined by pH-ISE conductivity titration (Denver Instrument Model 270) and found to be 1.85 H^+ sites per 1 g of solid acid at 25 °C.



Scheme 2. Preparation steps for fabricating sulfuric acid-functionalized magnetic Fe_3O_4 nanoparticles.

Fig. 1 shows the FTIR spectra of both the unfunctionalized and functionalized magnetic nanoparticles. The Fe–O stretching vibration near 580 cm^{-1}, O–H stretching vibration near 3432 cm^{-1}, O-H deformed vibration near 1625 cm^{-1} were observed for both in Fig. 1(a) and 1(b). The significant features observed for Fig. 1(b) are the appearance of the peaks at 476, 808, and 1090 cm^{-1} are ascribed to the asymmetric stretching vibration, symmetric stretching vibration and bending vibration Si–O–Si groups respectively. The wider and stronger peak at about 3448 cm^{-1} demonstrates that there are some free Si-OH in the samples [21]. The presence of sulfonyl group is confirmed by 1217 and 1124 cm^{-1} bands that were covered by a stronger absorption of Si-O bond at 1090 cm^{-1}. In addition, the Si-OH group peak at 900 cm^{-1} was disappeared for Fe_3O_4@Silica sulfuric acid [22]. The increase in the intensities of the band at 2800–3700 cm^{-1} suggests that there are more OH groups under the magnetic nanoparticle surface after the sulfonation. On the other hand, the band in this region became much broader [1]. All these observations confirm that the sulfonic groups have functionalized the surface of the magnetic nanoparticles (MPs).

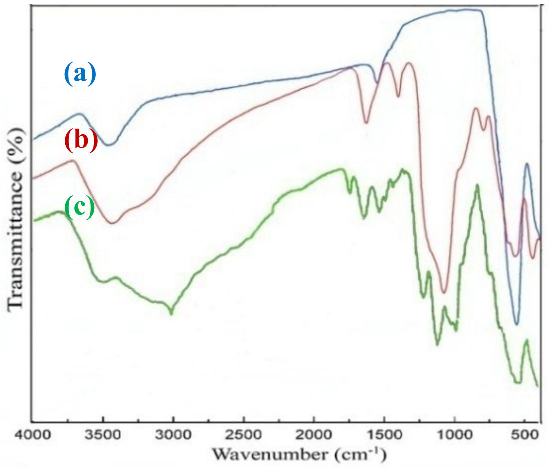


Fig. 1. The comparative FT-IR spectra for (a) Fe_3O_4, (b) Fe_3O_4@SiO_2 and (c) MNPs-SO_3H.

Fig. 2 presents the XRD-diffraction patterns of the prepared MNPs and MNPs-SO_3H. The same peaks were observed in the both of the MNPs and MNPs-SO_3H XRD patterns, indicating retention of the crystalline spinel ferrite core structure during the silica-coating process. The XRD patterns of the particles (JCPDS card No. 85-1436) show six characteristic peaks reveal a cubic iron oxide phrase (2θ = 30.35, 35.95, 43.45, 53.70, 57.25, 62.88, 71.37, 74.46). These are related to their corresponding indices (2 2 0), (3 1 1), (4 0 0), (3 3 1), (4 2 2), (3 3 3), (4 4 0) and (5 3 1) respectively [29]. The broad peaks at 2θ from 23° to 27° shown in Fig. 2(b) are ascribed to amorphous silica [23].

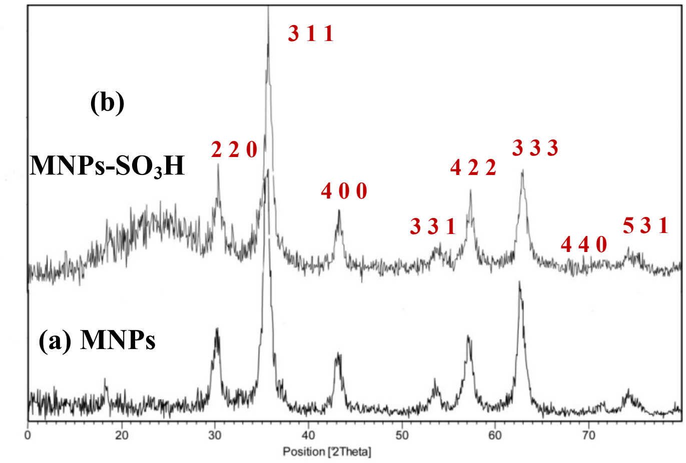


Fig. 2. XRD patterns of (a) Fe_3O_4 and (b) MNPs-SO_3H.

