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Fe_3O_4@silica sulfuric acid nanoparticles: An efficient reusable nanomagnetic catalyst as potent solid acid for one-pot solvent-free synthesis of indazolo[2,1-*b*]phthalazine-triones and pyrazolo[1,2-*b*]phthalazine-diones

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Multi-component reaction

A B S T R A C T

Regarding the green chemistry's goals, silica-coated magnetite nanoparticles (MNPs) open up new avenue to introduce an amazing and efficient system for facilitating catalyst recovery in different organic reactions. Therefore, in this paper the preparation of sulfuric acid functionalized silica-coated magnetite nanoparticles with core–shell structure (Fe_3O_4@silica sulfuric acid) are presented by using Fe_3O_4 spheres as the core and silica sulfuric acid nanoparticles as the shell. The catalyst was characterized by infrared spectroscopy (FT-IR), scanning electron microscope (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) spectroscopy, and vibrating sample magnetometer (VSM). Ability of this nanomagnetic solid acid catalyst in the one-pot three-components condensation reaction of phthalhydrazide, aromatic aldehydes and cyclic or acyclic 1,3-diketones are also described. Utilization of easy reaction conditions, catalyst with high catalytic activity and good reusability, and simple magnetically work-up, makes this methodology as an interesting option for the economic synthesis of indazolo[2,1-*b*]phthalazine-triones and pyrazolo[1,2-*b*]phthalazine-diones.

1. Introduction

In recent years, to minimize waste and atom economy in the use of raw materials, the target of science and technology has been shifting toward more environment friendly, sustainable resources and reusable catalysts [1]. 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 [2–4]. Functionalized magnetic nanoparticles can be easily separated and recycled from the products by an external magnet. This kind of separation prevents the loss of solid catalyst in the process and is not time-consuming. It also enhances products purity and optimizes operational costs [5–8].

In the past few decades, heterocyclic chemistry has been one of the most important disciplines in organic synthesis and pharmaceutical chemistry [9]. Heterocycles containing the phthalazine moiety are a class of compounds, which are highly recognized in the field of medicine and organic chemistry [10] due to their antimicrobial [11], anticonvulsant [12], antifungal [13], anticancer [14] and anti-inflammatory activities [15].

Moreover, these compounds also could be promising materials for new luminescence or fluorescence probes. Generally, the formation of phthalazine derivatives was carried out by the treatment of phthalhydrazide with aromatic aldehydes and cyclic or acyclic 1,3-diketones under acidic conditions [16]. Many of the reported methods are efficient, however, in some methods the catalyst recovery/reuse is not possible [17–22]. Therefore, the discovery of new and inexpensive catalysts for the preparation of phthalazine derivatives under mild conditions is of prime importance.

On the other hand, multicomponent coupling reactions (MCRs) have become powerful tools in organic, combinatorial and medicinal chemistry [23] with the rapid generation of molecular complexity and diversity with predefined functionality [24]. Solvent-free multicomponent is an eco-friendly approach, which opens up numerous possibilities for conducting rapid organic synthesis and functional group transformations [25–28].

The aim of this protocol is to highlight the synergistic effects of the combined use of multicomponent coupling reactions under solvent-free conditions and application of solid Brönsted acid catalyst supported on nanostructure materials with inherent magnetic property for the development of new eco-compatible strategy for heterocyclic synthesis. Therefore, we now wish to explore a straightforward convergent one-pot synthesis of indazolo[2,1-*b*]phthalazine-triones and pyrazolo[1,2-*b*]phthalazine-diones derivatives using Fe_3O_4@silica

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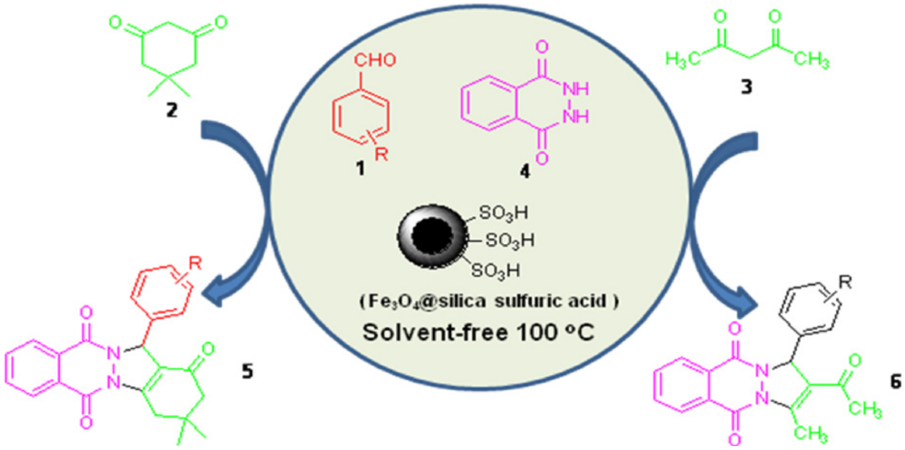


Scheme 1. Preparation of indazolo [2,1-*b*] phthalazine-triones and pyrazolo[1,2-*b*]phthalazine-diones catalyzed by Fe_3O_4@silica sulfuric acid.

sulfuric acid as an proficient, mild, harmless to the environment, recyclable, non-toxic and magnetic powerful solid acid catalyst with good stability toward humidity, under solvent-free conditions through domino Knoevenagel condensation/Michael addition/intramolecular cyclodehydration sequence (Scheme 1).

