

# Application of immobilized sulfonic acid on the cobalt ferrite magnetic nanocatalyst (CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@SO<sub>3</sub>H) in the synthesis of spirooxindoles

Bardia Zamani-Ranjbar-Garmroodi<sup>1</sup> · Mohammad A. Nasseri<sup>1</sup> · Ali Allahresani<sup>1</sup> · Kaveh Hemmat<sup>1</sup>

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#### Abstract

Sulfonic acid immobilized on the surface of magnetically cobalt ferrite/silicate is a green, convenient, efficient and recyclable catalyst which can be applied in organic reactions ranges from lab to industry goals as a solid acid to achieve high yield products. After synthesizing (CoFe<sub>2</sub>O<sub>4</sub>/SiO<sub>2</sub>/SO<sub>3</sub>H), it was also characterized by using different techniques such as FT-IR, XRD, EDX, VSM, TEM, SEM, TGA and so on which everyone approved presented structure. In this study, we are on to use this catalyst in a certain multicomponent reaction that is a common way to produce heterocycle compounds in order to synthesis spirooxindole derivatives which possess biological capabilities as anticancer and antimicrobial drugs. Hence, the three-component reaction of malononitrile, dimedone and isatin were performed in one pot under optimized situations of 80 °C temperature, reflux condition and water/ethanol (1:1) mixture as the solvent. Also, the present study shows unique advantages, such as simple synthesis of the catalyst, high magnetic properties, easy separation of catalyst with a permanent magnet, and the application of inexpensive and available precursors. At the end of the reaction, we gained the high yields of product at a short time that represents the high catalytic activity of the catalyst.

Keywords Cobalt ferrite · Solid acid · MCRs · Spirooxindole

# Introduction

Green chemistry is a branch of chemistry that tries to make the chemical process registered with the environment. One of the fields that green chemistry has always dealt with is Catalysis. Hence, the researches around the green catalysts have been

Mohammad A. Nasseri manaseri@birjand.ac.ir

<sup>&</sup>lt;sup>1</sup> Department of Chemistry, College of Sciences, University of Birjand, Birjand 97175-615, Iran

promoted until heterogenous acids stepped into the arena [1, 2]. Actually despite high catalytic activity of homogeneous Bronsted acids such as sulfuric acid, they have some disadvantages which made them inefficient; for instance problems in separation, hard work up and sulfate wastes that come from neutralization of containing solutions and specifically inefficiency in complying with requirements for a reusable catalyst are just only a few typical issues. So researches around it led to turning them solid; for this purpose, metal oxide and organic compounds can be applied, but they are expensive compounds which also possess less active sites. So that sulfonic acid is a good vantage point which has no drawbacks associated with them. As a result, the production of these kinds of eco-friend catalysts resolved those drawbacks [3–22].

Therefore, heterogenous catalysts have been progressed by transforming them to magnetic nanoparticles (MNPs) that made them easier to recover in the solution by using an external magnet. Also, these catalysts are less toxic and possess high catalytic performance in chemical reactions. One common type of these magnetic nanocatalysts are ferrite materials. Ferrites with general formula  $MFe_2O_4$  that M refers to a divalent cation are very important catalysts which are used in a wide range of affairs such as industrially important reactions and public health. The features are like being inexpensive, thermal stability and capability of reducing wastes in chemical industries for environmental demands causes that this kind of catalyst makes common [23–41].

By considering all these interpretations, we used cobalt ferrite immobilized  $SiO_2/SO_3H$  in a one-pot multicomponent reaction. A multi-component reaction is an effective method to producing a diversity-oriented synthesis of the large scale of heterocycle compounds like spirooxindoles that possess a considerable impact on biological systems and also pharmaceutical activities, and it was always a big challenge to produce oxindole derivatives in the field of organic chemistry [42–46].