The components of the Fe_3O_4, Fe_3O_4@SiO_2 and MNPs-SO_3H nanoparticles were analysis by using energy dispersive spectrometer (EDS) in Fig 3(a), (b) and (c), respectively. The presence of Si, O, and Fe signals in Fig. 3(b) indicates that the iron oxide particles were loaded into silica, and the higher intensity of Si peak compared with Fe peaks indicates Fe_3O_4 nanoparticles were trapped by SiO_2. The characteristic peak of S in Fig. 3(c) indicates that the iron oxide nanoparticles have been coated by SO_3H. According to the above analysis, it could be concluded MNPs-SO_3H have been successfully synthesized.

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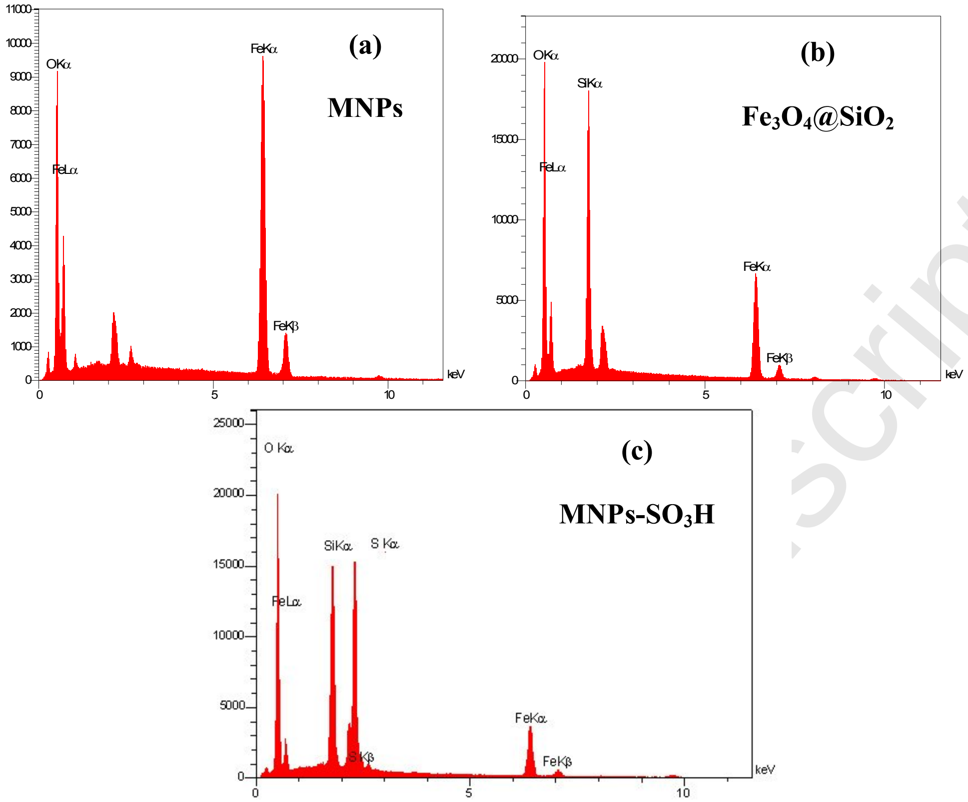

Fig. 3. The EDS spectra of (a) Fe_3O_4, $Fe_3O_4@SiO_2$ and (c) MNPs-SO_3H nanoparticles.

The thermogravimetric analysis (TGA) curves of the Fe_3O_4 MNPs, and MNPs-SO_3H show the mass loss of the organic materials as they decompose upon heating (Fig. 4). The initial weight loss from the Fe_3O_4 MNPs up to 126 ˚C is due to the removal of physically adsorbed solvent and surface hydroxyl groups. The TGA curve of the MNPs-SO_3H was divided into several regions corresponding to different mass lose ranges. The first region, which occurred below 160 °C, displayed a mass loss that was attributable to the loss of adsorbed solvent or trapped water from the catalyst. The weight loss at higher temperature (250-350°C) could be mainly attributed to the evaporation and subsequent decomposition of SO_3H groups. Thus, the catalyst was stable up to 200 °C, confirming that it could be safely used in organic reactions at temperatures in the range of 100 °C [7, 1].