2. Results and discussions

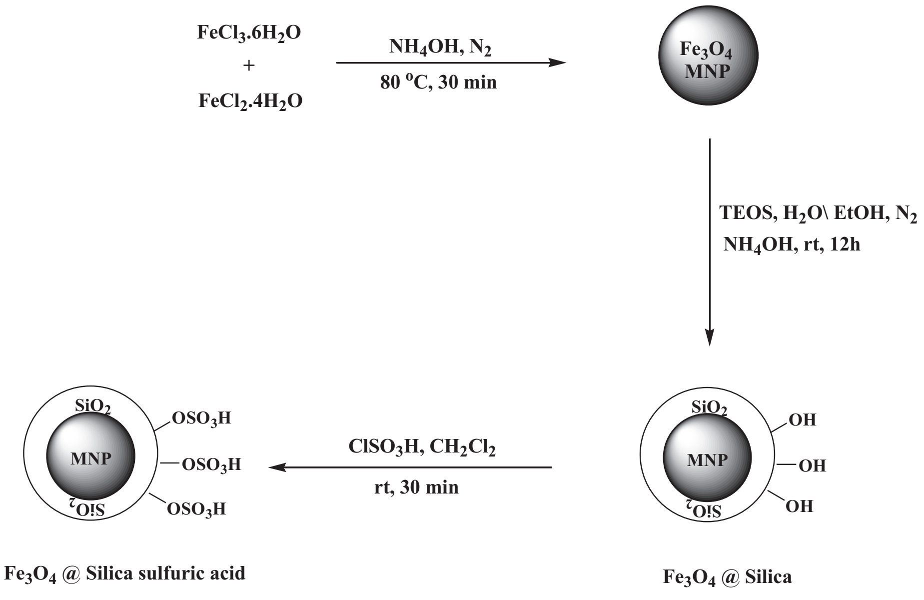
Fe_3O_4@silica sulfuric acid core–shell composite, that Fe_3O_4 spheres as the core and silica sulfuric acid nanoparticles as the shell, was prepared by a simple, low cost and convenient method. Magnetite nanoparticles were synthesized by the co-precipitation of $FeCl_2$ and $FeCl_3$ in ammonia solution. To improve the chemical stability of magnetite nanoparticles, their surface engineering was successfully performed by the suitable deposition of silica onto nanoparticles surface by the ammonia-catalyzed hydrolysis of tetraethylorthosilicate (TEOS). Next, The SiO_2 spheres served as support for the immobilization of SO_3H groups by simple mixing of core–shell composite and chlorosulfonic acid in CH_2Cl_2 (Scheme 2).

Fe_3O_4@silica sulfuric acid nanocomposite was characterized by FT-IR, SEM, HRTEM, XRD, VSM and ion exchange pH-analysis. The ion-exchange pH-analysis demonstrated a loading of 1.89 mmol $SO_3H\,g^{-1}$.

The FT-IR spectra of Fe_3O_4@silica sulfuric acid is shown in Fig. 1. The FT-IR analysis of the Fe_3O_4@silica sulfuric acid exhibits basic characteristic peak at approximately 580 cm^{-1}, which was attributed to the presence of Fe—O vibration and the bands at 1092 cm^{-1}, 800 cm^{-1} and 447 cm^{-1} come from Si—O—Si asymmetric stretching vibration, symmetric stretching vibration and bending vibration, respectively. 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 1092 cm^{-1}. In addition, the Si—OH group peak at 900 cm^{-1} was disappeared for Fe_3O_4@silica sulfuric acid [29]. The spectrum also shows a broad OH stretching absorption around 2800–3700 cm^{-1}.

The morphology and particle size distribution of Fe_3O_4, Fe_3O_4@SiO_2 and Fe_3O_4@silica sulfuric acid nanostructures were performed by measuring SEM using a Philips XL30 scanning electron microscope. According to Fig. 2, Fe_3O_4@silica sulfuric acid has spherical shape with nano dimension ranging from 90 to 170 nm.

Transmission electron microscopy (TEM) revealed that iron oxide nanoparticles had entrapped in the silica shell successfully, in which an average particle size is about 40–60 and the diameter of



Scheme 2. Schematic diagram for the synthesis of Fe_3O_4@silica sulfuric acid.

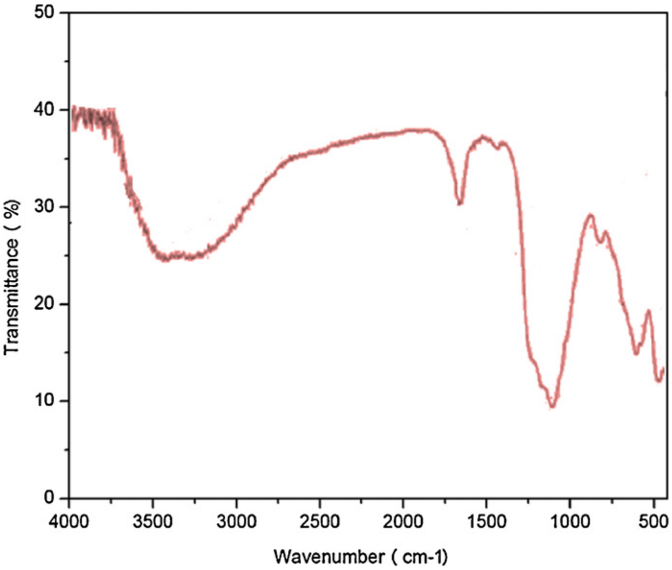


Fig. 1. FT-IR spectra of Fe_3O_4@silica sulfuric acid. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

the magnetic core is about 20–40 nm, much smaller than the sizes obtained from the SEM measurements (Fig. 3). Images of the silica-coated magnetic nanoparticles display dark MNP cores surrounded by an amorphous silica shell.

The magnetic property of the catalyst was studied by vibrating-sample magnetometer (VSM). The diagram of magnetization for $Fe_3O_4@SiO_2$ and Fe_3O_4@silica sulfuric acid MNPs are depicted in Fig. 4. The saturation magnetization of $Fe_3O_4@SiO_2$ and Fe_3O_4@silica sulfuric acid MNPs were found to be 17 and 38 emu/g,

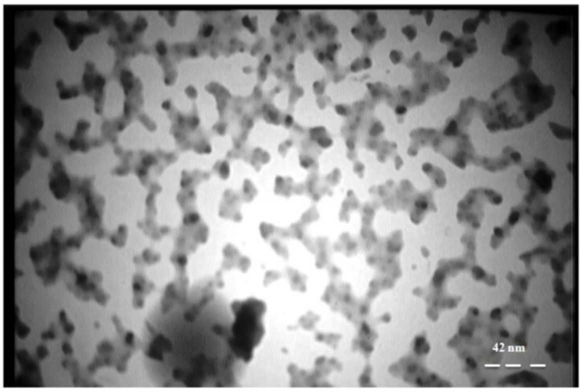


Fig. 3. TEM image of Fe_3O_4@silica sulfuric acid.