As we noticed before, herein, we synthesized  $CoFe_2O_4@SiO_2@SO_3H$ (Scheme 1) to examine catalytic activity in the three component reaction of



Scheme 1 Preparation of catalyst (CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@SO<sub>3</sub>H)

malononitrile, dimedone and isatin in 80 °C at the reflux and solvent ethanol/ water (1:1) condition which led to the synthesis of spirooxindole derivatives (Scheme 2). In the end, the corresponding heterogeneous nanocatalyst was also characterized by FT-IR, VSM, SEM–EDX, and XRD which will be mentioned below.

## Experimental

#### Materials

Reagents (Dimedone, Isatin, Malononitrile and their own dependent derivatives) and solvents (Ethanol, N-hexane, DMSO, CHCl<sub>3</sub>, THF, and CH<sub>3</sub>CN) were purchased from Merck. Purity determinations of the products were accomplished by TLC on silica-gel polygram SILG/UV 254 plates. Melting points were measured on an Electrothermal 9100 apparatus.

#### **Characterization techniques**

IR spectra were taken on a Perkin Elmer 781 spectrometer in KBr pellets and reported in cm<sup>-1</sup>. <sup>1</sup>HNMR and <sup>13</sup>CNMR spectra were measured on a Bruker DPX-250 Avance instrument at 250 MHz and 62.9 MHz in CDCl<sub>3</sub> or DMSO-d<sub>6</sub> with chemical shift given in ppm relative to TMS as an internal standard. Powder X-ray diffraction (XRD) was performed on a Bruker D<sub>8</sub>-advance X-ray diffractometer with Cu K $\alpha$  ( $\lambda$ =0.154 nm) radiation. The magnetic properties were determined by using a vibrating sample magnetometer (VSM) leak shore 7200 at 300 K VSM leak shore. TGA was also recorded using a Perkin-Elmer Diamond TG/DTA thermal analyzer in an argon flow rate (100 ml/min) with increasing the heating rate of 10 °C min<sup>-1</sup>. The scanning electron microscope (SEM) (Mitra3TEScan-XMU) was used for recording surface morphology. Transmission electron microscopy (TEM) was performed on a Philips EM208 microscope and was operated at 100 kV.



Scheme 2 Synthesis of spirooxindole derivatives catalyzed by CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@SO<sub>3</sub>H

## **Catalyst preparation**

# Preparation of CoFe<sub>2</sub>O<sub>4</sub> magnetic nanoparticles

The 0.001 mol (0.183 g) of  $Co(NO_3)_2 \cdot 6H_2O$  and 0.002 mol of  $Fe(NO_3)_3 \cdot 9H_2O$ (0.808 g) have been dissolved in 100 ml of distilled water and the solution placed in ultrasonication for 30 min. After that, a 20 ml solution of NaOH (2 M) added to the mixture drop wisely right as a black precipitate was slowly forming. Then the mixture was heated in 80 °C for 2 h. Finally, the black precipitate ( $CoFe_2O_4$ ) washed with ethanol as far as the solution becomes neutralized. Eventually, the product was placed in the oven at 80 °C for 2 h [47].

# Synthesis of CoFe<sub>2</sub>O<sub>4</sub> coated by SiO<sub>2</sub> (CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>)

After synthesizing of  $CoFe_2O_4$  MNPs, 0.04 g of ferrite was dispersed at ethanol in an ultrasonication homogenizer device for 20 min. After that 40 ml of water, 1 ml TEOS (tetraethyl orthosilicate) and 5 ml of ammonia solution were added into the flask slowly as mixture stirred. After 24 h stirring of the solution, it was washed with ethanol and separated using the external magnet and finally placed in the oven at 80 °C for 4 h [48].

## Synthesis of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@SO<sub>3</sub>H nanocomposite

The 1 g of  $CoFe_2O_4$ @SiO<sub>2</sub> nanocomposite was entered into a flask and after adding 20 ml of dichloromethane as the solvent, the mixture dispersed for 30 min in the ultrasonicate instrument. After that, 4 ml of chlorosulfonic acid drop wisely added to the mixture and then stirred for 5 h. Eventually, the catalyst separated from containing the solution and after washing the residue, dried in room temperature for 2 h [3].