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Fig. 4. TGA curve of (a) Fe_3O_4 MNPs, and (b) MNPs-SO_3H nanoparticles.

Fig. 5 shows SEM images of the relative nanoparticles. It can be seen from Fig. 5(a) that magnetite (Fe_3O_4) particles have a mean diameter of about 28-35 nm and a nearly spherical shape. The SEM image shown in Fig. 5(b) demonstrates that most of Fe_3O_4@SiO_2 nanoparticles are spherical with particle size in the about 120 nm. Fig. 5(c) shows that Fe_3O_4@SiO_2-SO_3H nanoparticles are nearly spherical with nano dimension ranging from 120 to 150 nm in size and smoother surface.

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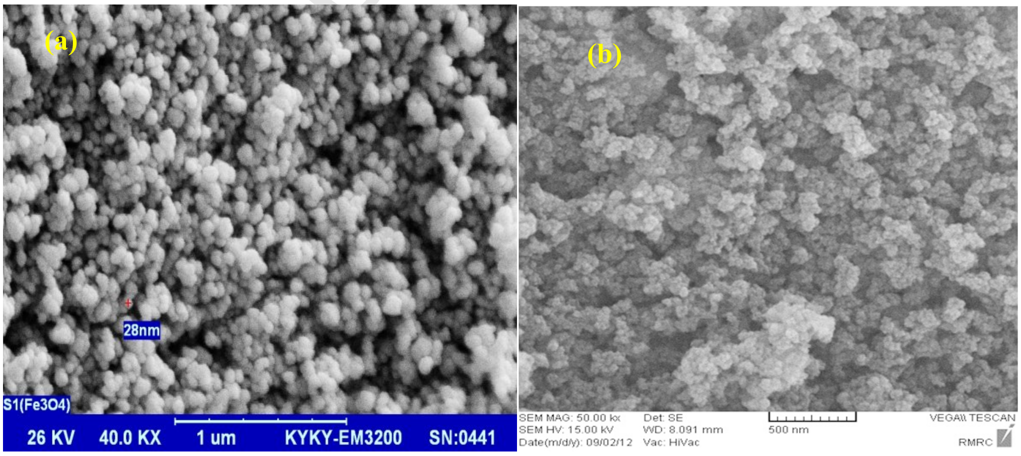

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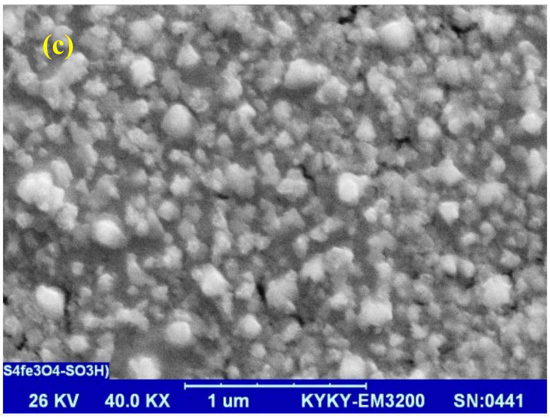

Fig. 5. The SEM image of (a) Fe_3O_4 (b) Fe_3O_4@SiO_2 and (c) MNPs-SO_3H nanoparticles.

The magnetic property of the catalyst was studied by vibrating-sample magnetometer (VSM) in Fig. 6. The magnetization curve for Fe_3O_4 nanoparticles, Fe_3O_4@SiO_2 and MNPs-SO_3H are shown in Fig. 6. The saturation magnetization of Fe_3O_4@SiO_2 and MNPs-SO_3H were found to be 22.67 and 45.87 emu/g, respectively, which are much lower than bare Fe_3O_4 MNPs (67.22 emu/g) [19].

