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Synthesis, characterization and catalytic application of Fe_3O_4@Cys–SO_3H for preparation of 2*H*-indazolo[1,2-*b*]phthalazine-triones

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ABSTRACT

The surface of Fe_3O_4 magnetic nanoparticles (MNPs) was modified by L-cysteine through condensation of COOH groups of L-cysteine and OH groups on the surface of Fe_3O_4. The –SH group of prepared Fe_3O_4@Cys MNPs oxidized to –SO_3H group and Fe_3O_4@Cys–SO_3H as an environmentally friendly magnetic nanoparticle was prepared. The MNPs were characterized by FT-IR, XRD, SEM and TEM studies. Then, the catalytic activity of the MNPs was evaluated as an effective and reusable catalyst for one-pot synthesis of 2*H*-indazolo [1,2-*b*] phthalazine-triones derivatives. The results show that the catalytic activity of Fe_3O_4@Cys–SO_3H was comparable to that of other reported heterogeneous and homogeneous catalysts.

Keywords: *Fe_3O_4@Cys–SO_3H, L-cysteine, Fe_3O_4, 2H-indazolo [1,2-b] phthalazine-triones.*

1. Introduction

Magnetic nanoparticles (MNPs) due to their excellent physical and chemical properties, such as superparamagnetism, easy separation under external magnetic fields, strong adsorption ability and high surface area [1], have many applications in drug delivery [2], removal of heavy metal ions and dyes in wastewater [3] and catalysis [4]. However, some properties of magnetic nanoparticles such as a tendency to deform and aggregate during the course of reactions will limit their applications [5]. Thus, to overcome this problem and improve their properties for the special application, it is necessary to modify these particles with functionalization and modification of their surface.

Recently, modification of magnetic nanoparticles with a series of polymers and some small organic compounds have been extensively investigated [6]. Among them, surface modified Fe_3O_4 have attracted intensive attention due to various applications as a catalyst in organic synthesis [6,7]. Also, several research studies have reported the preparation of the L-cysteine functionalized Fe_3O_4 magnetic nanoparticles (Cys–Fe_3O_4 MNPs) and their application for removing metal ions [8-10] and as a catalyst in organic synthesis [11,12].

Phthalazine derivatives have attracted considerable interest over the past decade due to their excellent and wide variety of pharmacological and biological activities [13], such as anticonvulsant [14], cardiotonic [15], and vasorelaxant activities [16]. Moreover, fused phthalazines have multiple biological activities such as anti-cancer [17], anti-fungal [18], anti-microbial [19], and anti-inflammatory activities [20]. Therefore, the introduction of new methods for the efficient synthesis of fused phthalazines can be useful.

Recently, several methods for the preparation of 2*H*-indazolo[1,2-*b*]phthalazine-triones via condensation of phthalhydrazide, cyclic-1,3-diketones, and aldehydes by various catalysts have been reported [21-32]. Despite the usefulness of this reported methods, some of them have limitations such as low product yields, long reaction times, harsh reaction conditions and use of an expensive or toxic catalyst. Thus, a cost-effective, catalytically efficient and simple procedure is still strongly desired for the synthesis of 2*H*-indazolo [1,2-*b*]phthalazine-triones.

In continuation with our recent studies on the design of a new nanocatalyst for organic synthesis [33,34], herein,

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we have investigated preparation of a new and efficient functionalized Fe_3O_4 MNPs with cysteine (Fe_3O_4@Cys–SO_3H) and studied their performances as novel strong, recoverable, and stable catalysts for the synthesis of 2*H*-indazolo[1,2-*b*]phthalazine-triones.

