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# Synthesis and characterization of Co (III) salen complex immobilized on cobalt ferrite-silica nanoparticle and their application in the synthesis of spirooxindoles

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M. A. Nasseri, Department of Chemistry, College of Sciences, University of Birjand, Birjand 97175-615, Iran. Email: manaseri@birjand.ac.ir The preparation, characterization and catalytic application of Co (III) salen complex loaded on cobalt ferrite-silica nanoparticle [CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@ Co (III) salen complex] are described. Co (III) salen complex loaded on ferrite cobalt-silica nanoparticles is characterized by transmission electron microscopy, scanning electron microscopy coupled with energy-dispersive X-ray, vibrating-sample magnetometer and Fourier transform-infrared analyses. The thermal stability of the material is also determined by thermal gravimetric analysis. An average crystallite size is determined from the full-width at half-maximum of the strongest reflection by using Scherrer's approximation by powder X-ray diffractometry. The efficiency of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co (III) salen complex is investigated in the synthesis of spirooxindoles of malononitrile, various isatins with 1,3-dicarbonyles. The nanocatalyst demonstrated excellent catalytic activity that gave the corresponding coupling products in good to excellent yields. Moreover, the recoverability and reusability of CoFe2O4@SiO2@Co (III) salen complex is investigated where nanocatalyst could be recovered and reused at least five times without any appreciable decrease in activity and selectivity, which confirmed its high efficiency and high stability under the reaction conditions and during recycling stages.

#### **KEYWORDS**

Co (III) salen complex, cobalt ferrite, nanoparticle, spirooxindole

# **1** | INTRODUCTION

Schiff base ligands with more flexible structures are easily synthesized and form complexes with almost all metal ions. Many salen complexes show excellent catalytic activity in various reactions.<sup>[1-9]</sup> Salen complexes are one out of 10 superior catalysts synthesizing organic material. On the other hand, immobilizing them on nanomagnetic substrates could create a new methodology of organic material. One of the most important challenges in catalysis is to transform a successful homogeneous catalyst into a heterogeneous one, due to the intrinsic advantages of heterogeneous systems, namely easy catalyst

separation/recycling and products separation.<sup>[10,11]</sup> Heterogenization of metal complexes has been carried out using supports, such as zeolite, clays, silicious materials and activated carbon.<sup>[12–20]</sup> With the advancement of nanoscience, magnetic nano-sized particles are becoming increasingly interesting due to their unique applications, such as their uses for cell separation, magnetic resonance imaging, drug delivery systems, protein separation and cancer treatments through hyperthermia.<sup>[21–28]</sup> Also, magnetic nanoparticles (MNPs) can be good candidates as support materials for heterogeneous catalysts, because of easy synthesis, high surface area, excellent thermal and chemical stability, surface modification

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ability, and low toxicity and cost. Moreover, the application of an external magnet readily separates the catalystloaded MNPs from the reaction products to eliminate the need for filtration and facilitate catalyst recycling. This improvement highlights the advantages of both homogeneous (selectivity, activity) and heterogeneous (separation, recovery, recycling) catalysts.<sup>[29–34]</sup> CoFe<sub>2</sub>O<sub>4</sub> nanoparticles have been studied extensively by the scientific community due to applications in areas such as highdensity information storage, electromagnetic wave absorption and biomedicine.<sup>[35,36]</sup> Compared with some magnetic platforms such as Fe<sub>3</sub>O<sub>4</sub>, which is fairly reactive to acidic and oxidative environments, and  $\gamma$  -Fe<sub>2</sub>O<sub>3</sub>, which is not thermally stable, CoFe<sub>2</sub>O<sub>4</sub> is stable in acidic environments and thermal conditions.<sup>[37–43]</sup>

On a different note, oxindoles occupy an important place in the area of heterocyclic chemistry because they are frequently found in numerous natural and synthetic products along with useful biological activities. Oxindole derivatives often appear as important structural components in biologically active and natural compounds, which include antibacterial, antiprotozoal, anti-inflammatory activities, and progesterone receptors (PRs) agonists.<sup>[44–48]</sup>