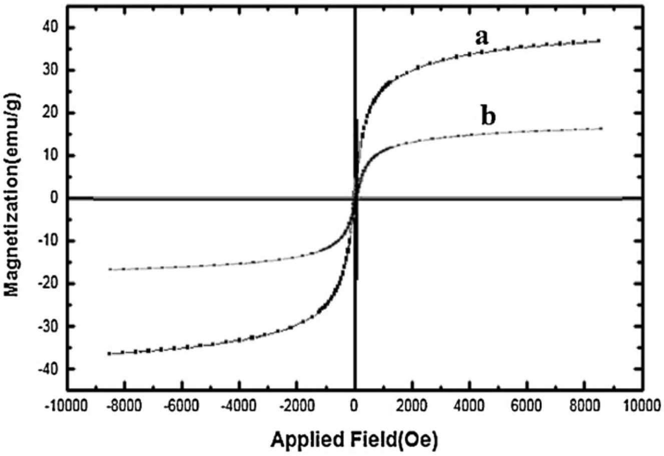


Fig. 4. VSM magnetization curves of the (a) $Fe_3O_4@SiO_2$ and (b) Fe_3O_4@silica sulfuric acid nanoparticles.

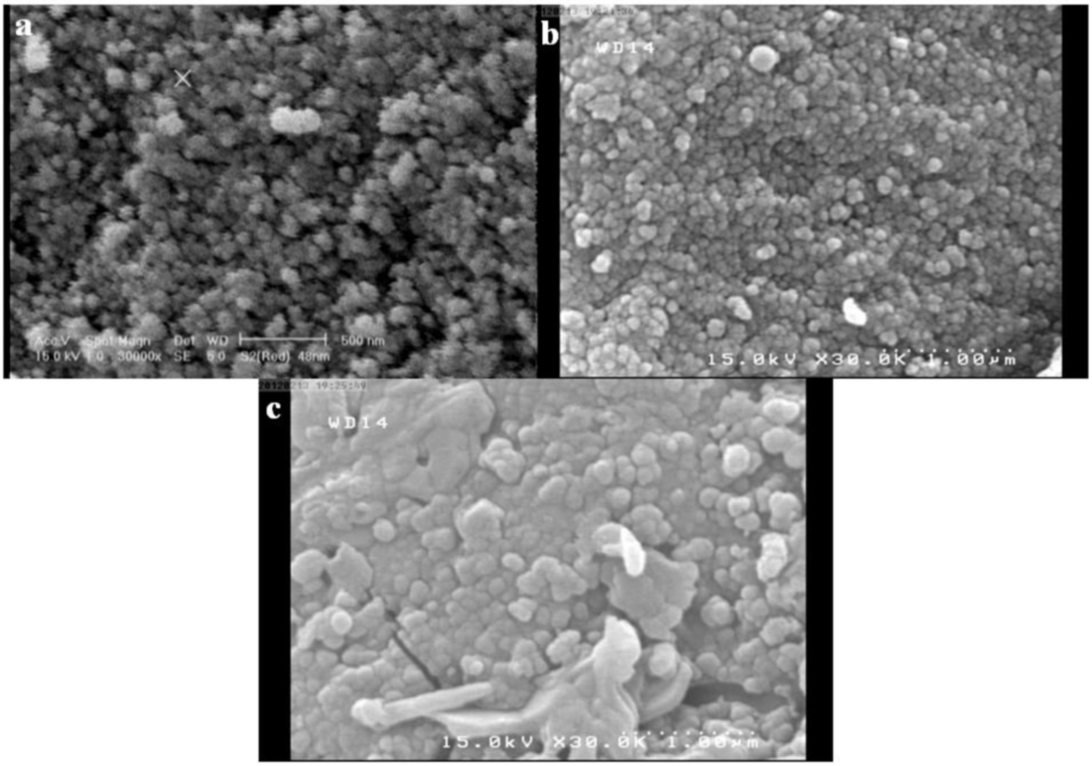


Fig. 2. SEM images of (a) Fe_3O_4, (b) $Fe_3O_4@SiO_2$ and (c) Fe_3O_4@silica sulfuric acid.