2. Experimental

2.1. General information

All Chemical materials and solvents were purchased from Merck. Melting points were measured by an Electro-Thermal IA 9100 melting point apparatus. ^1H and ^{13}C NMR spectra were recorded in DMSO on a Bruker Advance DRX - 400 MHz instrument using TMS as an internal standard. Fourier transform infrared (FT-IR) spectra were obtained with potassium bromide pellets in the range of 400-4000 cm^{-1} with a Shimadzu FT-IR 8600 spectrophotometer. Nanostructures were characterized using a Philips Xpert X-ray powder diffraction (XRD) diffractometer (CuKα, radiation, λ=0.154056), at a scanning speed of 2°/min from 10° to 80° (*2θ*). Transmission electron microscopy (TEM) measurements were carried out on a Zeiss-EM10C-100 kV instrument. The scanning electron microscope (SEM) was visualized by a Sigma Zeiss, Oxford Instruments Field Emission Scanning Electron Microscope.

2.2. Preparation of Fe_3O_4@Cys-SO_3H MNPs

Fe_3O_4 magnetite nanoparticles (MNPs) were synthesized according to our previous reports with a diameter about 15 nm [33,34]. Fe_3O_4 was functionalized with L-cysteine by stirring of mixture of Fe_3O_4 (5 g), L-cysteine (17 mmol, 2.06 g) and triethyl amine (17 mmol, 2.3 mL) in dry toluene (150 mL) at 110 ℃ for 24 h. The obtained nanoparticles were collected with a magnet (1.4 T) and washed with toluene (2 × 100 mL), dichloromethane (2 × 100 mL) and water-methanol (50:50, 2 × 100 mL) and finally dried at 100 °C for 24 h. For the conversion of –SH groups to -SO_3H groups, prepared Fe_3O_4@Cys–SH (5 g), hydrogen peroxide (50 mL), methanol (15 mL), and sulfuric acid 98% (2 drops) were added into a round-bottom flask and stirred at room temperature for 12 h. Then, the obtained MNPs were washed with distilled water (3 × 10 mL) and separated, dried and added to sulfuric acid (10 % W/W, 30 mL). The mixture was stirred for 4 h at room temperature and Fe_3O_4@Cys–SO_3H was separated by a magnet (1.4 T) and dried at 100 °C for 24 h. The amount of sulfonic acid groups of catalyst were evaluated by acid-base titration in the presence of phenolphthalein indicator before and after the conversion of –SH to –SO_3H group. The results show that the surface of 1 g of the magnetic nanocatalyst includes 0.02 mmol –SO_3H.

2.3. General procedure for synthesis of 2H-indazolo[1,2-b]phthalazine-triones

A mixture of phthalhydrazide (1 mmol), aromatic aldehydes (1 mmol), 1,3-cyclicdiketone (1 mmol) and Fe_3O_4@Cys–SO_3H MNPs (0.08 g) was refluxed in ethanol (5 mL) for 5-10 min. After completion of the reaction (monitored by TLC), 10 mL hot ethanol was added to the mixture and the obtained precipitate was dissolved. Then, magnetic nanocatalyst was separated with a magnet (1.4 T) and the solution was filtered and cooled at room temperature. The solid product was separated and characterized by IR, ^1H, ^{13}C NMR and comparison of their physical data with other reported data.

Selected spectral data

3,3- Dimethyl-13- (4-nitrophenyl)-3,4- dihydro-1H-indazolo[1,2-b]phthalazine-1,6,11(2H,13H)-trione ***(4a)****:*

Yellow solid. m.p.= 214-216 °C. IR (KBr): ($\bar{\nu}$ = 3020, 1722, 1656, 1620, 1601, 1400, 1082 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ= 0.92 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 2.03 (d, *J* = 16.0 Hz, 1H, CH), 2.22 (d, *J* = 16.0 Hz, 1H, CH), 2.36 (d, *J* = 20.0 Hz, 1H, CH), 2.20 (d, *J* = 16.0 Hz, 1H, CH), 6.34 (s, 1H, CH), 7.25 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H, H-Ar), 7.94-8.02 (m, 4H, H-Ar) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ= 28.2, 31.7, 35.8, 37.3, 49.8. 64.7, 119.2, 123.7, 126.9, 127.8, 129.4, 129.8, 130.7, 132.6, 133.3, 142.9, 147.8, 150.6, 154.7, 159.1, 191.3 ppm.

