

# Highly efficient protocol for the aromatic compounds nitration catalyzed by magnetically recyclable core/shell nanocomposite

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**Abstract** An efficient protocol for the nitration of aromatic compounds in the presence of a catalytic amount of sulfuric acid-functionalized silica-based magnetic core/shell nanocomposite was reported. The designed products were obtained in high yields in relatively short reaction times at room temperature under solvent-free conditions. The nanocatalyst was simply recovered from the reaction mixture by using an external magnet and efficiently reused for several times. The characterization of particle size, morphology and elemental analysis of the nanocatalyst were provided by scanning electron microscopy, transmission electron microscopy and energy-dispersive X-ray spectroscopy analyses, respectively.

**Keywords** Nanocatalyst · Core/shell · Nitration · Solid acid · Magnetic nanoparticles · Aromatic compounds

## Introduction

The nitration of aromatic compounds could be performed by using various reagents. The nitro aromatic compounds are widely used for the synthesis of dyes, pharmaceuticals, perfumes, plastics and explosives. The classical nitration is commonly performed in strongly acidic polar medium such as nitric acid and concentrated sulfuric acid [1, 2]. These conditions lead to excessive acid waste which is not eco-friendly, due to expensive treatment and corrosion of the

reactors. These problems have generated many efforts for finding alternative methods for the nitration reaction. Therefore, various nitrating agents have been studied under different conditions in the presence of various catalysts [3–12].

Due to significant advantages, hybrid and magnetic organic–inorganic nanocomposite catalysts have become of considerable interest in both academic and industrial fields. Among them, supported magnetic metal nanoparticles have emerged as a new class of nanocatalysts. Nanocatalysts generally exhibit higher catalytic activity than classic heterogeneous acid catalysts, because they have high specific surface area. Sulfuric acid-functionalized silica-coated magnetite nanoparticles as a recyclable strong solid acid catalyst have opened up a new road to introduce an amazing and efficient system for the facilitating catalyst recovery in different organic reactions. Other organic and inorganic compounds grafted on magnetic nanoparticles coated with silica which could be used as heterogeneous magnetic nanocatalysts in chemical reactions [13–15].

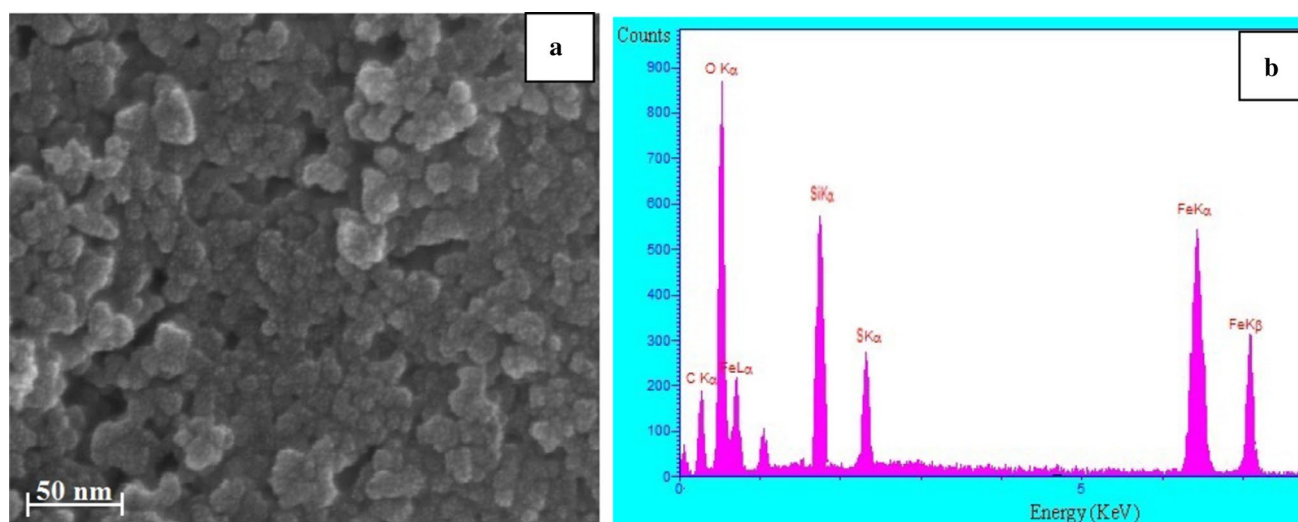
Due to importance of nitration and in connection with our previous researches on design and development of nanocatalysts [16–23], herein, the nitration of aromatic and heteroaromatic compounds was performed by using sulfuric acid-functionalized silica-based magnetic nanocomposite along with sodium nitrate under solvent-free conditions at room temperature. This research can be classified as a new and green approach for the efficient and rapid nitration of aromatic compounds by using a recyclable nanocatalyst under mild reaction conditions.