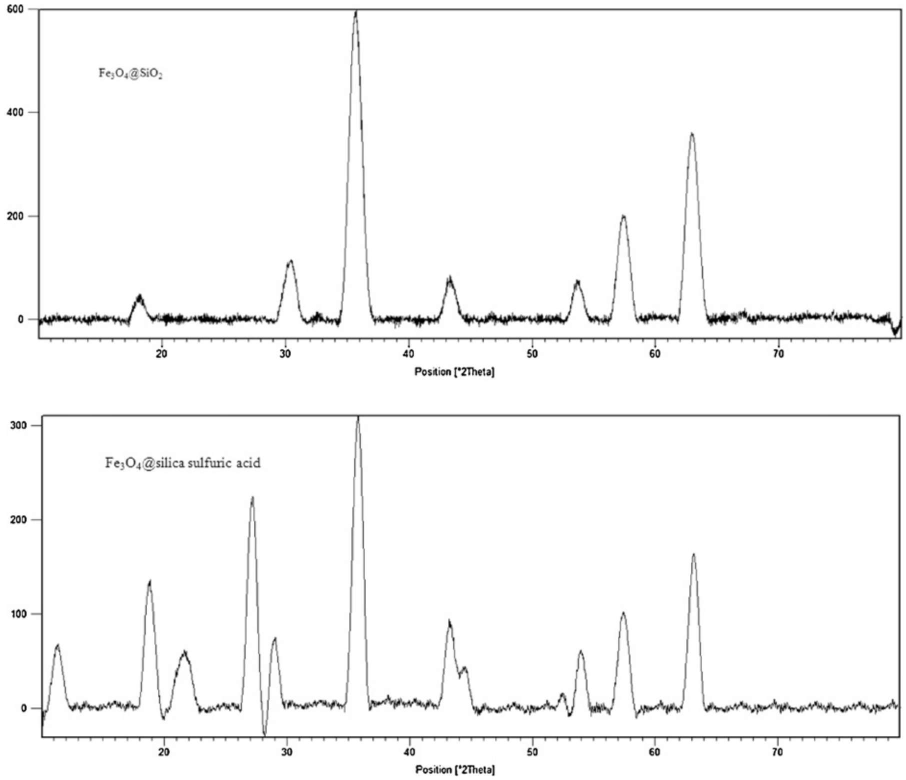


Fig. 5. X-ray diffraction for Fe_3O_4@SiO_2 and Fe_3O_4@silica sulfuric acid.

respectively, which are much lower than bare Fe_3O_4 MNPs (63.2 emu/g) [30].

The structure of Fe_3O_4@SiO_2 and Fe_3O_4@silica sulfuric acid were analyzed by X-ray diffraction (XRD) spectroscopy. XRD diagram of the bare MNPs displayed patterns consistent with the patterns of spinel ferrites described in the literature (Fig. 5) [29]. The same peaks were observed in the both of the Fe_3O_4@SiO_2 and Fe_3O_4@silica sulfuric acid XRD patterns, indicating retention of the crystalline spinel ferrite core structure during the silica-coating process.

The average MNPs core diameter of Fe_3O_4@SiO_2 and Fe_3O_4@silica sulfuric acid were calculated to be 7.4 and 8.9 nm, respectively from the XRD results by Scherrer's equation [31,32].

After characterization of the Fe_3O_4@silica sulfuric acid catalyst, we have tested its catalytic activity in the preparation of phthalazine derivatives. In the preliminary stage of investigation, we focused on a three-component process for the model reaction of phthalhydrazide (1 mmol), dimedone (1 mmol) and bezaldehyde (1.1 mmol) under solvent-free conditions at 100 °C in the absence and presence of Fe_3O_4@silica sulfuric acid. It was found that in the absence of nanomagnetic solid acid catalyst, only trace of the desired product was observed on TLC plate even after 2 h of heating (Table 1). When the reaction was performed in the presence of Fe_3O_4@silica sulfuric acid, it proceeded rapidly to give the desired product.

It should be pointed out that in the presence of Fe_3O_4 nano particle or Fe_3O_4@SiO_2, this three-component process was sluggish and even after 2 h of heating a considerable amount of starting material recovered unchanged (Table 1).

As shown in Table 1, 0.075 g of the magnetic nano Fe_3O_4@silica sulfuric acid and solvent-free conditions are the best operative experimental conditions (Table 1). Increasing the amount of catalyst does not improve the yield of the product any further, whereas decreasing the amount of catalyst leads to decrease in the product yield (Scheme 3).

Subsequently, with optimal conditions in hand, to study the scope and limitations of the protocol, a wide range of substituted aldehydes, phthalhydrazide and cyclic or acyclic diketones such as dimedone and acetylacetone were allowed to undergo three-component condensation in the presence of Fe_3O_4@silica sulfuric acid under solvent free conditions (Table 2).

As shown in Table 2, the aldehydes with both electron donating and withdrawing groups were participated in the condensation reaction with equal efficiency. Thus, the nature and position of substitution in the aromatic ring did not affect the reactions much. The meta-substituted aromatic aldehydes (Table 2, entries 6–8) as well as sterically hindered ortho-substituted aromatic aldehydes (Table 2, entry 11), both undergo condensation reaction without any difficulty.

The possibility of the magnetic recycling of catalyst was also examined. For this reason, the reaction of benzaldehyde, dimedone, and phthalhydrazide in the presence of Fe_3O_4@silica sulfuric acid was studied. In this procedure, after completion of the reaction, hot ethanol was added and the catalyst was easily separated from the product by attaching an external magnet onto the reaction vessel, followed decantation of the reaction solution. The remaining catalyst was washed with ethanol to remove residual product and dried under vacuum and reused in a subsequent reaction. For example, the reaction of benzaldehyde, dimedone, and phthalhydrazide afforded to the corresponding product at 100% conversion and isolated yield of 88 to 83% in six consecutive runs. The average chemical yield for six consecutive runs was 85%, which clearly demonstrates the practical recyclability of this catalyst (Fig. 6).

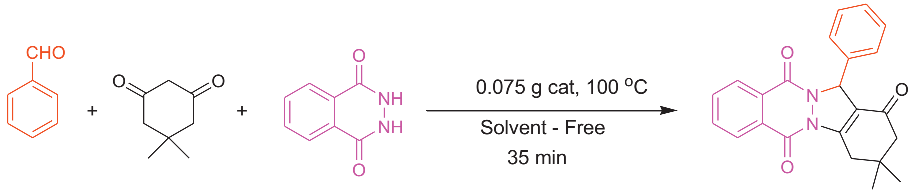
It should be point out that no special handling precaution regarding exposure to air/moisture need to be taken in the use of Fe_3O_4@silica sulfuric acid as catalyst.

A comparison of the efficacy of Fe_3O_4@silica sulfuric acid catalyst with some of those reported in the literature is presented in Table 3. The model reaction of, dimedone, phthalhydrazide and benzaldehyde was considered as a representative example

Table 1
The one-pot three component reaction of phthalhydrazide (1 mmol), dimedone (1 mmol) and bezaldehyde (1.1 mmol) under different conditions.