13- (4- Chlorophenyl)-3,3- dimethyl-3,4- dihydro- 1H-indazolo[1,2-b]phthalazine-1,6,11(2H,13H)-trione ***(4b)****:*

Yellow solid. m.p.=262-264 °C. IR (KBr): $\bar{\nu}$ = 3010, 1716, 1659, 1620, 1601, 1079, 705 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ= 0.88 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 1.98 (d, *J* = 16.0 Hz, 1H, CH), 2.17 (d, *J* = 16.0 Hz, 1H, CH), 2.37 (d, *J* = 20.0 Hz, 1H, CH), 2.46 (d, *J* = 16.0 Hz, 1H, CH), 6.23 (s, 1H, CH), 7.17 (d, *J* = 8.0 Hz, 2H, H-Ar), 7.22 (d, *J* = 8.0 Hz, 2H, H-Ar), 7.94-8.00 (m, 4H, H-Ar) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ= 27.7, 30.0, 34.8, 37.0, 52.4, 64.5, 119.2, 122.2, 123.5, 127.6, 128.9, 130.7, 132.7, 132.9, 134.1, 143.9, 147.4, 151.3, 154.1, 159.9, 193.2 ppm.

3. Results and Discussion

3.1. Preparation of Fe_3O_4@ Cys–SO_3H

L-cysteine is a biocompatible, water-soluble, sulfur-containing amino acid with three functional groups (–SH, –NH, –COOH). L-cysteine can be bound to the surface of Fe_3O_4 nano particles (NPs) by –SH [10-12], –NH, or –COOH [9] groups. In this research, for preparation of Fe_3O_4@Cys–SO_3H, we evaluated the

reaction of L-cysteine with Fe_3O_4 MNPs (Scheme 1). At first, the Fe_3O_4 MNPs were synthesized by the chemical coprecipitation method based on our previous reports [33,34]. According to the isoelectric structures of cysteine in different pH values (Fig. 1), to prepare the desired Fe_3O_4@Cys–SO_3H, the condensation reaction between the COOH groups of L-cysteine and OH groups on the surface of Fe_3O_4 MNPs was carried out in the presence of triethylamine at pH = 8. Finally, the obtained Fe_3O_4@Cys–SH was oxidized to Fe_3O_4@Cys–SO_3H by H_2O_2 and H_2SO_4 (Scheme 1).

3.2. Characterization of Fe_3O_4@Cys–SO_3H

Characterization of the prepared novel Fe_3O_4@Cys–SO_3H was performed by several physiochemical methods such as FT-IR, XRD, SEM, and TEM.

The FT-IR spectra of the bare Fe_3O_4, L-cysteine, Fe_3O_4@Cys and Fe_3O_4@Cys–SO_3H are shown in Fig. 2. The band at 572 cm^{-1} correspond to the stretching vibration of the Fe–O bond of bare Fe_3O_4. Also, the peaks at 1633 and 3429 cm^{-1} are attributed to the stretching vibration of the hydroxyl (–OH) groups on the surface of the Fe_3O_4 nanoparticles (Fig. 2a).

In the spectrum of L-cysteine (Fig. 2b), the bands appeared at 3463 cm^{-1} are assigned to NH stretching amino group. Furthermore, –OH stretching frequencies of the COOH group are observed as a broadband at 2750–3200 cm^{-1}. A weak band at 2582 cm^{-1} showed the presence of SH group in the cysteine molecule. Meanwhile, the peaks at 1623 and 1406 cm^{-1} belonged to the symmetric and asymmetric stretching vibrations of COO^-. The band at 1583 cm^{-1} is related to N–H bending vibration.