## **Catalytic activity**

## General procedure for the synthesis of spirooxindole derivatives

First, 0.01 g of the  $CoFe_2O_4@SiO_2@SO_3H$  was dispersed for 30 min and after that an amount of 1 mmol from isatin, malononitrile and dimedone with ethanol/ water (ratio 1:1) were mixed, and the final mixture was placed in 80 °C at the reflux condition. After completing the reaction by passing a certain time, the containing solution was separated by centrifuging and the crude product extracted and washed with ethyl acetate, and then  $Na_2SO_4$  was added to dehydrating the product. After that, the solvent was removed by using a rotary evaporator and finally the product recrystallized in hot ethanol to gain the pure product. Moreover, the catalyst was washed and applied for several times to examine reusability. Structural assignments of the products are based on their <sup>1</sup>HNMR, <sup>13</sup>CNMR and IR spectra.

#### Selected spectral data

**2-Amino-2',5-dioxo-5,6,7,8-tetrahydrospiro-[chromene-4,3'-indoline]-3-carbonitr ile: (Table 1, Entry 5)** White solid, M.p. > 250 °C. <sup>1</sup>H-NMR (250 MHz, DMSO-d<sub>6</sub>), ppm: 1.91 (2H, t, CH<sub>2</sub>), 2.14 (2H, m, CH<sub>2</sub>), 2.66 (2H, t, CH<sub>2</sub>), 6.66 (1H, d, ArH), 6.90 (1H, t, ArH), 7.11 (1H, d, ArH), 7.21 (1H, t, ArH), 7.35 (2H, s, NH<sub>2</sub>), 10.65 (1H, s, NH). <sup>13</sup>CNMR (62.8 MHz, DMSO-d<sub>6</sub>), ppm: 19.85, 26.87, 36.40, 46.94, 57.64, 109.19, 111.92, 117.46, 121.85, 123.37, 128.56, 134.64, 142.18, 158.69, 166.12, 178.23, 195.12. IR/cm<sup>-1</sup>: 3354 (N–H), 3290 (N–H), 3165 (C–H, sp<sup>2</sup>), 2950 (C–H, sp<sup>3</sup>), 2203 (CN), 1713 (C=O), 1652 (N–C=O), 1472 (C–H, Ar).

Table 1 The synthesis of spirooxindole derivatives by CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@SO<sub>3</sub>H



Entry	Isatin		Carbonyl com-	Product	Time (min)	Yield (%)
	R	$\mathbb{R}^1$	pound			
1	Н	Н	3a	4a	60	20
2	$NO_2$	Н	3a	4a	10	50
3	Br	Н	3a	4a	60	30
4	Me	Н	3a	4a	60	20
5	Н	Н	3b	4a	15	90
6	$NO_2$	Н	3b	4a	15	91
7	Br	Н	3b	4a	10	78
8	Me	Н	3b	4a	15	90
9	Н	Н	3c	4b	2	98
10	$NO_2$	Н	3c	4b	2	98
11	Br	Н	3c	4b	2	93
12	Me	Н	3c	4b	10	85