Entry	Solvent	Catalyst (g)	*T* (°C)	Time (min)	Yield[a] (%)
1	CH_3CN	0.075	Reflux	120	30
2	EtOH	0.075	Reflux	120	35
3	EtOH-H_2O	0.075	Reflux	120	40
4	H_2O	0.075	Reflux	120	35
5	Solvent-free	–	100	120	Trace
6	Solvent-free	0.025	100	60	60
7	Solvent-free	0.05	100	60	73
8	Solvent-free	0.075	100	35	88
9	Solvent-free	0.075	110	35	75
10	Solvent-free	0.075	120	35	71
11	Solvent-free	0.075	80	40	55
12	Solvent-free	0.075	50	60	45
13	Solvent-free	0.1	100	40	80
14	Solvent-free	0.15	100	40	81
15	Solvent-free	0.1 (Fe_3O_4)	100	120	11
16	Solvent-free	0.1 (Fe_3O_4@SiO_2)	100	120	13

[a] Isolated yield.



Scheme 3. Solvent-free three component reaction of phthalhydrazide (1 mmol), dimedone (1 mmol) and bezaldehyde (1.1 mmol).

(Table 3). As it is seen in addition to having the general advantages attributed to the inherent magnetic property of nanocatalysts, Fe_3O_4@silica sulfuric acid is an equally or more efficient catalyst for this three-component reaction.

3. Experimental

3.1. General

Iron (II) chloride tetrahydrate (99%), iron (III) chloride hexahydrate (98%), aromatic aldehydes and other chemical materials were purchased from Fluka and Merck companies and used without further purification. Products were characterized by comparison of their physical data, IR and ^{1}H NMR and ^{13}C NMR spectra with known samples. NMR spectra were recorded on a Bruker Advance DPX 400 MHz instrument spectrometer using TMS as internal standard. IR spectra were recorded on a BOMEM MB-Series 1998 FT-IR spectrometer.

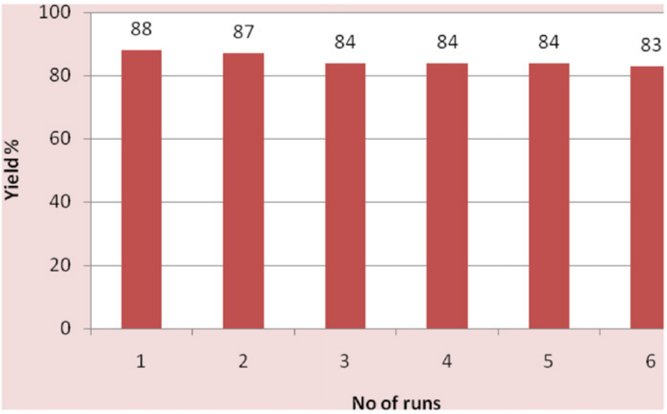


Fig. 6. Recyclability of Fe_3O_4@silica sulfuric acid.

The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/UV 254 plates. X-ray diffraction (XRD) patterns of samples were taken on a Philips X-ray diffractometer Model PW 1840. The particle morphology was examined by SEM (Philips XL30 scanning electron microscope) and TEM (Zeiss – EM10C – 80 kV).

3.2. Preparation of Fe_3O_4 superparamagnetic nanoparticles, MNPs

MNPs were synthesized by co-precipitation of $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ in ammonia solution, according to the reported procedure [34]: 15.136 g (55.987 mmol) $FeCl_3.6H_2O$ and 6.346 g (31.905 mmol) $FeCl_2{\cdot}4H_2O$ were dissolved in 0.64 L deionized water under nitrogen at 90 °C and added to a ammonium hydroxide 25% solution (0.08 L) with vigorous mechanical stirring. After the color of bulk solution turned to black the reaction was carried out for 60 min in N_2 atmosphere. The resulting black MNPs were isolated by applying a permanent external magnet, washed 3 times with deionized water and then dried under vacuum at 60 °C for 12 h.

3.3. Preparation of silica coated magnetic nanoparticles, Fe_3O_4@silica

The synthesized Fe_3O_4 nanoparticles (2 g) were diluted with 0.12 L water and 0.45 L ethanol. The suspension was dispersed under ultrasonification for 25 min. In the presence of a constant nitrogen flux and at room temperature, ammonium hydroxide 25% solution (0.01 L) was added to the suspension. Then under continuous mechanical stirring, 0.002 L TEOS was slowly added to this dispersion and after stirring for 12 h, silica was formed on the surface of 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. Then dried under vacuum at 60 °C overnight [35].

Table 2
Solvent-free synthesis of indazolo[2,1-*b*]phthalazine-triones and pyrazolo[1,2-*b*]phthalazine-diones catalyzed by Fe_3O_4@silica sulfuric acid.

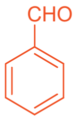
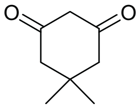
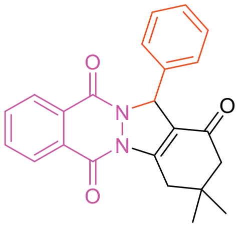
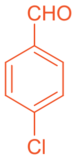
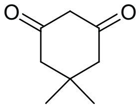
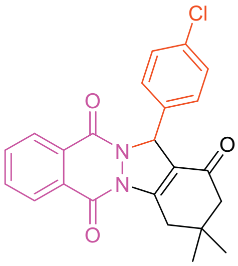
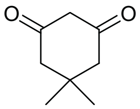
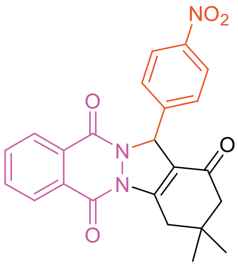
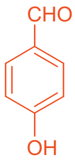
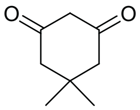
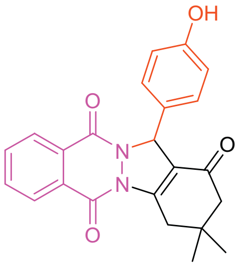
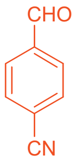
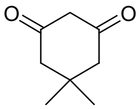
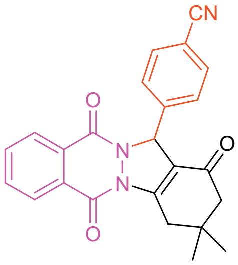
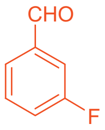
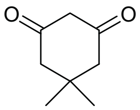
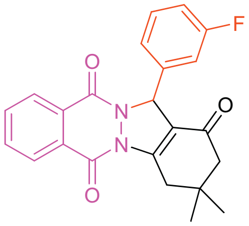
Entry	Aldehyde	Diketone	Product	Time (min)	Yield[a] (%)
1				35	88
2				35	90
3				30	94
4				40	85
5				30	92
6				35	90