Fig. 2c showed characteristic bands of both Fe_3O_4 and hydrosulfide, amino and carboxylic groups of cysteine in Fe_3O_4@Cys. The bands at 2580 and 1585 cm^{-1} can be attributed to the S–H stretching and NH bending vibration, respectively. Also, the asymmetric and symmetric stretching vibrations of carbonyl group bond were observed at 1626 and 1406 cm^{-1}. The wavenumber separation between the asymmetric and symmetric stretching vibrations of carbonyl group shows the monodentate interaction between the carboxylate head and metal atom [35].

Furthermore, the strong peak at 572 cm^{-1} corresponding to the Fe–O bond stretching vibration of Fe_3O_4, confirmed the existence of L-cysteine on the Fe_3O_4 surface. These results and disappearance of the broad peaks at 2750–3200 cm^{-1} belong to stretching frequencies of the COOH group of L-cysteine, this indicates that L-cysteine bonding of the surface of Fe_3O_4 MNPs through condensation interaction between the –OH group on the Fe_3O_4 surface and the –COOH group of L-cysteine.

The disappearance of the peaks at 2582 cm^{-1} in Fig. 2d confirmed the conversion of –SH group to -SO_3H group in Fe_3O_4@Cys–SO_3H. In addition, the sulfonic acid bond can be observed at 1222 and 638 cm^{-1}, which are attributed to the O=S=O asymmetric and symmetric stretching vibrations and S-O stretching vibration of the sulfonic groups (-SO_3H), respectively.

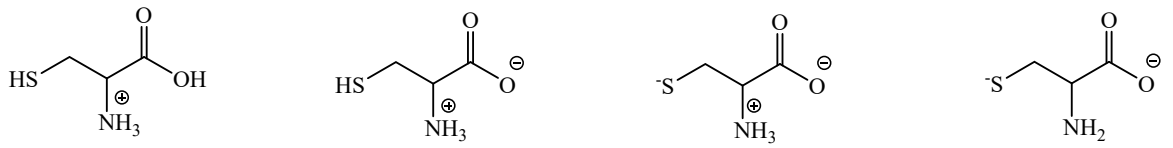
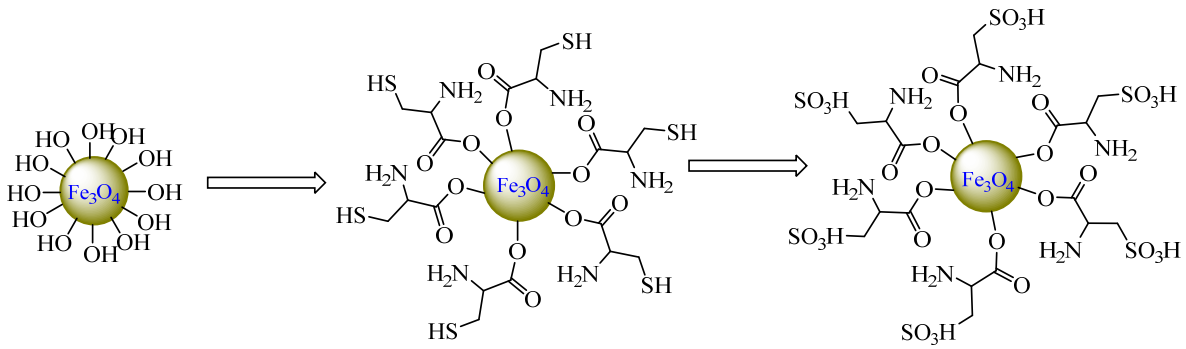


Fig. 1. Structures of cysteine in different pH values.



Scheme1. The reaction sequence for the synthesis of Fe_3O_4@Cys–SO_3H.