## Results and discussion

The sulfuric acid-functionalized silica-based magnetic nanocomposite as a heterogeneous magnetic nanocatalyst

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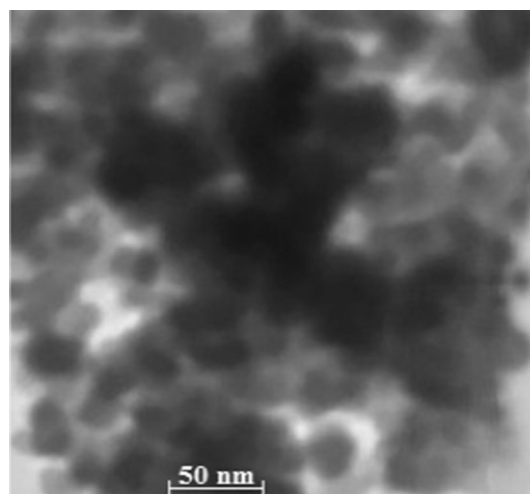
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**Fig. 1** a SEM image and b EDX pattern of the nanocatalyst

was prepared according to the literature-described procedures, except modifications on the use of the iron salts and their molar ratio and also procedure that enhanced the magnetic property and efficiency of the nanocatalyst [19]. In this regard, iron chloride salts were dissolved in distilled water and a solution of concentrated aqueous ammonia was added to the initial solution and gamma-Fe<sub>2</sub>O<sub>3</sub> nanoparticles were obtained. Then, these nanoparticles were diluted via a solution of water, ethanol and concentrated aqueous ammonia. A solution of tetraethyl orthosilicate (TEOS) in ethanol was then added to the mixture, and core/shell nanoparticles were obtained. Then, chlorosulfonic acid was added to the solution in *n*-hexane. After that, HCl was removed from the reaction pot. The resulted SO<sub>3</sub>H-functionalized core/shell nanoparticles were separated using an external magnet.

The particles size was studied via scanning electron microscopy (SEM), and the identification of SO<sub>3</sub>H-functionalized magnetic core/shell nanocatalyst was based on the analysis of SEM images that clearly showed a monodisperse spherical shape of the nanoparticles (Fig. 1a). The average particles size of the nanoparticles was approximately 25–30 nm. Also, energy-dispersive X-ray spectroscopy (EDX) spectra of the nanocatalyst indicated the presence of Si, S, O and Fe elements in the nanocatalyst (Fig. 1b). In addition, the structure of magnetized silica and magnetized silica sulfuric acid core/shell nanostructures have been analyzed by X-ray diffraction (XRD) spectroscopy in the literature [19]. Herein, similar peaks have been obtained for both of them and also SO<sub>3</sub>H-functionalized magnetic core/shell nanocatalyst in XRD patterns, which indicated the crystalline nanostructures magnetic cores during the silica-coating and sulfonation steps.



**Fig. 2** TEM image of the core/shell nanoparticles

To confirm the core/shell nanostructure of the SO<sub>3</sub>H-functionalized magnetic nanocatalyst, the transmission electron microscopy (TEM) images were provided (Fig. 2). It showed suitable spherical morphologies and arranged core/shell structures of the nanocatalyst. During the seeded sol-gel method, the thickness of silica shell of the magnetic nanoparticles can be appropriately adapted by controlling the addition amount of silica source TEOS. In comparison with the large-size support solid, nanoparticles with small particle sizes have larger specific surface area and better dispersion in the solvent, which can have practical effects to the catalysis.

The catalytic activity of the nanocatalyst was investigated in a pilot experiment for the nitration of toluene. The optimum condition for the reaction was using 4 mg of the