Several procedures of this strategy, which have been recently reported in the literatures, are reaction of isatin, malononitrile and dimedone in the presence of GN/SO<sub>3</sub>H,<sup>[49]</sup> ZnFe<sub>2</sub>O<sub>4</sub>,<sup>[50]</sup> borax,<sup>[51]</sup> Al-ITQ-HB,<sup>[52]</sup> sodium stearate,<sup>[53]</sup> TEBA,<sup>[54]</sup> AIUM,<sup>[55]</sup> B-CD,<sup>[56]</sup> DES,<sup>[57]</sup> Ni NPS,<sup>[58]</sup> SBA-PR-NH<sub>2</sub><sup>[59]</sup> and NEt<sub>3</sub>.<sup>[60]</sup>

In continuation of our ongoing research on the development of eco-friendly organic synthesis, particularly by nano-catalysts,<sup>[61–71]</sup> up to now, salen complexes that are stabled on a magnetic nano-substrate have not been used in multi-component synthesis of spirooxindole. In this paper, we introduce Co (III) salen complex immobilized cobalt ferrite-silica nanoparticle on [CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co (III) salen complex] as an efficient, active and recyclable magnetic nano-catalyst that can be used for different organic functional group transformations in green processes. Then, we studied its catalytic activity in the synthesis of spirooxindoles by the coupling of various isatins with 1,3-dicarbonyles and malononitrile. The yield and selectivity of the corresponding delivered products were also found to be high to excellent. Also, the present study shows unique advantages, such as high magnetic properties, simple synthesis of the catalyst, easy separation of catalyst with a permanent magnet, and the application of inexpensive and available precursors. Moreover, the catalytic systems exhibited high durability and reusability under the applied reaction conditions. The reactivity, reusability and stability of the catalyst against the reaction processes have also been improved (Scheme 1).

#### 2 | EXPERIMENTAL

#### 2.1 | Chemicals

Reagents and solvents were purchased from Merck or Fluka chemical companies. Purity determinations of the products were accomplished by thin-layer chromatography (TLC) on silica-gel polygram SILG/UV 254 plates. Melting points were measured on an Electro thermal 9100 apparatus. IR spectra were taken on a Perkin Elmer 781 spectrometer in KBr pellets and reported in cm<sup>-1</sup>. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were measured on a Bruker DPX-250 Avance instrument at 250 MHz and 62.9 MHz



SCHEME 1 Synthesis of spirooxindole derivatives catalyzed by CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co (III) salen complex

in CDCl<sub>3</sub> or DMSO-d<sub>6</sub> with chemical shift given in ppm relative to TMS as internal standard. The morphology of the products was determined by using CMPhilips10 model transmission electron microscopy (TEM) at an accelerating voltage of 100 kV. Power 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 thermal gravimetric analysis (TGA) curves were recorded under air atmosphere using TGA/DTA Shimadzu-50 with platinum pan. The samples were heated in air from 25 to 800°C with a heating rate of 10°C per min. The weight losses as a function of temperature were recorded. The magnetic properties were determined by using vibrating-sample magnetometer (VSM) leak shore 7200 at 300 kVsm leak shore. Scanning electron microscopy coupled with energy-dispersive X-ray (SEM-EDX) spectra were recorded by MIRA 3TESCAN-XMU and SAMx spectrometer.

# 2.2 | Catalyst preparation

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

n a balloon containing 100 mL of distilled water, 0.002 mol (0.808 g) of Fe (NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 0.001 mol (0.291 g) of Co (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were dissolved. Then, 1 M NaOH solution (20 mL) was added drop by drop to the previous solution and sonicated (60 W, 30 min). The mixture was then heated for 2 h at 80°C. CoFe<sub>2</sub>O<sub>4</sub> nanoparticles (black precipitate) were separated using an external magnet, rinsed with distilled water and ethanol, and dried in an oven at 80°C for 10 h.<sup>[72]</sup>

## 2.2.2 | Preparation of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell

An appropriate amount of  $CoFe_2O_4$  nanoparticles (0.150 g) was dispersed in EtOH/H<sub>2</sub>O (4:1, 100 mL) for 30 min. Then, tetraethylorthosilicate (0.5 mL) was added dropwise to the mixture followed by addition of ammonia solution (0.8 mL). For 24 h, the mixture was stirred. Using a permanent magnetic, the achieved  $CoFe_2O_4@SiO_2$ nanoparticles were separated. Then, they were washed with distilled water and dried under vacuum.<sup>[73]</sup>