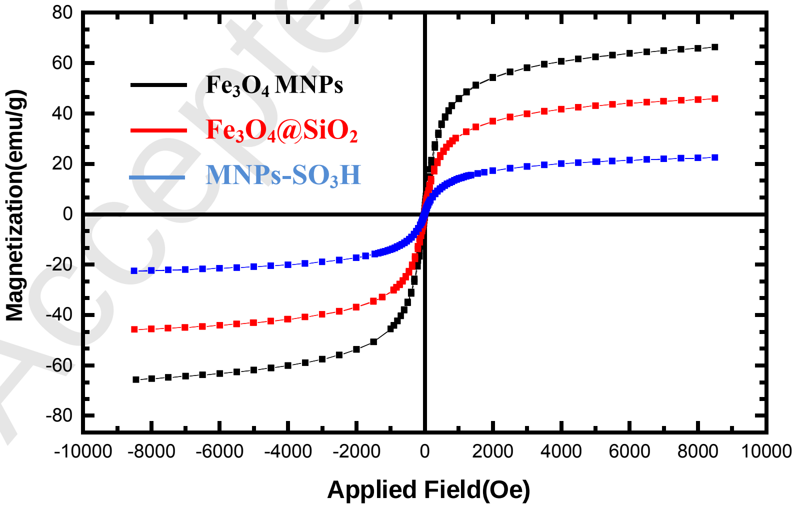

Fig. 6. Magnetization curves for the prepared Fe_3O_4 MNPs, Fe_3O_4@SiO_2 and MNPs-SO_3H at room temperature.

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After characterization of the solid acid catalyst, we have tested its catalytic activity in the preparation of amidoalkyl naphthol derivatives. In a typical experimental procedure, a mixture of aldehyde (2 mmol), β-naphthol (2 mmol), amide (2.4 mmol) and MNPs-SO_3H (0.02 g) as a model study were taken in round bottom flask and stirred for a certain period of time as required to complete the reaction (as indicated by TLC) at 100 °C in a preheated oil bath. As shown in Table 1, the best result was obtained by carrying out the reaction using 0.02 g of MNPs-SO_3H at 100 °C under solvent-free conditions (Table 1, Entry 8). Furthermore, no reaction was observed when the mixture was heated to 100 °C for 6 h in the absence of catalyst (Table 1, Entry 10).

Table 1
Optimization of the amount of catalyst and the reaction temperature for the preparation of amidoalkyl naphthols. [a]

Entry	Catalyst (g)	Temperature (°C)	Time (min)	Yield[b] (%)
1	0. 008	90	60	55
2	0.010	90	45	67
3	0.015	90	35	78
4	0.020	90	15	90
5	0.025	90	15	90
6	0.020	70	60	70
7	0.020	80	30	83
8	0.020	100	10	95
9	0.020	110	10	95
10	-	100	12 (h)	0

[a] Reaction conditions: benzaldehyde (2 mmol), β-naphthol (2 mmol), and acetamide (2.4 mmol) under solvent-free conditions.
[b] Isolated yields.

Using these optimized reaction conditions, we extended the reaction to substituted aromatic and aliphatic aldehydes, which reacted with amides/urea and β-naphthol in Table 2. As evident from the results, this procedure is uniformly effective for both aliphatic and aromatic aldehydes. The aliphatic aldehydes such as n-butyraldehyde and propionaldehyde were subjected under the reaction conditions and corresponding desired products were isolated in excellent yields. Aromatic aldehydes with both activating and deactivating groups such as Me, OMe, Cl, $N(Me)_2$, F and NO_2 reacted to afford the corresponding products in high yields. It was shown that

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aromatic aldehydes with electron-withdrawing groups reacted faster than those with electron-releasing groups as expected and sterically hindered aromatic aldehydes required longer reaction times. The rate of reaction of these aldehydes decreased compared to aldehydes with electron-donating groups, but the yield of the corresponding products was higher than benzaldehydes with electron-donating groups. In addition, urea, acetamide and benzamide underwent smooth transformation under the reaction conditions, whereas the reaction was unsuccessful with thiourea.

Table 2

Synthesis of amidoalkyl naphthols in the presence of MNPs-SO_3H without solvent.[a]