**Table 1** Comparison of the efficiency of the present nanocatalyst with literature reports in the nitration of toluene

Entry	Reagent/catalyst	Solvent	Temp (°C)	Time (min)	Yield <sup>a</sup> (%)
1	HNO <sub>3</sub> /ZBS-15 [24]	S.F.	100	240	55
2	HNO <sub>3</sub> /P <sub>2</sub> O <sub>5</sub> /silica gel [25]	S.F.	r.t.	7	56
3	Ph <sub>2</sub> PCI/I <sub>2</sub> /AgNO <sub>3</sub> [26]	S.F.	r.t.	60	66
4	HNO <sub>3</sub> /lanthanide(III) nosylates [27]	(CH <sub>2</sub> Cl) <sub>2</sub>	r.t.	960	98
5	HNO <sub>3</sub> /Yb(N(SO <sub>2</sub> C <sub>4</sub> F <sub>9</sub> ) <sub>2</sub> ) <sub>3</sub> /MCM-41 [28]	(CH <sub>2</sub> Cl) <sub>2</sub>	40	240	99
6	Magnetic nanocatalyst/NaNO <sub>3</sub>	S.F.	r.t.	3	95

<sup>a</sup> Isolated yield

SO<sub>3</sub>H-functionalized magnetic nanocatalyst and NaNO<sub>3</sub> at room temperature under solvent-free conditions. The isolated product was obtained in 95% yield after 3 min.

To compare the efficiency of the magnetic nanocatalyst with some other reports in nitration of toluene, we have investigated other works that are listed in Table 1. Ph<sub>2</sub>PCI/I<sub>2</sub>/AgNO<sub>3</sub> carries out the reaction at room temperature in 60 min in 86% yield (entry 1). HNO<sub>3</sub>/P<sub>2</sub>O<sub>5</sub>/silica gel gives the product at room temperature in 7 min in 92% yield (entry 2). HNO<sub>3</sub>/ZBS-15 gives the product at 100 °C in 240 min in 100% yield (entry 3). Another reagent is HNO<sub>3</sub>/lanthanide(III) nosylates that carries out the reaction in 1,2-dichloroethane at room temperature in 960 min in 98% yield (entry 4). HNO<sub>3</sub>/Yb(N(SO<sub>2</sub>C<sub>4</sub>F<sub>9</sub>)<sub>2</sub>)<sub>3</sub>/MCM-41 gives the product in 1,2-dichloroethane at 40 °C in 240 min in 96% yield (entry 5). Our method carries out the nitration reaction at room temperature in 3 min in 95% yield (entry 6). As a result, the SO<sub>3</sub>H-functionalized magnetic nanocatalyst is the best, highly efficient and environmentally friendly reagent for the nitration of aromatic compounds.

Subsequently, to investigate the efficiency and generality of this catalyst in the nitration of aromatic compounds the reaction was extended to other aromatic compounds in obtained optimized conditions (Table 2). According to the table, it is obvious that *o*-xylene (entry 2), 4-methoxybenzaldehyde (entry 8) and *p*-cresol (entry 13) are regioselectively converted into the corresponding nitro compounds by the SO<sub>3</sub>H-functionalized magnetic core/shell nanocatalyst in excellent yields. The efficiency and applicability of the SO<sub>3</sub>H-functionalized magnetic core/shell nanocatalyst in the nitration of aromatic compounds also were investigated. As indicated in Table 2, the best result for the heteroaromatic compounds was obtained for 4-nitrobiphenyl after 60 min (entry 22). Furthermore, other heteroaromatic compounds such as 2-phenyl-1*H*-imidazole and imidazole were regioselectively converted into the corresponding nitro compound by sodium nitrate in excellent yields in the presence of the nanocatalyst.

Finally, the reusability of the core/shell nanocatalyst was examined in the model reaction (Fig. 3). After completion of the reaction, nanoparticles were separated by using an

external magnet and simply washed, dried and reused in subsequent reactions. It was observed that the catalyst can be reused for eight times without any significant decrease in efficiency. After separation from the reaction mixture, the nanocatalyst was washed with methanol/diluted HCl solution (to remove Na<sup>+</sup> as NaCl and to regenerate the catalyst's active sites) and then dried in an oven at 60 °C. Before reusing the recycled catalyst, it was weighted in any cycle, and after that, it was reused in subsequent runs. Furthermore, fresh catalyst was added to reciprocate decreased mass loss, if it was considerable.