# 2.2.3 | Preparation of 4-[(E)-{(2-[(E)-(2hydroxybenzylidene)amino]phenyl)imino} methyl]benzene-1,3-diol

2,4- Dihydroxyl benzaldehyde (0.690 g, 5 mmol) was dissolved in dry chloroform (35 mL). Then, *o*phenylenediamine (5 mmol, 0.54 g) in dry chloroform (30 mL) was added drop by drop to the mixture, and then stirred for 6 h at 0°C. The crude solid yellow product was filtered, and salicylaldehyde (0.52 mL, 5 mmol) in dry EtOH (10 mL) was added. Then the reaction mixture was stirred for 2 h under reflux conditions under N<sub>2</sub> atmosphere. Upon completion, the solvent was filtered and dried at 80°C for 12 h to obtain 4-[(E)-{(2-[(E)-2-hydroxybenzylidene) amino]phenyl)imino}methyl]benzene-1,3-diol.

# 2.2.4 | Procedure for the synthesis of Co (III) salen complex

Co  $(OAC)_2$ ·4H<sub>2</sub>O (0.249 g, 1 mmol) in ethanol (10 mL) was added to a suspension of ligand (0.332 g, 1 mmol) and NaOH (67 mg, 1.67 mmol) in ethanol (20 mL). This suspension was stirred under reflux conditions for 1.5 h. Then, LiCl (5.8 mmol, 0.247 g) was added to the reaction mixture and stirred for 1 h, and the product was filtered and washed with hot water and methanol. The product was dried at 80°C for 12 h to obtain Co (III) salen complex.

# 2.2.5 | Preparation of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co (III) salen complex

Co (III) salen complex was synthesized as reported in the literature. The homogeneous Co (III) salen complex was chemically grafted onto the surface of  $CoFe_2O_4@SiO_2$ .

In 100 mL of dry toluene, 1.5 g of  $CoFe_2O_4@SiO_2$  was sonicated for 2 h. Then, homogeneous Co (III) salen complex was added. The mixture was stirred under reflux conditions in an inert atmosphere for 48 h. After the reaction completed, the corresponding Co (III) salen complex was washed with dry toluene and EtOH. Under vacuum, the corresponding nanocatalyst (1.95 g) was dried in an oven for 10 h at 80°C.<sup>[74]</sup>

# 2.3 | Catalytic activity

## 2.3.1 | General procedure for the preparation of oxindole derivatives

To a mixture of 1,3-dicarbonyl compounds (1.0 mmol), isatin (1.0 mmol) and malononitrile (1.0 mmol) in water/ethanol mixture (1:1), was added  $CoFe_2O_4@SiO_2@Co$  (III) salen complex (10 mg). The mixture was stirred at 80°C for an appropriate reaction time (Table 1), and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was dissolved in ethyl acetate, and  $CoFe_2O_4@SiO_2@Co$  (III) salen complex MNPs were separated by external magnet. Then the solvent was removed from solution under reduced pressure, and the resulting

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#### TABLE 1 The synthesis of oxindole derivatives by CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co (III) salen complex



	Isatin						
Entry	R	$\mathbb{R}^1$	Cyclic ketone	Product	Time (min)	Yield (%)	TON
1	Н	Н	3a	4a	10	98	296.96
2	$NO_2$	Н	3a	4a	10	95	287.87
3	Cl	Н	3a	4a	10	98	296.96
4	Н	PhCH <sub>2</sub>	3a	4a	25	82	248.48
5	NO <sub>2</sub>	Et	3a	4a	10	92	278.78
6	OMe	Н	3a	4a	25	85	257.57
7	Me	Н	3a	4a	10	83	251.51
8	Br	Me	3a	4a	10	87	263.63
9	Н	Н	3b	4b	2	98	296.96
10	$NO_2$	Н	3b	4b	2	98	296.96
11	Cl	Н	3b	4b	2	93	281.81
12	Н	PhCH <sub>2</sub>	3b	4b	10	85	257.57
13	$NO_2$	Et	3b	4b	2	93	281.81
14	OMe	Н	3b	4b	5	87	263.63
15	Me	Н	3b	4b	5	82	248.48
16	Br	Me	3b	4b	2	88	266.66
17	Н	Н	3c	4c	2	98	296.96
18	$NO_2$	Н	3c	4c	2	98	296.96
19	Cl	Н	3c	4c	2	95	287.87
20	Н	PhCH <sub>2</sub>	3c	4c	10	84	254.54
21	$NO_2$	Et	3c	4c	2	93	281.81
22	OMe	Н	3c	4c	5	81	245.45
23	Ме	Н	3c	4c	5	85	257.57
24	Br	Me	3c	4c	5	90	272.72