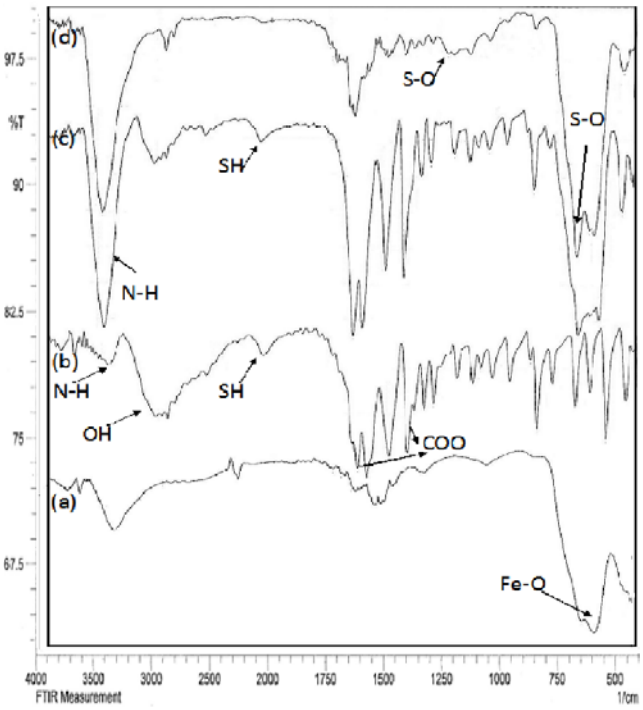


Fig. 2. (a) Fe_3O_4, (b) L-cysteine, (c) Fe_3O_4@Cys and (d) Fe_3O_4@Cys–SO_3H.

XRD patterns of the bare Fe_3O_4, Fe_3O_4@Cys are shown in Fig. 3. The MNP patterns have peaks at 2θ = 30.11°, 35.57°, 43.17°, 57.15°, and 62.77°, which are identical to pure magnetite and matched well with the XRD pattern of the standard Fe_3O_4 from Joint Committee on Powder Diffraction Standards (JCPDS No. 19-692) [36]. In other words, the XRD patterns represent similar diffraction peaks and this indicates that the coating agent does not significantly affect the crystal structure of the magnetite nanoparticles after modification and shows that the Fe_3O_4@Cys MNPs has been synthesized correctly.

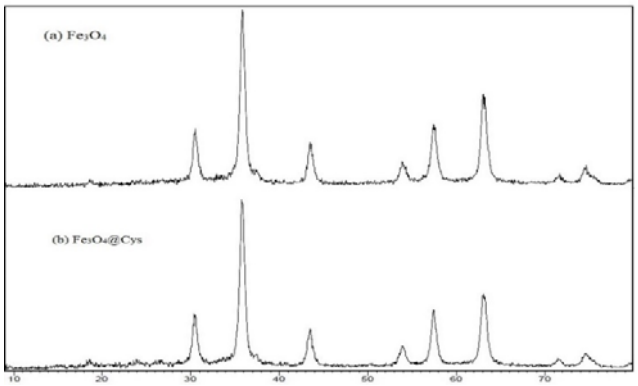


Fig. 3. XRD patterns of (a) Fe_3O_4, (b) Fe_3O_4@Cys.

The morphology of Fe_3O_4 and morphology of Fe_3O_4@Cys MNPs were also observed by TEM and SEM. As shown in Fig. 4, the TEM and SEM images show that Fe_3O_4 particles were spherical with uniform size, and showed good dispersity. Furthermore, it was found that the diameter of Fe_3O_4 nanoparticles obtained was about 15 nm and Fe_3O_4@Cys microspheres were obtained with a diameter of about 20 nm.