## Experimental

### General

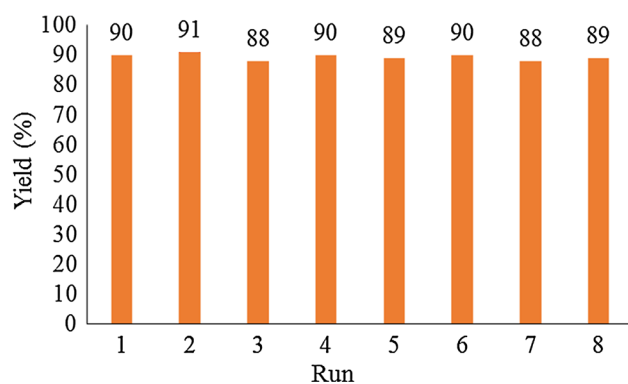
All solvents, chemicals and reagents were purchased from Merck, Fluka and Sigma-Aldrich and used without purification. Melting points were measured on an Electrothermal 9100 apparatus and were uncorrected. SEM images were taken with Zeiss-DSM 960A microscope with attached camera. EDX spectra were recorded on Numerix DXP-X10P. TEM images were obtained through Zeiss-EM 900 electron microscope operating at 80 kV. Some reactions and products were confirmed by a gas chromatography manufactured by Teif Gostar Faraz Co., Iran. XRD measurements were carried out using a JEOL JDX-8030 (30 kV, 20 mA).

### Preparation of the magnetic nanoparticles

First, FeCl<sub>3</sub>·6H<sub>2</sub>O (10 mmol) and FeCl<sub>2</sub>·4H<sub>2</sub>O (10 mmol) were dissolved in distilled water (100 mL) in a three-necked round-bottom flask (250 mL). Then, the resulting solution was heated at 90 °C under N<sub>2</sub> atmosphere with rapid stirring for 2 h. A solution of concentrated aqueous ammonia (10 mL, 25 wt%) was added dropwise to the solution for 45 min. Then, the reaction mixture was cooled to room temperature and the resulting gamma-Fe<sub>2</sub>O<sub>3</sub> magnetic particles collected with a magnet.

**Table 2** Nitration of aromatic and heteroaromatic compounds in the presence of the core/shell nanocatalyst at room temperature under solvent-free conditions

Entry	Substrate	Products	Time (min)	Yield <sup>a</sup> (%)	Mp/bp (°C)	
					Found	Reported
1	Toluene	4-Nitrotoluene	3	95	50–51	51–52 [29]
2	o-Xylene	4-Nitro-o-xylene	3	92	29–31	30–31 [30]
3	1,3,5-Trimethylbenzene	2-Nitro-1,3,5-trimethylbenzene	3	90	40–43	43–45 [31]
4	Chlorobenzene	4-Nitrochlorobenzene	4	95	80–82	81–83 [31]
5	Bromobenzene	4-Nitrobromobenzene	4	92	124–126	125–127 [32]
6	<i>N,N</i> -Dimethylaniline	<i>N,N</i> -Dimethyl-4-nitroaniline	3	98	160–163	162–165 [33]
7	Anisole	4-Nitroanisole	3	97	53–57	54–57 [34]
8	4-Methoxybenzaldehyde	3-Nitro-4-methoxybenzaldehyde	6	93	96–99	99–101 [35]
9	Phenol	4-Nitrophenol	5	92	109–111	108–110 [36]
10	4-Chlorophenol	4-Chloro-2-nitrophenol	22	90	87–89	91 [37]
11	3-Chlorophenol	2-Nitro-5-chlorophenol	30	95	43–45	42–43 [38]
12	4-Bromophenol	4-Bromo-2-nitrophenol	34	95	80–83	84 [39]
13	<i>p</i> -Cresol	4-Methyl-2-nitrophenol	20	93	29–31	31 [39]
14	[1,1'-Biphenyl]-4-ol	3-Nitro-[1,1'-biphenyl]-4-ol	30	94	63–65	66 [40]
15	Acetanilide	Nitroacetanilide	5	95	150–152	149–151 [41]
16	2-Phenyl-1 <i>H</i> -imidazole	2-(4-Nitrophenyl)-1 <i>H</i> -imidazole	30	92	230–232	229–231 [42]
17	Benzophenone	3-Nitrobenzophenone	15	90	95–99	94–95 [43]
18	1-Methylimidazole	1-Methyl-4-nitroimidazole	60	78	134–136	134–135 [44]
19 <sup>b</sup>	Imidazole	4-Nitroimidazole	90	87	313–317	315 [45]
20 <sup>b</sup>	Naphthalene	1-Nitronaphthalene	75	94	53–56	55–57 [46]
21 <sup>b</sup>	4-Nitroimidazole	1,4-Dinitro-1 <i>H</i> -imidazole	80	80	93–95	92–94 [47]
22 <sup>b</sup>	Biphenyl	4-Nitrobiphenyl	60	95	113–116	115 [48]

<sup>a</sup> Isolated yield<sup>b</sup> In refluxing dichloromethane**Fig. 3** Reusability study of the nanocatalyst in the pilot experiment

### Preparation of the core/shell

The prepared gamma-Fe<sub>2</sub>O<sub>3</sub> nanoparticles (1.0 g) were initially diluted via the sequential addition of water (20 mL), ethanol (60 mL) and concentrated aqueous ammonia (1.5 mL, 28 wt%). A solution of TEOS (0.45 mL) in ethanol (10 mL)

was then added dropwise to the dispersion under stirring conditions. After 12-h vigorous stirring, the resulting product was collected by magnetic separation and washed with ethanol.