Reaction conditions: isatin (1.0 mmol), 1,3-dicarbonyl (1.0 mmol) and malononitrile (1.0 mmol) in E-tOH/H<sub>2</sub>O (1:1), at 80 °C, 10 mg CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@SO<sub>3</sub>H **2-Amino-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro** [chromene-4,3'-indoline]-**3-Carbonitrile:** (Table 1, Entry 9) White solid, M.p. > 250 °C. <sup>1</sup>H-NMR (250 MHz, DMSO-d<sub>6</sub>) ppm: 0.96 (6H, s, 2CH<sub>3</sub>), 2.13 (2H, s, CH<sub>2</sub>), 2.40 (2H, s, CH<sub>2</sub>), 6.71– 7.24 (4H, ArH, 2H, NH<sub>2</sub>, m), 10.35 (1H, s, NH). <sup>13</sup>C-NMR (62.8 MHz, DMSO-d<sub>6</sub>) ppm: 27.43, 28.05, 32.31, 47.25, 50.43, 57.89, 109.76, 111.23, 117.72, 122.41, 123.40, 128.54, 134.79, 142.39, 152.01, 159.34, 164.51, 178.44, 195.36. IR/cm<sup>-1</sup>: 3372 (N–H), 3316 (NH), 3141 (C–H, sp<sup>2</sup>), 2923 (C–H, sp<sup>3</sup>), 2189 (CN), 1719 (C=O), 1656 (N–C=O), 1602 (C–H, Ar), 1471 (C–H, Ar).

## **Result and discussion**

 $CoFe_2O_4@SiO_2@SO_3H$  was used in a model reaction of isatin, malononitrile, and dimedone which led to a certain product called spirooxindole (Scheme 2). With regarding the advantages of this solid acid such as easy recovery, non-toxicity, high catalytic performance, easy synthesizing and reusability, this catalyst can be a suitable choice in catalysis. Eventually, this catalyst was characterized by different techniques including XRD, EDX, IR, TEM, SEM, TGA and VSM.

#### **FT-IR spectroscopy**

Herein we discuss the IR spectroscopy of the catalyst which performed in the range of 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. Based on Fig. 1, we can see a broadening absorption at  $3212 \text{ cm}^{-1}$  which belongs to OH-stretching of absorbed water molecules; furthermore, the peak located at 594 cm<sup>-1</sup> is dealing with the bending mode of CO–O and Fe–O bonds (Fig. 1a). Another sharp and strong absorption at 1091 cm<sup>-1</sup> is due to the stretching band or asymmetric vibrations of Si–O–Si and the peak locating around 794 cm<sup>-1</sup> is because of symmetric vibration of Si–O–Si. Also, the absorption band presenting at 459 cm<sup>-1</sup> is because of the bending vibration of O–Si–O. Finally, a broad peak in



the range of 1091 cm<sup>-1</sup> represents S–O absorption which is directly alluded to SO<sub>3</sub>H groups and coated on the surface of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub> nanocomposites (Fig. 1b).

In comparison to other spectra mentioned in other articles, about (a) that represents uncoated cobalt ferrite, we can exemplify Demirelli et al. which has a metal–oxygen band revealed in 560 cm<sup>-1</sup> comparing to this spectrum in 594 cm<sup>-1</sup> it is partial differences in shift; also in order to compare Si–O–Si bands in (b) we can reference it to Kurtan et al. and Runowski et al. which there are MnFe<sub>2</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub> in the former and later coated by silicate. In these articles, asymmetric and symmetric vibrations of Si–O–Si respectively are revealed at 1080 cm<sup>-1</sup> and around 800 cm<sup>-1</sup> which in comparing both data to this one, concludes that there are no significant differences in presented peak for CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@SO<sub>3</sub>H. The same conclusion happens for O–Si–O vibration that is based on noted articles and concedes 460 cm<sup>-1</sup> while herein it shows at 459 cm<sup>-1</sup> [49–51].

# X-ray diffraction (XRD) analysis of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@SO<sub>3</sub>H

Figure 2 shows the XRD patterns of synthesized (a)  $CoFe_2O_4$  and (b)  $CoFe_2O_4$ @  $SiO_2@SO_3H$ . Corresponding the peaks of phase analysis shows that all the peaks belong to  $CoFe_2O_4$  and cobalt ferrite-silicon oxide phase which both proves the structure. Based on the results, the existence of a broad peak at  $2\theta = 23.6^{\circ}$  approves the silicate immobilization and also sulfonic acid functionalization over the cobalt ferrite MNPs. The average grain size of the  $CoFe_2O_4@SiO_2@SO_3H$  is calculated by using the Debye–Scherrer formula. From the well-known Scherrer formula the average crystallite size, *L* is:

$$L = \frac{K\lambda}{\beta\cos\theta},$$

Fig. 2 XRD pattern of  $CoFe_2O_4$ (a).  $CoFe_2O_4@SiO_2@SO_3H$  (b)



where  $\lambda$  is the X-ray wavelength (nm),  $\theta$  is the Bragg's angle, *K* is a constant related to crystallite shape, normally taken as 0.9, and  $\beta$  is the full width of the diffraction line at the half maximum intensity. The average crystallite size of synthesized products was thus calculated at about 42.41 nm [52–54].

# Energy-dispersive X-ray (EDX) pattern of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@SO<sub>3</sub>H

Figure 3 demonstrates energy-dispersive X-ray spectroscopy (EDX) of  $CoFe_2O_4@SiO_2@SO_3H$  nanocomposite. This analyze is recorded because of the determination of elemental composition in the catalyst. The results show that Co, Fe, S, Si, and O are existing in the sample. We should note that there is no impurity in the product.

## Vibrating sample magnetometer (VSM) analysis of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@SO<sub>3</sub>H

The magnetic properties of (a)  $CoFe_2O_4$  (b)  $CoFe_2O_4@SiO_2$  and (c)  $CoFe_2O_4@SiO_2@SO_3H$  were studied by a vibrating sample magnetometer (VSM) at 300 K (Fig. 4). Figure 4 shows the absence of the hysteresis phenomenon and indicates that the product has superparamagnetism at room temperature. The saturation magnetization values for  $CoFe_2O_4$ ,  $CoFe_2O_4@SiO_2$  and  $CoFe_2O_4@SiO_2@SO_3H$  were 39.124, 30.387 and 13.614 emu/g, respectively [52, 54].

## Thermal gravimetric analysis (TGA)

Figure 5 presents the thermogravimetric analysis (TGA) of  $CoFe_2O_4@SiO_2@SO_3H$  nanoparticles. The TGA curve was separated into three areas according to three mass loss ranges. The first area, which occurred below 150 °C, showed a mass loss



Fig. 3 The EDX pattern of  $CoFe_2O_4@SiO_2@SO_3H$ 



Fig. 4 Magnetization curves of  $CoFe_2O_4$  (a).  $CoFe_2O_4@SiO_2$  (b).  $CoFe_2O_4@SiO_2@SO_3H(c)$ 



Fig. 5 TGA curve of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H MNPs

that was attributed to the loss of physically adsorbed solvent and surface hydroxyl groups. The second region (150–600 °C) shows that the silica-coated MNPs are thermally stable. Finally, the third area that occurred between 600 and 800 °C belongs to the mass loss of SO<sub>3</sub>H groups.

#### Transmission electron microscopy (TEM)

The grain size of the  $CoFe_2O_4@SiO_2@SO_3H$  was investigated by TEM. They have a narrow distribution of sizes, from 55 to 68 nm (Figs. 6, 7). The average size



Fig. 6 TEM images of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@SO<sub>3</sub>H



Fig. 7 Particle size distribution of  $CoFe_2O_4@SiO_2@SO_3H$  nanoparticle

of  $CoFe_2O_4@SiO_2@SO_3H$  NPs is determined, and average size distribution of 62.90 nm is observed for  $CoFe_2O_4@SiO_2@SO_3H$  NPs (Fig. 7).

#### Scanning electron microscopy (SEM)

SEM analysis of the product (Fig. 8) provided information on the size and morphology of  $CoFe_2O_4@SiO_2@SO_3H$  nanoparticles.