Entry	R[1]	R[2]	Product	Time (min)	Yield[b] (%)	Mp (lit. mp)[ref]
1	C_6H_5	CH_3	**4a**	10	93	242-244 [245–246][24]
2	4-$CH_3C_6H_4$	CH_3	**4b**	30	85	223-224 [222–223][24]
3	4-$N(CH_3)_2C_6H_4$	CH_3	**4c**	35	80	120-122 [123–125][24]
4	4-$CH_3OC_6H_4$	CH_3	**4d**	20	83	184-186 [183–185][24]
5	3-$NO_2C_6H_4$	CH_3	**4e**	7	97	253-254 [256–258][25]
6	4-FC_6H_4	CH_3	**4f**	10	93	228-230 [230–232][24]
7	2,4-$Cl_2C_6H_3$	CH_3	**4g**	7	93	202-203 [201–203][24]
8	2,5-$(CH_3O)_2C_6H_3$	CH_3	**4h**	10	90	253-254 [251–253][24]
9	3,4-$(CH_3O)_2C_6H_3$	CH_3	**4i**	10	87	236-237 [235–237][24]
10	2-ClC_6H_4	CH_3	**4j**	20	85	214-216 [213–215][24]
11	2-$NO_2C_6H_4$	CH_3	**4k**	25	87	217-219 [218–219][25]
12	3-OH,4-$CH_3OC_6H_3$	CH_3	**4l**	10	90	236-238
13	2,3-$(CH_3O)_2C_6H_3$	CH_3	**4m**	10	93	231-233
14	2-FC_6H_4	CH_3	**4n**	20	80	244-245
15	$C_{10}H_7$	CH_3	**4o**	10	95	229-230
16	CH_3CH_2	CH_3	**4p**	10	85	179-181 [179–180][26]
17	$CH_3CH_2CH_2$	CH_3	**4q**	10	90	222-223 [224–226][26]
18	C_6H_5	C_6H_5	**4r**	10	82	238-240 [237–238][26]
19	3-$NO_2C_6H_4$	C_6H_5	**4s**	7	92	230-233 [232–234][26]
20	4-$CH_3OC_6H_4$	C_6H_5	**4t**	20	80	209-211 [208–210][26]
21	2-ClC_6H_4	C_6H_5	**4u**	20	80	285-287 [284–285][25]
22	C_6H_5	NH_2	**4v**	10	83	177-178 [177–179][26]
23	3-$NO_2C_6H_4$	NH_2	**4w**	7	88	190-192 [193][27]
24	4-$CH_3C_6H_4$	NH_2	**4x**	20	77	113-115 [115–117][28]

[a] Reaction conditions: β-naphthol 2 mmol, aldehyde 2 mmol, amide 2.4 mmol, MNPs-SO_3H 0.02 g, at 100 °C.
[b] Isolated yields.

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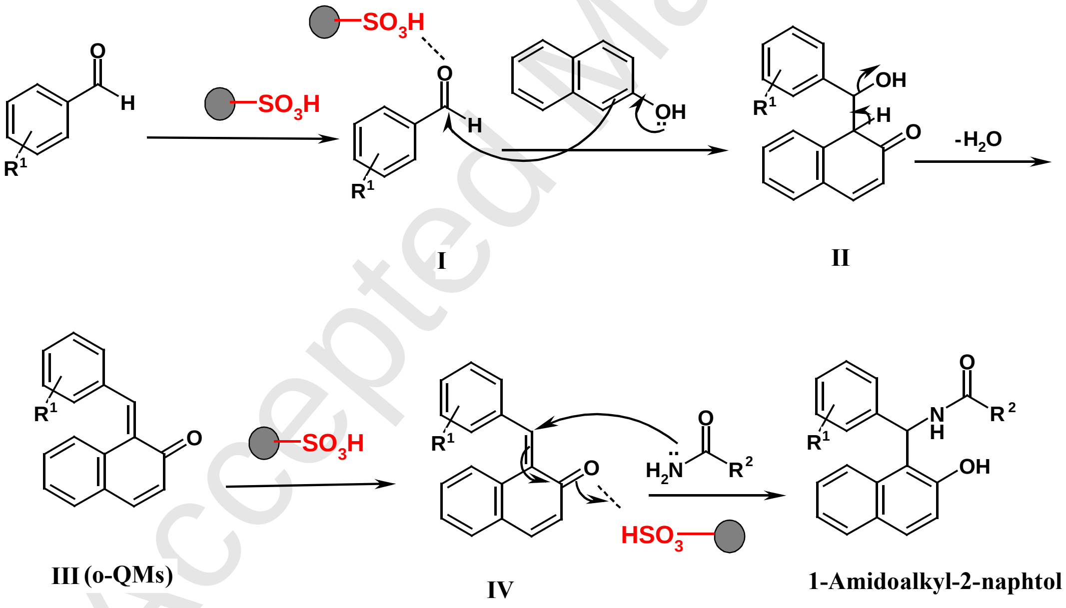
In a plausible mechanism (Scheme 3) which is supported by the literature [24, 27]; at first, aromatic aldehyde is activated by acidic group of MNPs to produce **I**. Then, β-naphthol attacks to the carbonyl group of the activated aldehyde, and affords intermediate **II**. Next, by removing H_2O from II, ortho-quinone methides (o-QMs, **III**) is prepared. MNPs-SO_3H again activates intermediate **III** to give **IV** as a Michael acceptor. Afterward, Michael addition of amide or urea to intermediate **IV** affords the expected 1-amidoalkyl-2-naphthol. The aromatic aldehydes with electron-withdrawing groups reacted faster as compared with those having electron-releasing groups. As per earlier report [24], the lower energy of LUMO of the alkene containing electron-withdrawing groups (a carbonyl group as in o-QM intermediate) as compared to that of alkene containing electron-donating groups may be responsible for making the present reaction faster.