Reaction conditions: isatin (1.0 mmol), 1,3-dicarbonyl (1.0 mmol) in EtOH:H2O (1:1), at 80°C, 10 mg CoFe2O4@SiO2@Co (III) salen complex.

product was purified by recrystallization using ethanol to afford the pure oxindole product in excellent purity and yield. Structural assignments of the products are based on their <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and IR spectra (for the NMR spectrum of the products, see SI, PP. S1-S6).

#### 2-Amino-2',5-dioxo-5,6,7,8-tetrahydrospiro-

*[chromene-4,3'-indoline]-3-carbonitrile* (Compound 9, Table 1): white solid, mp > 250°C. <sup>1</sup>H-NMR (250 MHz, DMSO-d<sub>6</sub>) 1.92 (2H, m, CH<sub>2</sub>), 2.12 (2H, m, CH<sub>2</sub>), 2.58 (2H, m, CH<sub>2</sub>), 6.66 (d,1H, *J* = 7.39 Hz, Ph), 6.89 (t, 1H,

*J* = 7.39 Hz, Ph), 7.13 (d, 1H, *J* = 7.39 Hz, Ph), 7.23 (t, 1H, *J* = 7.39 Hz, Ph), 7.36 (s, 2H, NH<sub>2</sub>), 10.66 (s, 1H, NH). <sup>13</sup>C-NMR (62.9 MHz, DMSO-d<sub>6</sub>) 195.11 (C=O), 178.21 (C=O), 166.11 (C), 158.71 (C), 142.1 (C), 134.59 (C), 128.51 (CH), 123.31 (CH), 121.81 (CH), 117.41 (CH), 112.91 (C ≡ N), 109.21 (C), 57.61 (C), 46.91 (C), 36.41 (CH<sub>2</sub>), 26.81 (CH<sub>2</sub>), 19.81 (CH<sub>2</sub>). IR (KBr, cm<sup>-1</sup>) 3352, 3295, 3175, 2952, 2204, 1713, 1655, 1352, 1216, 1076. Anal. calcd for C<sub>17</sub>H<sub>13</sub>N<sub>3</sub>O<sub>3</sub>: C, 66.44; H, 4.26; N, 13.67%. Found: C, 66.42; H, 4.31; N, 13.72%.

### 2-Amino-7,7-dimethyl-2',5-dioxo-5,6,7,8tetrahydrospiro-[chromene-4,3'-indoline]-3-

*carbonitrile* (Compound **17**, Table 1): white solid, mp > 250°C. <sup>1</sup>H-NMR (250 MHz, DMSO-d<sub>6</sub>) 1.00 (3H, s, CH<sub>3</sub>), 1.14 (3H, s, CH<sub>3</sub>), 2.08–2.11 (2H, m, CH<sub>2</sub>), 2.55 (2H, m, CH<sub>2</sub>), 6.69 (d,1H, J = 7.3 Hz, Ph), 6.89 (t, 1H, J = 7.3 Hz, Ph), 7.09 (d, 1H, J = 7.3 Hz, Ph), 7.21 (t, 1H, J = 7.4 Hz, Ph), 7.34 (s, 2H, NH<sub>2</sub>), 10.64 (s, 1H, NH) .<sup>13</sup>C-NMR (62.9 MHz, DMSO-d<sub>6</sub>) 195.29 (C=O), 178.49 (C=O), 166.57 (C), 159.19 (C), 152.39 (C), 142.47 (C), 134.82 (CH), 128.58 (CH), 123.39 (CH), 122.15 (CH), 117.75 (C), 112.21 (C  $\equiv$  N), 109.69 (C), 57.95 (C), 50.44 (CH<sub>2</sub>), 47.22 (C), 32.34 (CH<sub>2</sub>), 28.01 (CH<sub>3</sub>), 27.09 (CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 3376, 3312, 3144, 2928, 2196, 1724, 1656, 1348, 1224, 1056. Anal. calcd for C<sub>19</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>: C, 68.05; H, 5.11; N, 12.53%. Found: C, 67.86; H, 5.14; N, 12.65%.