Table 2 (*Continued*)

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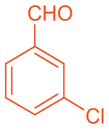
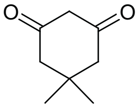
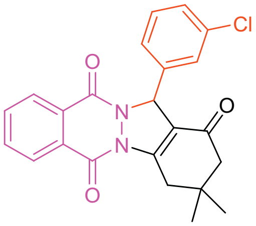
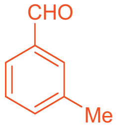
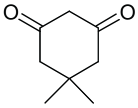
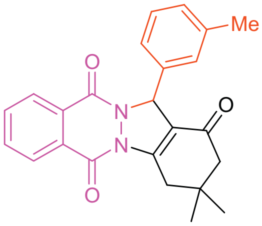
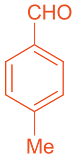
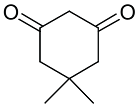
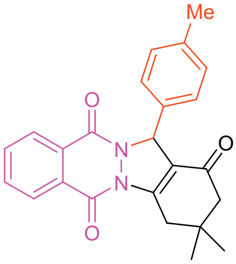
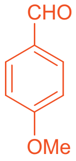
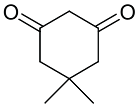
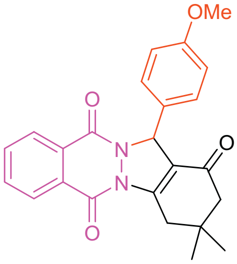
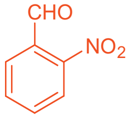
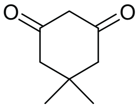
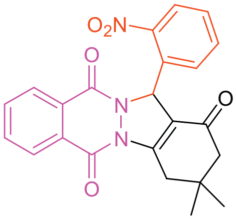
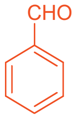
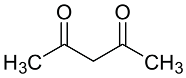
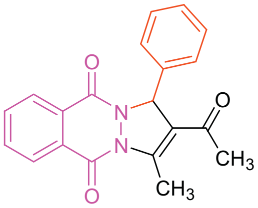
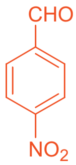
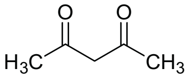
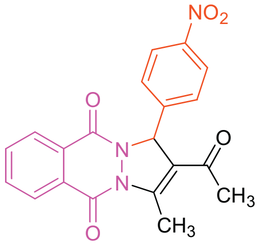
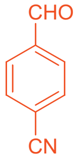
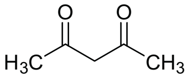
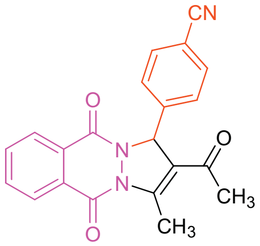
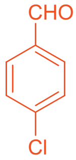
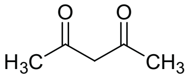
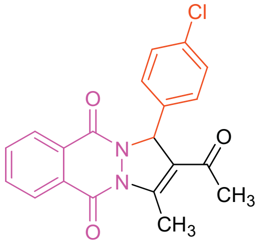
7				35	90
8				35	88
9				40	86
10				40	85
11				35	90
12				45	85

Table 2 (*Continued*)

Entry	Aldehyde	Diketone	Product	Time (min)	Yield[a] (%)
13				35	88
14				35	87
15				40	84

[a] Isolated yield.

3.4. *Preparation of SO_3H functionalized silica-coated magnetite nanoparticles, Fe_3O_4@silica sulfuric acid*

A 0.5 L 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 into the flask and dispersed by ultrasonic for 10 min in CH_2Cl_2 (0.075 L). chlorosulfonic acid (1.75 g, *ca.* 0.001 L, 15 mmol) in CH_2Cl_2 (0.02 L) 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_3O_4@silica sulfuric acid was separated from the reaction mixture by a magnetic field and washed several times with dried CH_2Cl_2. Finally, Fe_3O_4@silica sulfuric acid was dried under vacuum at 60 °C.

3.5. *Sulfonic acid loading of Fe_3O_4@silica sulfuric acid*

Sulfonic acid loading was calculated based on titration of the proton-exchanged brine solutions. To an aqueous solution of NaCl (1 M, 0.025 L) with an initial pH 5.9, the Fe_3O_4@silica sulfuric acid (100 mg) was added and the resulting mixture stirred for 24 h after which the pH of solution decreased to 2.10. This is equal to a loading of 1.98 mmol $SO_3H\,g^{-1}$ of acidic catalyst. Additionally, this result confirmed by back-titration analysis of the catalyst.

3.6. *Typical procedure for the preparation of 3,4-dihydro-3,3-dimethyl-13-phenyl-2H-indazolo[2,1-b]phthalazine-1,6,11-trione*

A mixture of phthalhydrazide (0.16 g, 1 mmol), dimedone (0.14 g, 1 mmol), benzaldehyde (0.13 g, 1.2 mmol), and Fe_3O_4@silica sulfuric acid (0.1 g) was heated at 100 °C for 35 min (TLC). After satisfactory completion of the reaction and cooling, the reaction mixture was washed with hot ethanol and the catalyst was removed by a magnetic field. The solid residue was isolated and purified by recrystallization in hot EtOH. The desired pure product(s) was characterized by comparison of their physical data with those of known.