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Scheme 3. Possible mechanism for the synthesis of amidoalkyl naphthol using MNPs-SO_3H.

A comparison of the efficacy of MNPs-SO_3H catalyst with some of those reported in the literature is presented in Table 3 for the preparation of N-[Phenyl-(2-hydroxynapthalen-1-yl)-methyl]acetamide **(4a)**. The results showed that MNPs-SO_3H is a better catalyst with respect to reaction times and yields of the products. Also, it is seen in addition to having the general

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advantages attributed to the inherent magnetic property of nanocatalysts, MNPs-SO_3H is an equally or more efficient catalyst for this three component reaction.

Table 3

Comparison of MNPs-SO_3H with other catalysts reported in the literature for the synthesis of N-[phenyl-(2-hydroxynapthalen-1-yl)-methyl]acetamide.[a]

Entry	**Catalyst**	**Amount; condition**	**Time**	**Yield[b] (%)**	**Ref.**
1	p-TSA	10 mol%; solvent-free, 125 ˚C	5 h	85	30
2	Sulphamic acid	50 mol%; solvent-free, 30 ˚C	15 min	88	18
3	Silica sulfuric acid	0.02 g; solvent-free, r.t	2 h	85	22
4	Montmorillonite K10	0.1 g; solvent-free, 125 ˚C	1.5 h	90	31
5	SiO_2–$HClO_4$	0.6 mol%; solvent-free, 125 ˚C	40 min	90	21
6	MNPs-SO_3H	0.02 gr, solvent-free, 100 ˚C	10 min	93	This work

[a] Reaction conditions: β-naphthol (2 mmol), benzaldehyde (2 mmol), and acetamide (2.4 mmol).
[b] Isolated yields.

The reusability is one of the important properties of this catalyst. The recyclability of MNPs-SO_3H was investigated for the reaction of 3-nitrobenzaldehdye, acetamide and β-naphthol. After completion of reaction the separated catalyst can be reused after washing with acetone and drying at 80 ˚C. It was shown that the catalyst could be reused for the next cycle without any appreciable loss of its activity (Fig 7). The effect of catalyst was unchanged which was determined by measuring the acidic site loading of the reused MNPs-SO_3H and hence conforming the purity of MNPs-SO_3H.

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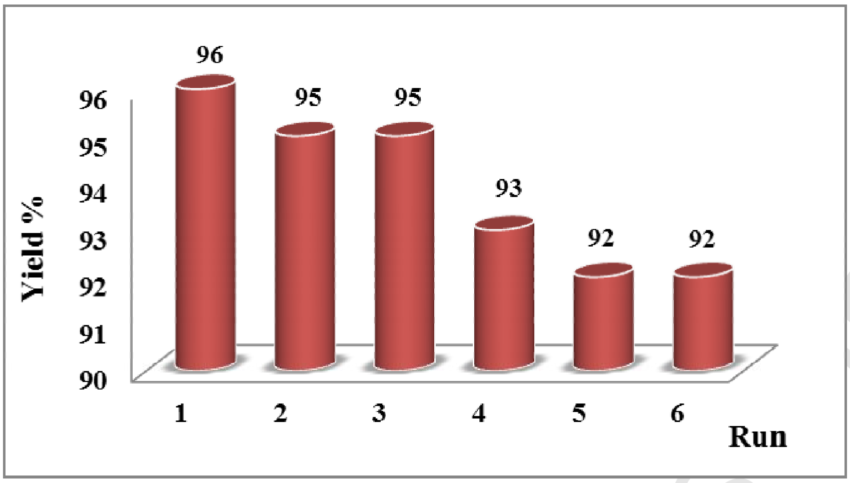

Fig. 7. Recyclability of MNPs-SO_3H in the reaction of β-naphthol (2 mmol), 3-nitrobenzaldehdye (2 mmol), acetamide (2.4 mmol), catalyst (0.02 g) at 100 °C.