2'-Amino-2,5'-dioxo-5'H-spiro [indoline-3,4'pyrano[3,2-c]chromene]-3'-carbonitrile (Compound 1, Table 1): white solid, mp > 250°C. <sup>1</sup>H-NMR (250 MHz, DMSO-d<sub>6</sub>): 6.82 (1H, d, J = 7.59 Hz, Ph), 6.91 (1H, t, J =7.58 Hz, Ph), 7.16 (1H, d, J = 7.22 Hz, Ph), 7.31 (1H, d, J = 7.61 Hz, Ph), 7.43 (1H, t, J = 7.5 Hz, Ph), 7.47 (1H, t, J = 8.1 Hz, Ph), 7.51 (1H, d, J = 8.3 Hz, Ph), 7.52 (2H, s, NH<sub>2</sub>), 7.94 (1H, d, *J* = 8.1 Hz, Ph), 10.64 (1H, s, NH). <sup>13</sup>C-NMR (62.9 MHz, DMSO-d<sub>6</sub>) 177.41 (C=O), 158.9 (C=O), 155.7 (C), 155.5 (C), 152.39 (CH), 142.59 (CH), 134.09 (CH), 133.49 (CH), 129.38 (C), 125.39 (C), 124.49 (CH), 123.11 (CH), 122.51 (CH), 117.41 (CH), 117.08 (C), 112.89 (C  $\equiv$  N), 109.89 (C), 101.89 (C), 70.19 (C), 57.49 (C). IR (KBr, cm<sup>-1</sup>): 3415, 3241, 3260, 2218, 1719, 1679, 1623, 1581. Anal. calcd for C<sub>20</sub>H<sub>11</sub>N<sub>3</sub>O<sub>4</sub>: C, 67.23; H, 3.10; N, 11.76%. Found: C, 67.39; H, 3.12; N, 11.65%.

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# 3 | RESULTS AND DISCUSSION

 $CoFe_2O_4$  was synthesized from Fe  $(NO_3)_3 \cdot 9H_2O$  and Co  $(NO_3)_2 \cdot 6H_2O$ . Then, an appropriate amount of  $CoFe_2O_4$  nanoparticles was dispersed in EtOH/H<sub>2</sub>O followed by drop-wise addition of tetraethylorthosilicate to achieve  $CoFe_2O_4@SiO_2$  nanoparticles. Finally, homogeneous Co (III) salen complex was immobilized on to the  $CoFe_2O_4@SiO_2$  [corresponding heterogeneous  $CoFe_2O_4@SiO_2@Co$  (III) salen complex; Scheme 2].

Co (III) salen complex loaded on ferrite cobalt-silica nanoparticles is characterized by TEM, SEM–EDX, VSM, Fourier transform-infrared (FT-IR) analyses, TGA and XRD.

## FT-IR spectroscopy

The FT-IR at 4000 to 400 cm<sup>-1</sup> for (a) CoFe<sub>2</sub>O<sub>4</sub>, (b) CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>, and (c) CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co (III) salen complex nanoparticles were studied by FT-IR spectroscopy, and the results are shown in Figure 1. The broadening absorption peak at 3347 cm<sup>-1</sup> belongs to OH-stretching of absorbed water molecules. The peak located at 605 cm<sup>-1</sup> is attributed to the bending mode of Co-O and Fe-O. In spectrum 1b, the absorption band present at about 1099 cm<sup>-1</sup> is due to the stretching band vibrations of Si-O-Si. The absorption band present at about 467 cm<sup>-1</sup> is due to the bending of Si-O-Si or O-Si-O. In spectrum 1c, the absorption peak at 1611 cm<sup>-1</sup> belongs to C=N stretching band vibrations in CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co (III) salen complex.

#### Transmission electron microscopy

The grain sizes of (a)  $CoFe_2O_4$ , (b) $CoFe_2O_4$ @SiO<sub>2</sub>, and  $CoFe_2O_4$ @SiO<sub>2</sub>@Co (III) salen nanoparticles were investigated by TEM. They have a narrow distribution of sizes, from 18 to 30 nm (Figures 2 and 3).