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

Entry	Catalyst	Catalyst loading (mol %)	Time (min)	Yield (%)	Ref.
1	p-Toluenesulfonic acid	30	10	93	[9]
2	(S)-camphorsulfonic acid.	10	35	80	[16]
3	$[bmim]BF_4/H_2SO_4$	15	30	96	[20]
4	$Mg(HSO_4)_2$	11.5	10	85	[21]
5	Silica supported PPA	0.1 g	7	91	[33]
6	Fe_3O_4@silica sulfuric acid	0.075 g	35	88	This work

3.7. Selected spectral data

3,4-Dihydro-3,3-dimethyl-13-(4-nitrophenyl)-2-H-indazolo[2,1-*b*]phthalazine-1,6,11(13H)-trione (Table 2, entry 3): M.P. = 225–227 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 1.10 (s, 3H), 1.14 (s, 3H), 2.27 (s, 2H), 3.20 (AB system, dd, 1H, J = 18.8 Hz and J = 2.0 Hz), 3.32 (AB system, d, 1H, J = 18.8 Hz), 6.44 (s, 1H), 7.79–7.82 (m, 2H), 7.96–8.01 (m, 2H), 8.09–8.12 (m, 4H). ^{13}C NMR (DMSO-d_6, 100.6 MHz): δ = 28.3, 28.4, 34.8, 37.7, 50.6, 64.2, 116.8, 123.8, 127.2, 128.0, 128.9, 129.2, 129.7, 134.3, 135.0, 145.3, 147.6, 152.3, 154.4, 155.9,192.3. IR (KBr) (ν_{max}, cm^{-1}): 2973, 1697, 1617, 1660, 1525, 1368, 1148, 1102, 858, 701.

3,4-Dihydro-3,3-dimethyl-13-(3-flourophenyl)-2-H-indazolo[2,1-*b*]phthalazine-1,6,11(13H)-trione (Table 2, entry 6): M.P. = 225–227 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 1.11 (s, 3H), 1.13 (s, 3H), 2.27 (s, 2H), 3.18 (AB system, dd, 1H, J = 19.1 Hz and J = 2.2 Hz), 3.33 (AB system, d, 1H, J = 19.2 Hz), 6.31 (s, 1H), 7.08–7.12 (pt, 1H), 7.31–7.39 (m, 3H), 7.96–7.98 (m, 2H), 8.01–8.12 (m, 1H), 8.26–8.29 (m, 1H). ^{13}C NMR (DMSO-d_6, 100.6 MHz): δ = 28.3, 28.4, 34.7, 37.7, 50.7, 64.3, 114.7, 115.2, 117.0, 124.1, 127.5, 129.0, 129.7, 130.5, 134.2, 135.0, 140.8, 152.9, 154.3, 155.9, 161.3, 163.7, 192.3. IR (KBr) (ν_{max}, cm^{-1}): 2957, 2877, 1663, 1629, 1603, 1471, 1357, 1314, 1271, 1142, 778, 701, 684.

3,4-Dihydro-3,3-dimethyl-13-(4-hydroxyphenyl)-2-H-indazolo[2,1-*b*]phthalazine-1,6,11(13H)-trione (Table 2, entry 4): M.P. = 225–227 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 1.10 (s, 3H), 1.14 (s, 3H), 2.27 (d, 2H, J = 4.8 Hz), 3.16 (AB system, dd, 1H, J = 17.8 Hz and J = 2.0 Hz), 3.32 (AB system, d, 1H, J = 17.2 Hz), 6.20 (s, 1H), 6.86 (d, 2H, J = 8.8 Hz), 7.22 (d, 2H, J = 8.4 Hz), 7.94–7.99 (m, 2H), 8.10–8.12 (m, 1H), 8.25–8.27 (m, 1H), 9.47 (br, 1H_{OH}). ^{13}C NMR (DMSO-d_6, 100.6 MHz): δ = 28.4, 28.5, 34.7, 37.7, 50.8, 64.4, 115.2, 115.3, 118.0, 127.1, 127.9, 128.1, 129.2, 129.4, 134.1, 134.9, 151.4, 154.0, 155.8, 157.7, 192.4. IR (KBr) (ν_{max}, cm^{-1}): 3363(OH), 2960, 1674, 1657, 1634, 1362, 1271, 847, 704.

3,4-Dihydro-3,3-dimethyl-13-(4-methylphenyl)-2H-indazolo[2,1-*b*]phthalazine-1,6,11(13H)-trione (Table 2, entry 9): M.P. = 224–226 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.17 (s, 6H), 2.25 (s, 3H), 2.28 (s, 2H), 3.18 and 3.37 (AB system, s, 2H, J = 18.85 Hz), 6.36 (s, 1H), 7.08–7.2 (m, 4H), 7.8 (m, 2H), 8.2–8.3 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 21.6, 28.8, 29.1,35.0, 38.4, 51.3, 65.1, 118.9, 127.4, 128.0, 128.3, 129.3, 129.5, 129.7, 133.8, 134.8, 138.8, 151.1, 154.6, 156.3, and 192.4. IR (KBr) (ν_{max}, cm^{-1}): 2897, 1663, 1654, 1603, 1600, 1497, 1085, 827, 790, 687, 627, 495.

3,4-Dihydro-3,3-dimethyl-13-(4-chlorophenyl)-2-H-indazolo[2,1-*b*]phthalazine-1,6,11(13H)-trione (Table 2, entry 2): M.P. = 224–226 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.22 (s, 6H), 2.30 (s, 2H), 3.26 (AB system, d, 1H, J = 18.9 Hz), 3.43 (AB system, d, 1H, J = 18.8 Hz), 6.42 (s, 1H), 7.27–7.36 (m, 4H), 7.90–7.92 (m, 2H), and 8.31–8.40 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 23.3, 28.4, 30.8, 34.7, 51.6, 64.0, 117.8, 125.6, 127.9, 128.1, 128.5, 129.2, 129.6, 134.0, 135.0, 142.3, 149.6, 152.0, 154.4, 156.0,192.4.