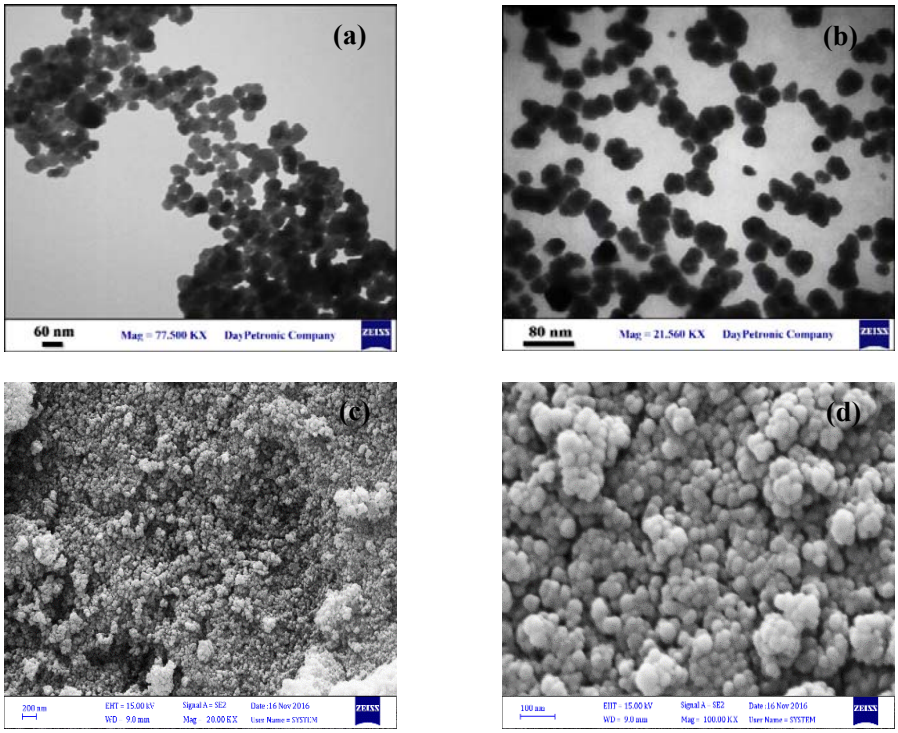


Fig. 4. TEM images of Fe_3O_4 (a), Fe_3O_4@Cys (b) and SEM images of Fe_3O_4 (c), Fe_3O_4@Cys (d).

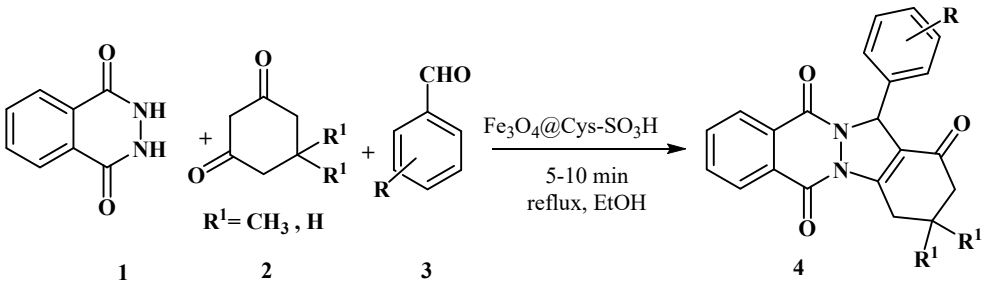
3.3. Method development

The prepared Fe_3O_4@Cys–SO_3H MNPs were tested as catalysts in the synthesis of 2*H*-indazolo [1,2-*b*]phthalazine-triones derivatives by the reaction of phthalhydrazide (**1**), dimedone (**2**) and 4-nitrobenzaldehyde (**3a**) (Scheme 2, Table 1). The amount of Fe_3O_4@Cys–SO_3H MNPs was examined, and the results are summarized in Table 1. It can be seen that 0.08 g Fe_3O_4@Cys–SO_3H gave the best yield (93%) in the shortest time (5 min) (Table 1, entry 4).

A comparison between the result of the use of Fe_3O_4@Cys–SO_3H and some of the recently used catalysts for the synthesis of 2*H*-indazolo [1,2-*b*]phthalazine-triones derivatives are summarized in Table 1 (entry 6-10). Although some of these methods have convenient protocols with good to high yields, the majority of these methods suffer at least from one of the following disadvantages such as the longer reaction time, the use of toxic organic solvents, excess reagents, and harsh reaction conditions. Table 1 shows that the heterogeneous catalyst of Fe_3O_4@Cys–SO_3H is the best in comparison to other mentioned catalysts.