**SCHEME 2** Preparation of catalyst CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co (III) salen complex





**FIGURE 1** Fourier transform-infrared (FT-IR) spectra of (a)  $CoFe_2O_4$ , (b)  $CoFe_2O_4$ @SiO<sub>2</sub> and (c)  $CoFe_2O_4$ @SiO<sub>2</sub>@Co (III) salen complex

## X-ray diffraction analysis

Figure 4 shows the XRD patterns of synthesized (a)  $CoFe_2O_4$  and (b)  $CoFe_2O_4@SiO_2$  nanoparticles. All the peaks correspond to the  $CoFe_2O_4$  phase, which shows the formation of cobalt ferrite and cobalt ferrite-silica structure. The average grain sizes of the samples are calculated using the Debye–Scherrer formula, where  $\lambda$  is the X-ray wavelength,  $\theta$  is the Bragg's angle 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 14.5 and 17.2 nm.

#### Vibrating-sample magnetometer

The magnetic properties of (a)  $CoFe_2O_4$ , (b)  $CoFe_2O_4$ @SiO<sub>2</sub>, and (c)  $CoFe_2O_4$ @SiO<sub>2</sub>@Co (III) salen complex nanoparticles were studied by a VSM at 300 K (Figure 5). Figure 5 shows the absence of hysteresis phenomenon, and indicates that the product has super-paramagnetism at room temperature. The saturation



**FIGURE 3** Particle size distribution of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co (III) salen complex nanoparticle



**FIGURE 4** Powder X-ray diffractometry (XRD) pattern of (a) CoFe<sub>2</sub>O<sub>4</sub> and (b) CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>



FIGURE 2 Transmission electron microscopy (TEM) image of (a) CoFe<sub>2</sub>O<sub>4</sub>, (b) CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub> and (c) CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co (III) salen complex



**FIGURE 5** Vibrating-sample magnetometer (VSM) pattern of (a)  $CoFe_2O_4$ , (b)  $CoFe_2O_4$ @SiO<sub>2</sub> and (c)  $CoFe_2O_4$ @SiO<sub>2</sub>@Co (III) salen complex



**FIGURE 6** Thermal gravimetric analysis (TGA) pattern of (a) CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub> and (b) CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co (III) salen complex

magnetization values for  $CoFe_2O_4$ ,  $CoFe_2O_4$ @SiO<sub>2</sub> and  $CoFe_2O_4$ @SiO<sub>2</sub>@Co (III) salen nanoparticles were 39.124, 30.387 and 27.348 emu g<sup>-1</sup>.

### Thermal gravimetric analysis

The thermal behavior of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co (III) salen nanoparticles is shown in Figure 6. Significantly, the TGA curve of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub> shows a weight loss over the range of 90-165°C. This weight loss can be attributed to the loss of adsorbed water and dehydroxylation of internal -OH groups. The second weight loss step is over the range 250-460°C, which can be ascribed to even further decomposition of the materials (Figure 6a). As shown in Figure 6b, the amount of water decreased after the incorporation of Co (III) salen complex onto the CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>, indicating that the Co (III) salen complex has been successfully immobilized onto the CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>. The TGA curve of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co (III) salen complex shows a weight loss over the range of 90-160°C and 250-650°C, which is similar to the TGA curve of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>, and the organic parts were decomposed completely at 460-800°C (Figure 6b).

# Scanning electron microscopy coupled with energy-dispersive X-ray

Figures 7–9 show EDX of  $CoFe_2O_4$ ,  $CoFe_2O_4$ @SiO<sub>2</sub> and  $CoFe_2O_4$ @SiO<sub>2</sub>@Co (III) salen complex nanoparticles. These are recorded to investigate the elemental composition of nanoparticles. The results demonstrate that Co, Fe and O appear in  $CoFe_2O_4$  sample, and Co, Fe, Si and O appear in  $CoFe_2O_4$ @SiO<sub>2</sub> sample. Also, the results demonstrate that Co, Fe, Si, O, N and C appear in



FIGURE 7 Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM–EDX) of CoFe<sub>2</sub>O<sub>4</sub>



FIGURE 8 Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>



FIGURE 9 Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) of  $CoFe_2O_4@SiO_2@Co$  (III) salen complex

 $CoFe_2O_4@SiO_2@Co$  (III) salen nanoparticles. Note that no impurity is present in the products.