4. Conclusion

In this research, Fe_3O_4@silica sulfuric acid core–shell nanocomposite was successfully prepared and characterized by FT-IR, SEM, TEM, XRD and VSM. The catalytic activity of this solid acid nanocomposite, was probed through the one-pot synthesis of 2H-indazolo[2,1-*b*]phthalazine-1,6,11-trione and 1H-pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives by a three-component reaction of phthalhydrazide, cyclic or acyclic diketones and aromatic aldehydes. The attractive features of this method are simple procedure, cleaner reaction, use of reusable catalyst, easy workup and performing multicomponent reaction under solvent-free conditions.

Acknowledgement

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References

[1] Y. Zhang, Y. Zhao, C. Xia, J. Mol. Catal. A: Chem. 306 (2009) 107–112.
[2] C.G. Gill, B.A. Price, W.J. Jones, J. Catal. 251 (2007) 145–152.
[3] Y. Lin, H. Chen, K. Lin, B. Chen, C. Chiou, J. Environ. Sci. 23 (1) (2011) 44–50.
[4] N.M. Mahmoodi, S. Khorramfar, F. Najafi, Desalination 279 (2011) 61–68.
[5] A.R. Kiasat, S. Nazari, J. Mol. Catal. A: Chem. 365 (2012) 80–86.
[6] M. Khoobi, L. Mamani, F. Rezazadeh, Z. Zareie, A. Foroumadi, A.R. Ramazani, A. Shafiee, J. Mol. Catal. A: Chem. 359 (2012) 74–80.
[7] V.V. Costa, M.J. Jacinto, L.M. Rossi, R. Landers, E.V. Gusevskaya, J. Catal. 282 (2011) 209–214.
[8] A.H. Lu, E.L. Salabas, F. Schüth, Angew. Chem. Int. Ed. 46 (2007) 1222–1244.
[9] M. Sayyafi, M. Seyyedhamzeh, H.R. Khavasi, A. Bazgir, Tetrahedron 64 (2008) 2375–2378.
[10] R.G. Vaghei, R.K. Nami, Z.T. Semiromi, M. Amiri, M. Ghavidel, Tetrahedron 67 (2011) 1930–1937.
[11] S.S. El-Saka, A.H. Soliman, A.M. Imam, Afinidad 66 (2009) 167–172.
[12] L. Zhang, L.P. Guan, X.Y. Sun, C.X. Wei, K.Y. Chai, Z.S. Quan, Chem. Biol. Drug Des. 73 (2009) 313–315.
[13] C.K. Ryu, R.E. Park, M.Y. Ma, J.H. Nho, Bioorg. Med. Chem. Lett. 17 (2007) 2577–2580.
[14] J. Li, Y.F. Zhao, X.Y. Yuan, J.X. Xu, P. Gong, Molecules 11 (2006) 574–582.
[15] J. Sinkkonen, V. Ovcharenko, K.N. Zelenin, I.P. Bezhan, B.A. Chakchir, F. Al-Assar, K. Pihlaja, Eur. J. Org. Chem. 6 (2002) 2046–2053.
[16] D.S. Raghuvanshi, K.N. Singh, Tetrahedron Lett. 52 (2011) 5702–5705.
[17] G. Shukla, R.K. Verma, G.K. Verma, M.S. Singh, Tetrahedron Lett. 52 (2011) 7195–7198.
[18] G. Karthikeyana, A. Pandurangan, J. Mol. Catal. A: Chem. 361/362 (2012) 58–67.
[19] M.R. Nabid, S.J. Tabatabaei, R. Ghahremanzadeh, A. Bazgir, Ultrason. Sonochem. 17 (2010) 159–161.
[20] J.M. Khurana, D. Magoo, Tetrahedron Lett. 50 (2009) 7300–7303.
[21] H.R. Shaterian, F. Khorami, A. Amirzadeh, R. Doostmohammadi, M. Ghashang, J. Iran. Chem. Res. 2 (2009) 57–62.
[22] H.R. Shaterian, M. Ghashang, M. Feyzi, Appl. Catal. A 345 (2008) 128–133.
[23] X.N. Zhang, Y.X. Li, Z.H. Zhang, Tetrahedron 67 (2011) 7426–7430.
[24] M.S. Singh, S. Chowdhury, RSC Adv. 2 (2012) 4547–4592.
[25] M.A.P. Martins, C.P. Frizzo, D.N. Moreira, L. Buriol, P. Machado, Chem. Rev. 109 (2009) 4140–4182.
[26] R.S. Varma, Pure Appl. Chem. 73 (2001) 193–198.
[27] A. Khojastehnezhad, F. Moeinpour, A. Davoodnia, Chin. Chem. Lett. 22 (2011) 807–810.
[28] R. Kumar, K. Raghuvanshi, R.K. Verma, M.S. Singh, Tetrahedron Lett. 51 (2010) 5933–5936.
[29] M.Z. Kassaee, H. Masrouri, F. Movahedi, Appl. Catal. A 395 (2011) 28–33.
[30] Z. Lei, Y. Li, X. Wei, J. Solid State Chem. 181 (2008) 480–486.
[31] Y.L. Tsai, C.H. Chun, J.L. Ou, C.K. Huang, C.C. Chen, Desalination 200 (2006) 97–99.
[32] B.D. Cullity, S.R. Stock, Elements of X-ray Diffraction, 3rd ed., Prentice-Hall, Englewood Cliffs, 2001.
[33] H.R. Shaterian, A. Hosseinian, M. Ghashang, Arkivoc ii (2009) 59–67.
[34] K.D. Kim, S.S. Kim, Y.H. Choa, H.T. Kim, J. Ind. Eng. Chem. 13 (2007) 1137–1141.
[35] H.Y. Deng, C.C. Wang, J.H. Hu, W.L. Yang, S.K. Fu, Colloids Surf. A: Physicochem. Eng. Aspects 262 (2005) 87–93.