After optimizing the conditions, the efficiency and versatility of the Fe_3O_4@Cys–SO_3H as a catalyst for the preparation of other 2*H*-indazolo[1,2-*b*]phthalazine-trione derivatives were evaluated by various aromatic aldehydes. In all studied cases, the reaction proceeded smoothly to give the corresponding products **4a–o** (Table 2). A brief comparison of the present method with those previously reported in the literature in terms of reaction times and yields reveals the desired products were obtained in better yields (86-93%), and shorter times (5-10 minutes).

A proposed mechanism for the synthesis of 2*H*-indazolo[1,2-*b*]phthalazine-triones using Fe_3O_4@Cys–SO_3H as a catalyst is shown in scheme 3. It is thought that the sulfonic groups (SO_3H) on the catalyst can activate the carbonyl groups of aldehydes. Then, the reaction of dimedone in its enol form is expected to react with the aromatic aldehyde to raise Knoevenagel product **5**. The intermediate **5** may further undergo Michael addition with phthalhydrazide and produce intermediate **6**. This intermediate undergoes a cyclo condensation and dehydration reaction to afford the corresponding 2*H*-indazolo[1,2-*b*]phthalazine-trione derivatives **4**.



Scheme 2. Synthesis of 2*H*-indazolo[1,2-*b*]phthalazine-triones.

Table 1. Synthesis of 2*H*-indazolo[1,2-*b*] phthalazine-triones using different conditions.[a]

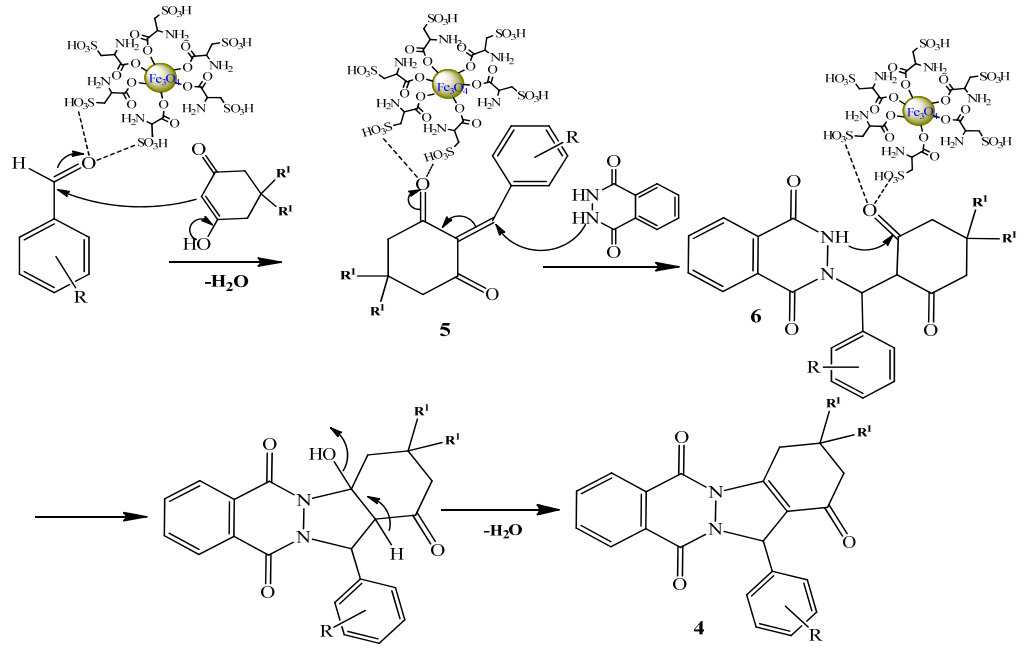
Entry	Catalyst	Catalyst amount	Solvent	Temp. (°C)	Time (min)	Yield (%)	Ref.
1	-	-	EtOH	78	30	-	-
2	Fe_3O_4	0.05 g	EtOH	78	30	31	-
3	Fe_3O_4@Cys–SO_3H	0.05 g	EtOH	78	7	87	-
4	Fe_3O_4@Cys–SO_3H	0.08 g	EtOH	78	5	93	-
5	Fe_3O_4@Cys–SO_3H	0.1 g	EtOH	78	5	93	-
6	p-Toluenesulfonic acid	30 (mol %)	-	80	10	93	[21]
7	Polyphosphoric acid-SiO_2	5 (mol %)	[bmim]BF_4	25	7	87	[22]
8	(*S*)-camphorsulfonic acid	20 (mol %)	-	25	20	92	[23]
9	Silica sulfuric acid	6.5 (mol %)	-	100	7	85	[25]
10	I_2	0.1 g	-	30	10	90	[26]