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Scanning electron microscopy analysis of the products (Figure 7–9) provided information on the size and



**FIGURE 10** The effect of different solvents in the synthesis of oxindole by  $CoFe_2O_4@SiO_2@Co$  (III) salen complex. Reaction conditions: isatin (1.0 mmol), 4-hydroxycoumarin (1.0 mmol) in EtOH:H<sub>2</sub>O (1:1), at 80°C, 10 min, 10 mg CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>



 $\label{eq:FIGURE 11} \begin{array}{l} \text{The effect of the amount of $CoFe_2O_4@SiO_2@Co$} (III)$ salen complex in the synthesis of oxindole. Reaction conditions: isatin (1.0 mmol), 4-hydroxycoumarin (1.0 mmol)$ in EtOH:H_2O$ (1:1)$, at $80°C$ } \end{array}$ 

morphology of  $CoFe_2O_4$ ,  $CoFe_2O_4$ @SiO<sub>2</sub> and  $CoFe_2O_4$ @SiO<sub>2</sub>@Co (III) salen nanoparticles. The results showed that the average product sizes of  $CoFe_2O_4$ ,  $CoFe_2O_4$ @SiO<sub>2</sub> and  $CoFe_2O_4$ @SiO<sub>2</sub>@Co (III) salen complex nanoparticles were 11.76–15.00 nm.

According to ICP-AES analysis, the Co loading was found to be 0.33 mmol  $g^{-1}$ .

# 3.2 | Catalytic activity of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@co (III) salen complex for the synthesis of oxindoles

In order to show the merit of synthesized nanocatalyst in organic reactions, Co (III) salen complex immobilized on



**FIGURE 12** The effect of time in the synthesis of oxindole by  $CoFe_2O_4@SiO_2@Co$  (III) salen complex. Reaction conditions: isatin (1.0 mmol), 4-hydroxycoumarin (1.0 mmol) in EtOH:H<sub>2</sub>O (1:1), at 80°C

cobalt ferrite-silica nanoparticles [CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co (III) salen complex] was used for the first time as an efficient and recyclable nanocatalyst for the synthesis of spirooxindoles by the coupling of various isatins with 1.3-dicarbonyls and malononitrile. For this purpose, isatins, 4-hydroxycoumarin and malononitrile were taken as model substrates. We examined this reaction in various solvents (Figure 10). The results indicate that different solvents affected the efficiency of the reaction. Acetonitrile and dichloromethane afforded low yields (50-56%), while the use of solvents such as water, ethanol, DMF and DMSO could improve the yields. Finally, when a mixture of ethanol and water (1:1) was used, the yield increased to 98% better than any other solvents examined here. In the absence of solvent, the yield of model reaction decreased to 35%.

Electrophilic reaction of isatin with two different nucleophiles is a fundamental strategy for constructing MCRs. As well as its action as a solvent, water and protic solvent also help in the enolization of dimedone by making hydrogen bonds with the OH and, thus, it increases the nucleophilic character of the methylene carbon (C-2) of dimedone. As a result, it helps to increase the reaction rate.<sup>[75]</sup>

We also changed the amount of catalyst. The results are summarized in Figure 11. Our results showed that the reaction yield was affected crucially by the catalyst concentration. Decreasing the catalyst concentration resulted in lower yields under the same conditions. With catalyst concentration increasing (> 10 mg), product decreased significantly. Consequently, this condensation was best catalyzed by 10 mg of  $CoFe_2O_4@SiO_2@Co$  (III)

TABLE 2 Comparison of results using CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co (III) salen complex with various catalysts