### Preparation of the SO<sub>3</sub>H-functionalized magnetic core/shell nanocatalyst

Initially, chlorosulfonic acid (0.5 g, 4.5 mmol) was added dropwise to a cooled solution of core/shell (1 g) in *n*-hexane (5 mL) over a 2-h period. After completion of the loading, the mixture was stirred for a further 3 h until the complete removal of HCl from the reaction pot. The resulted SO<sub>3</sub>H-functionalized silica-coated magnetic core/shell nanoparticles were separated by using an external magnet, washed with ethanol and then dried in an oven at 60 °C.

### General procedure for the nitration of aromatic compounds

A mixture of aromatic compound (1 mmol), sodium nitrate (1 mmol) and SO<sub>3</sub>H-functionalized magnetic core/shell

nanocatalyst (0.1 mmol) was pulverized in a mortar at room temperature for an appropriate time. The reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction,  $\text{CH}_2\text{Cl}_2$  (5.0 mL) was then added to the mixture and filtered. Evaporation of the solvent followed by recrystallization or column chromatography on silica gel of the crude product gave the corresponding nitrated compounds in good to excellent yields. The nanocatalyst was simply separated from the reaction mixture by using an external magnet, washed with methanol/diluted HCl solution and then dried in an oven at 60 °C. Before reusing the recycled catalyst, it was weighted in any cycle, and after that, it was reused in subsequent runs. Furthermore, fresh catalyst was added to reciprocate decreased mass loss, if it was considerable.

#### Spectral data of the selected products

*4-Nitrophenol* (Table 2, entry 9): Yellow solid; m.p. 109–111 °C. IR (KBr) 1338, 1494, 1546, 3320  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 6.17 (s, 1H, OH), 6.93 (*d*,  $J = 9.0$  Hz, 2H), 8.17 (*d*,  $J = 9.0$  Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 115.7, 126.3, 141.3, 161.3.

*4-Bromo-2-nitrophenol* (Table 2, entry 12): Yellow solid; m.p. 80–83 °C. IR (KBr) 1313, 1527, 3273  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.07 (*d*,  $J = 8.7$  Hz, 1H), 7.66 (*d*,  $J = 8.7$  and 2.4 Hz, 1H), 8.24 (*d*,  $J = 2.1$  Hz, 1H), 10.49 (s, 1H, OH).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 111.7, 121.7, 127.3, 140.3, 142.9, 154.1.

*1-Nitronaphthalene* (Table 2, entry 20): Yellow solid; m.p. 53–56 °C. IR (KBr) 1336, 1519  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.54 (*t*,  $J = 7.8$  Hz, 1H), 7.62 (*t*,  $J = 7.2$  Hz, 1H), 7.72 (*t*,  $J = 6.9$  Hz, 1H), 7.96 (*d*,  $J = 8.1$  Hz, 1H), 8.12 (*d*,  $J = 8.1$  Hz, 1H), 8.23 (*d*,  $J = 7.5$  Hz, 1H), 8.56 (*d*,  $J = 8.7$  Hz, 1H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 123.5, 124.4, 124.5, 125.5, 127.7, 129.0, 129.8, 134.7, 135.0.

*1,4-Dinitro-1H-imidazole* (Table 2, entry 21): Yellow solid; m.p. 93–95 °C. IR (KBr) 1245, 1517, 1557, 1638, 3150  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 9.43 (s, 1H), 8.99 (s, 1H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 120.0, 133.2, 147.2.

## Conclusion

In summary, we have described a simple, rapid and convenient method for the nitration of aromatic compounds in the presence of  $\text{SO}_3\text{H}$ -functionalized silica-coated magnetic core/shell nanoparticles as a nanocomposite catalyst along with sodium nitrate under solvent-free conditions at room temperature. The superiorities of the present method over previous reports include a very rapid reaction, readily

available reagents, high selectivity, recoverable catalyst, high yields and environmentally benign protocol. The efficiency and high activity of the present nanocatalyst were confirmed by excellent isolated yields of the products (Table 2) and several times reusability (Fig. 3).

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