## Evaluating the acidity of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@SO<sub>3</sub>H

In order to determine acidity of the catalyst, we have decided to choose the ion exchange to analyze a method for evaluating amounts of  $H^+$  on the surface of  $CoFe_2O_4@SiO_2@SO_3H$  for this purpose, about 50 mg of the catalyst was dissolved in the 25 ml aqueous solution of NaCl, 0.1 M, and primary pH was recorded; then,



Fig. 8 SEM images of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@SO<sub>3</sub>H

the mixture stirred for about 2 h; after that, the secondary pH was recorded. Finally, the result of subtraction of pHs which is assigned directly to the catalyst acidic capability contributed to proportional 0.02 mol of  $H^+$  instead of each gram of catalyst.

#### The catalytic activity of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@SO<sub>3</sub>H for the synthesis of spirooxindoles

To optimize the reaction conditions, a wide series of reactions was performed with 1 mmol of substrates malononitrile, isatin, and dimedone in the presence, and absence of the catalyst  $CoFe_2O_4@SiO_2@SO_3H$  nanocomposite and so changing the situations by using different solvents at 80 °<sub>C</sub>. For the first step, in the model reaction of 1 mmol from substrates with ethanol/water (ratio 1:1), the amount of catalyst was optimized based on (Fig. 9). So the best amount of  $CoFe_2O_4@SiO_2@SO_3H$  which lead to the product at a short time was 0.01 g of it that showed; whereas this reaction in the absence of catalyst after 30 min finished by only 20% yield.

**Fig. 9** The effect of different amounts of  $CoFe_2O_4 @SiO_2@$  $SO_3H$ . Reaction conditions: isatin (1.0 mmol), malononitrile (1.0 mmol), dimedone (1.0 mmol) in EtOH:H<sub>2</sub>O (1:1), at 80 °C. Final optimized amount of catalyst=0.01 g





Fig. 10 The effects of solvent on the yield of model reaction spirooxindoles. Reaction conditions: isatin (1.0 mmol), malononitrile (1.0 mmol), dimedone (1.0 mmol) in 10 mg  $CoFe_2O_4@SiO_2@SO_3H$ , at 80 °C

After an amount optimization, we have carried out the same reaction by changing solvent in a wide range of polarity (Fig. 10). Based on the experiments by considering of obvious rise in yield, we can conclude that the model reaction can be performed in polar solvents. So the best situation in the solvent was selected in a mixture of ethanol and water (1:1).

In the end, temperature optimization was performed and based on the results, after increasing temperature from room temp to 80 °C, an obvious increase in yield was observed (Fig. 11).

To expand the scope of catalyst  $CoFe_2O_4@SiO_2@SO_3H$  we have tested it in the reaction by changing substrates 1,3-diketone, malononitrile and isatin derivatives which in any reaction there was only a single substrate variable and other conditions (including temperature, solvent, etc.) have been considered constantly (Table 1). So, for comparing the yield, a range of time 2–60 min was recorded, and as a result, we find out that dimedone as a 1,3 dicarbonyl compound can accelerate the velocity of the reaction more efficiency than 1,3-cyclohexadione (Table 1, entries 9–12). The same result has been recorded for isatin when we investigated the effect of the substituent on the isatin because it has the electron-withdrawing groups such as nitro or halogens attached in the phenyl ring (Table 1, entries 2, 3, 6, 7, 10, 11). But by changing 4-Hydroxycoumarin instead of 1,3-diketones we observed that the rate of the reaction would not progress in comparison to other diketones (Table 1, entries 1–4).

In Scheme 3, we have presented the reasonable mechanism for preparation of spirooxindole derivatives. The  $CoFe_2O_4@SiO_2@SO_3H$  as an acidic catalyst that activates the carbonyl group of isatin, and then malononitrile because of the

**Fig. 11** The effect of temperature on the yield of the model reaction spirooxindoles. Reaction conditions: isatin (1.0 mmol), malononitrile (1.0 mmol), dimedone (1.0 mmol) in EtOH:H<sub>2</sub>O (1:1), 10 mg CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@SO<sub>3</sub>H





Scheme 3 The reasonable mechanism for the synthesis of spirooxindole derivatives

activated alpha hydrogens will have a nucleophilic attack on activated carbon to generate intermediate 2, This intermediate generates intermediate 3 by the elimination of Knoevenagel condensation, finally with adding of dimedone to this intermediate the corresponding product was synthesized. In all steps of the reaction, everywhere that the catalyst takes part in, the anionic intermediates were stabilized by heterogeneous solid acid  $CoFe_2O_4@SiO_2@SO_3H$ ; therefore, this catalyst has a huge effect on the reaction.