4. Conclusion

Sulfuric acid functionalized Fe_3O_4 nanoparticles is successfully achieved by a multiple synthetic procedure which is confirmed with XRD, FT-IR, TGA, VSM, and SEM. The most interesting features of the present work include durability as well as efficient catalytic activity for one-pot synthesis of amidoalkyl naphthols by one-pot three-component coupling of β-naphthol, aromatic and aliphatic aldehydes and urea or amides under solvent free at 100 °C, MNPs-SO_3H as an inexpensive and non-hazardous solid acid catalyst which can be handled easily and removed from the reaction mixtures by applying an external magnetic field. This method offers several advantages including short reaction time, excellent yields, simple work-up, ease of separation, and recyclability of the magnetic catalyst, as well as the ability to tolerate a wide variety of substitutions in the reagents.

Acknowledgments

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We gratefully acknowledge the financial support from the Research Council of the University of Kashan for supporting this work by Grant NO. (256722/IV).

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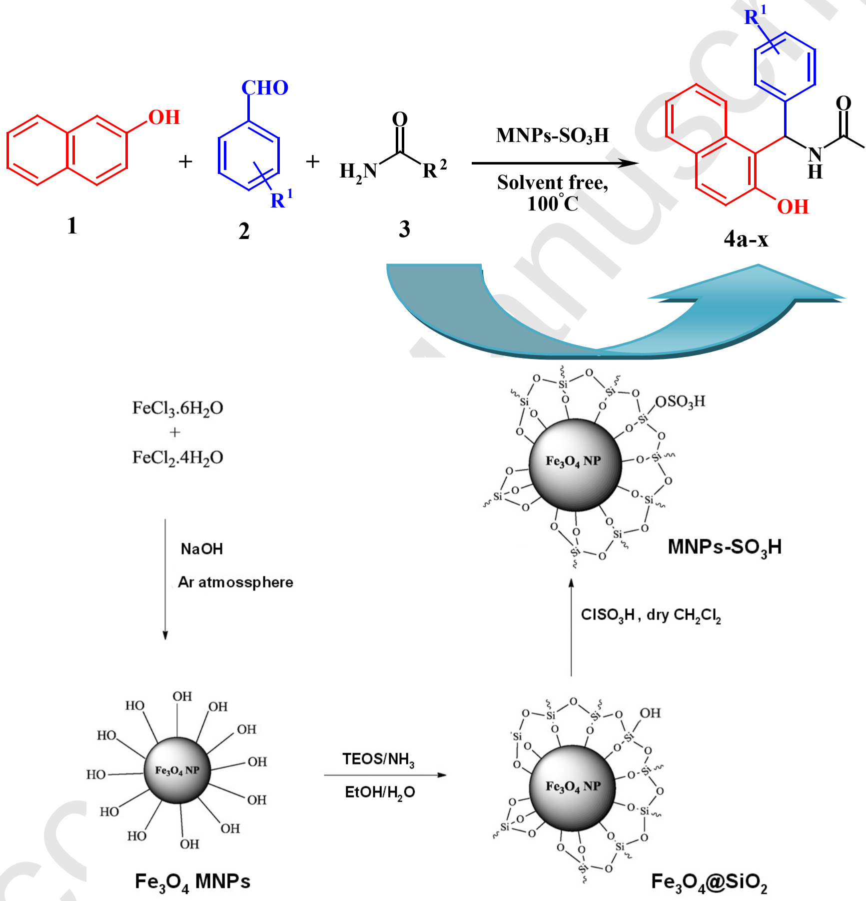
Graphical Abstract

A Magnetic nanoarticle-supported sulfuric acid as a highly efficient and reusable catalyst for rapid synthesis of amidoalkyl naphthols

Javad Safari*, Zohre Zarnegar



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highlights

- MNP-SO_3H was prepared and amidoalkyl naphthol was synthesized using this catalyst.
- Sulfuric acid functionalized Fe_3O_4 nanoparticles were caracterized by XRD, FT-IR, TGA, VSM, and SEM.
- The catalyst was separated by an external magnet and reused as such for the next experiment.

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