Entry	Catalyst	Solvent/T (°C)	Time (min)	Yield (%)	Reference
1	Sodium stearate	H <sub>2</sub> O/60°C	180	95	[46]
2	TEBA	H <sub>2</sub> O/90°C	120	88	[47]
3	AIUM (10 mol%)	DMSO/60°C	120	40	[48]
4	B-CD	H <sub>2</sub> O/60°C	480	88	[49]
5	DES (0.5 mL)	Urea: CHCl <sub>3</sub> /80°C	240	88	[50]
6	Ni NPS	Ethylene glycol	20	88	[51]
7	SBA-PR-NH <sub>2</sub>	H <sub>2</sub> O/ref.	5	80	[52]
8	NEt <sub>3</sub>	EtOH/ref.	30	80	[53]
9	ZnFe <sub>2</sub> O <sub>4</sub>	H <sub>2</sub> O/ref.	8	86	[43]
10	Borax (10 mol%)	EtOH/ref.	120	94	[44]
11	GN/SO <sub>3</sub> H	EtOH/water (1:1)/ref.	40	95	[42]
12	Al-ITQ-HB (10 mol%)	CDCl <sub>3</sub> /r.t.	120	91	[45]
13	CoFe <sub>2</sub> O <sub>4</sub> @ SiO <sub>2</sub> @ Co (III) salen complex	EtOH/water (1:1) / 80°C	2	98	This work

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



salen complex as the reaction was completed within a high yield. The effect of time of reaction was studied by carrying out the model reaction at different times, and the best result was obtained within 10 min (Figure 12).

In order to study the catalytic activity of  $CoFe_2O_4@SiO_2@Co$  (III) salen complex, this coupling was carried out in the absence of catalyst. In this case, the reaction proceeded in low yield (16%) over model reaction time. Oxindole was achieved with excellent yield (98%), using 10 mg catalyst within 10 min in a mixture of ethanol and water as solvent.

Co (III) complex showed that the system with the heterogeneous catalyst exhibits high catalytic efficiency with TON (296.96).

To further explore the scope and limitation of this protocol under the optimized conditions, particularly in regard to library construction, we evaluated using various 1,3-dicarbonyl and isatin compounds. The results are



 $\label{eq:FIGURE 13} FIGURE \ 13 \ \mbox{Recyclability of } CoFe_2O_4 @SiO_2 @Co \ (III) \ salen \ complex in the synthesis of oxindole$ 

**SCHEME 3** A plausible mechanism for the synthesis of spirooxindole in the presence of  $CoFe_2O_4@SiO_2@Co$  (III) salen complex

summarized in Table 1. In all cases, the reaction proceeded readily to afford the corresponding oxindoles in good to excellent yields (81–98%) in very short reaction times. TON showed the catalytic activity of the catalysts. Therefore, the TON of the catalyst was calculated and added to the main text, and the results showed that  $CoFe_2O_4@SiO_2@Co$  (III) salen complex is highly active in the synthesis of spirooxindole (296.96). As can be seen in Table 2, this catalyst showed good catalytic activity and good yields (98%) in shorter times compared with most of the reported works (Table 2).



 $\label{eq:FIGURE 14} \begin{array}{ll} \mbox{Transmission electron microscopy (TEM) image of recovered CoFe_2O_4@SiO_2@Co (III) salen complex after 2nd run \\ \end{array}$ 

Herein, we proposed a mechanism for the Co (III) salen complex nanoparticles supported on  $CoFe_2O_4@SiO_2$ -catalyzed preparation of spirooxindole in Scheme 3. Thus, we proposed that the cobalt (III) in Co (III) salen complex induces the polarization of the carbonyl group of isatin followed by the nucleophilic addition of malononitrile to isatin after this intermediate subsequently undergoes elimination via Knoevenagel condensation. The addition of dimedone to the intermediate afforded the spirooxindole derivatives.





**FIGURE 16** Scanning electron microscopy (SEM) of recovered CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co (III) salen complex after 2nd run

At the end of the reaction, the catalyst could be recovered by external permanent magnet. The recycled catalyst was washed with ethanol and subjected to a second reaction process. The results show that the yield of product after five runs was only slightly reduced (Figure 13).

For further investigation, the characterization of the recycled catalyst after two runs [TEM image (Figure 14), XRD spectrum (Figure 15) and SEM image (Figure 16)] was obtained and the results showed that the recovered catalyst did not show significant differences in the structure.

# 4 | CONCLUSION

In conclusion, the present work provided  $CoFe_2O_4@SiO_2@Co$  (III) salen complex for potential synthetic application.  $CoFe_2O_4@SiO_2@Co$  (III) salen complex is an efficient and reusable nanocatalyst for the synthesis of oxindoles, and is comparable with some other applied catalysts. The reaction was completed in a short period of time with small amounts of catalyst. In addition, it is easy to separate and recover the catalyst for catalytic recycling.

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#### SUPPORTING INFORMATION

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