[a]Reaction conditions: Phthalhydrazide (1 mmol), dimedone (1 mmol) and 4-nitrobenzaldehyde (1 mmol) and ethanol (5 mL).

Table 2. Synthesis of 2*H*-indazolo[1,2-*b*]phthalazine-triones.[a]

Product	R	R^1	Time (min)	Yield (%)	m.p. (°C)		Ref.
					Found	Reported	
4a	4-NO_2	CH_3	5	93	214-216	215-217	[24]
4b	4- Cl	CH_3	5	91	262-264	258-260	[21]
4c	3-NO_2	CH_3	5	90	268-270	270-272	[26]
4d	4-CH_3	CH_3	10	87	223-226	226-228	[25]
4e	2,4-Cl_2-C_6H_3	CH_3	5	92	218-220	220-222	[26]
4f	2-Cl	CH_3	10	86	266-268	266-268	[25]
4g	H	CH_3	10	89	205-207	207-208	[26]
4i	3-CH_3	CH_3	10	82	231-233	232-235	[26]
4j	4-Br	CH_3	10	86	265-267	266-268	[26]
4k	4-OMe	CH_3	10	80	218-220	220-221	[26]
4l	4-NO_2	H	5	87	223-225	224-226	[37]
4m	4-Cl	H	5	90	284-286	285-287	[37]
4n	2-Cl	H	10	85	275-277	273-275	[37]
4o	2,4-Cl_2-C_6H_3	H	5	90	280-282	283-285	[37]

[a]Reaction conditions: Phthalhydrazide (1 mmol), 1,3-cyclicdiketone (1 mmol) and aromatic aldehyde (1 mmol), Fe_3O_4@Cys–SO_3H (0.08 g) and ethanol (5 mL), reflux.



Scheme 3. Proposed mechanism for the synthesis of 2*H*-indazolo[1,2-*b*]phthalazine-triones catalyzed by Fe_3O_4@Cys–SO_3H.

3.4. Reusability

The reusability of Fe_3O_4@Cys–SO_3H was studied by the model reaction. After completion of the reaction, the catalyst was separated using a magnet, washed with ethanol and dried at 100 °C. After four successive runs, recycled Fe_3O_4@Cys–SO_3H showed no loss of noticeable efficiency with regard to reaction time and yield (The yields were 93, 91, 88 and 84%, respectively).

4. Conclusions

A simple procedure for the functionalization of Fe_3O_4 MNPs surface by L-cysteine through the condensation reaction between the COOH groups of L-cysteine and OH groups on the surface of Fe_3O_4 was introduced. Innovative Fe_3O_4@Cys–SO_3H MNPs has been used as an effective and reusable catalyst for one-pot synthesis of 2*H*-indazolo[1,2-*b*] phthalazine-triones derivatives. Serious analyses investigated the structure of the prepared catalysts. The significant advantages of our protocol are short reaction time, excellent yields, nanocatalyst stability, simple work-up and reusability of the catalyst.

Acknowledgments

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