The model reaction of spirooxindole has been performed by using 0.01 g  $CoFe_2O_4@SiO_2@SO_3H$  in the reaction of dimedone, isatin and malononitrile in 80 °C via solvent ethanol/water (1:1) to examine reusability of the catalyst. Based on the experiments, the results which are recorded in (Fig. 12) show that after five cycles, there is no specific reduction in the yield so we can use it for several times without problems of reusability.

To elucidate this strong durability, the recovered catalyst after the third run was studied by FT-IR, XRD characteristic methods. By comparing the FT-IR spectrum of the recovered catalyst by the corresponding fresh spectrum, there cannot be



Fig. 12 Recyclability of  $CoFe_2O_4@SiO_2@SO_3H$  in the synthesis of spirooxindoles. Reaction conditions: isatin (1.0 mmol), malononitrile (1.0 mmol), dimedone (1.0 mmol) in EtOH:H<sub>2</sub>O (1:1), 10 mg  $CoFe_2O_4@SiO_2@SO_3H$ , 80 °C



Fig. 13 a FT-IR spectrum, and b XRD pattern of the recovered catalyst after third recycle

found any change wherein, confirming the structure of the catalyst during the reaction. Also, the XRD image of the recovered catalyst corroborates that the results showed that the recovered catalyst did not show significant differences in the structure (Fig. 13).

To show the advantage and uniqueness of the present method, the catalyst  $CoFe_2O_4@SiO_2@SO_3H$  was compared with the previously reported catalyst for the preparation of spirooxindole (Table 2).

#### Conclusions

In conclusion, a facile methodology was developed for the preparation of biologically active spirooxindole derivatives using  $CoFe_2O_4@SiO_2@SO_3H$  nanoparticles as an efficient heterogeneous catalyst. The catalyst represents an outstanding activity in water/EtOH at 80 °C, which have high yields in short reaction times. The catalyst was characterized by FT-IR, VSM, EDX, TEM, TGA, SEM and XRD analyses. Then, the efficiency of the prepared  $CoFe_2O_4@SiO_2@SO_3H$  was studied in the reaction of malononitrile, isatins with 1,3-dicarbonyl compounds to synthesize

	1	0 24 2 5		2	
Entry	Catalyst	Solvent/ $T$ (°C)	Time (min)	Yield (%)	References
1	Sodium stearate	H <sub>2</sub> O/60 °C	180	95	[55]
2	TEBA	H <sub>2</sub> O/90 °C	120	88	[56]
3	B-CD	H2O/60 °C	480	88	[57]
4	GN/SO3H	EtOH/H <sub>2</sub> O (1:1)/ref.	40	95	[3]
5	NET <sub>3</sub>	EtOH/ref.	30	80	[58]
6	CoFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> @SO <sub>3</sub> H	EtOH/H <sub>2</sub> O (1:1)/80 °C	2	98	This work

 Table 2
 Comparison of results using CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@SO<sub>3</sub>H with various catalysts

Malononitrile (1 mmol), isatin (1 mmol), dimedone (1 mmol)

biologically spirooxindole derivatives, and the results showed excellent yields. In the end, advantages of this method are the low-cost catalyst, less toxicity (eco-friendly), clean reaction profiles, and reusability, the reaction was completed in a short period of time with small amounts of catalyst. In addition, it is easy to separate the catalyst for catalytic recycling. Finally, the catalyst could be readily reused for at least five consecutive runs without any metal leaching, or significant loss in catalytic activity. The analyses of the recovered catalyst demonstrated its stability and durability.

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