

## Synthesis, characterization and immobilization of cobalt (III) salen complex on $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ nanoparticle and their application in the synthesis of di-indolyloxindole

Kaveh Hemmat, Mohammad Ali Nasser<sup>\*</sup>, Ali Allahresani

Department of Chemistry, College of Sciences, University of Birjand, Birjand 97175-615, Iran.

Received 10 January 2019; received in revised form 28 April 2019; accepted 26 May 2019

### ABSTRACT

The preparation, characterization, and immobilization of cobalt (III) salen complex on  $\text{CoFe}_2\text{O}_4@\text{SiO}_2$  nanoparticle ( $\text{CoFe}_2\text{O}_4@\text{SiO}_2@ \text{Co(III)}$  salen complex) are described. Co(III) salen complex loaded on ferrite cobalt-silica nanoparticle is characterized by TEM, SEM-EDX, VSM and FT-IR analyses. The efficiency of  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@ \text{Co(III)}$  salen complex as a catalyst was carried out in the 3-indolylation reaction of indole with isatin derivatives in the water at 80 °C. Di-indolyloxindole was achieved with excellent yield (95%), using indole, isatin, and  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@ \text{Co(III)}$  salen complex within 2 h in water as solvent at 80 °C. Moreover, the recoverability and reusability of  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@ \text{Co(III)}$  salen complex were investigated.

**Keywords:** *Co(III) salen complex, Di-indolyloxindole, Indole, Cobalt ferrite, Isatin, Multicomponent.*

### 1. Introduction

Complex with almost all metal ions is formed using Schiff base ligands with more flexible structures which are easily synthesized. In various reactions, excellent catalytic activity is shown by many Schiff base complexes [1-9]. Heterogeneous systems have intrinsic advantages such as easy catalyst separation/recycling and products separation [10,11]. This is why that transforming a successful homogeneous catalyst into a heterogeneous one is an important challenge in catalysis. Supports including zeolite, clays, silicious materials, activated carbon and magnetic nanoparticles via non-covalent or covalent interactions were used for heterogenization of metal complexes [12-22]. Magnetic nanoparticles have some potential applications including exchange-coupled nanocomposite magnets, magnetic data storage, magnetic fluids, and biomedicine; this matter made them an interesting subject of investigation [23-27]. There is often a relationship between the nanoparticle size, shape, crystal structure, and composition and its magnetism

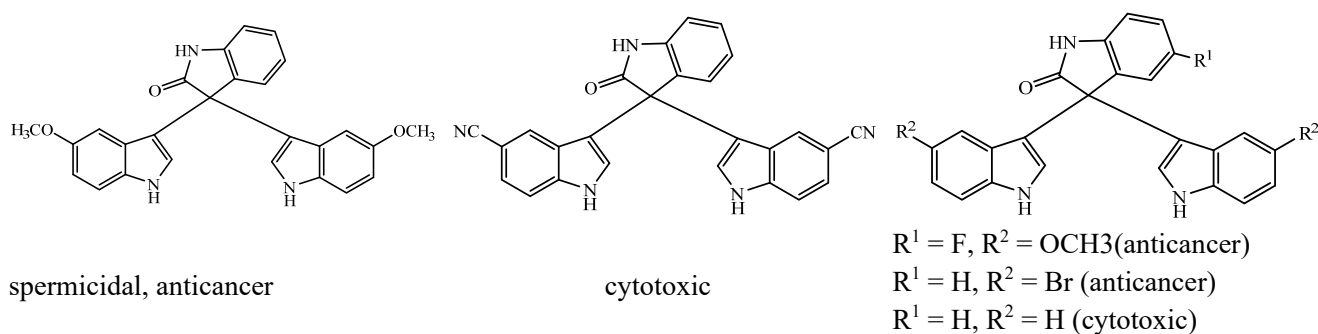
including anisotropy, magnetization, coercivity, and ordering temperature [28-32]. High anisotropy, coercivity, chemical stability, and mechanical hardness are interesting magnetic properties which made  $\text{CoFe}_2\text{O}_4$  an interesting subject for studying. Different chemical and physical approaches have been used to achieve considerable advances to synthesize magnetic nanostructures [33-37].

On the other hand, oxindole derivatives as important structural components in natural and synthetic product exhibit diverse biological and pharmacological activities such as anticancer, antibacterial, antiprotozoal and anti-inflammatory (Fig. 1) [38-40]. Oxindole derivatives are synthesized by the coupling of indole and isatin derivatives, aromatics in triflic acid [41], pyrazolones [42] and other routes [43].

From a synthetic point of view, there is still a challenge in the synthesis of oxindole derivatives in the field of organic chemistry. Therefore, introducing new and benign protocols for the synthesis of these valuable compounds is highly desirable for chemical and medicinal industries. In continuation of our previous attempt to the synthesis of spirooxindole derivatives, herein, we introduced the new heterogeneous catalyst by

<sup>\*</sup>Corresponding author.

E-mail address: manaseri@birjand.ac.ir (M.A. Nasser)



**Fig. 1.** Representative examples of pharmacologically active synthetic 3,3-bis(indol-3-yl)indolinones.

immobilization of Co(III) salen complex onto the surface of  $CoFe_2O_4@SiO_2$  magnetic nanoparticles and the corresponding heterogeneous magnetic nanocatalyst was applied for the synthesis of spirooxindole derivatives in green media.

## 2. Experimental

### 2.1. Materials and apparatus

Reagents and solvents were purchased from Merck or Fluka chemical companies. 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. IR spectra were taken on a Perkin Elmer 781 spectrometer in KBr pellets and reported in  $cm^{-1}$ . The morphology of the products was determined using CMPhilips10 model Transmission electron microscopy (TEM) at 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. Inductively coupled plasma (ICP) atomic emission spectroscopy was conducted with an OPTIMA 7300DV. The magnetic properties were determined by using vibrating sample magnetometer (VSM) leak shore 7200 at 300 K Vsm 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. Preparation of $CoFe_2O_4$ nanoparticles

0.001 mol of cobalt nitrate ( $Co(NO_3)_2 \cdot 6H_2O$ ) and 0.002 mol of ferrite nitrate ( $Fe(NO_3)_3 \cdot 9H_2O$ ) as precursor were accurately weighed and dissolved into 100 mL of deionized water. Then, 20 mL of solution NaOH 1 M was added to the reaction mixture and was placed under ultrasonic irradiation for 30 min. Then, the solution was stirred with a magnetic stirrer at 80 °C for 2 h to make a solid black product. The black magnetite solid was isolated by an external magnet and washed with deionized water three times and was then

dried at 80 °C for 10 h to obtain  $CoFe_2O_4$  nanoparticles [44].

### 2.3. Preparation of $CoFe_2O_4@SiO_2$ core-shell

0.150 g of  $CoFe_2O_4$  was dispersed in the mixture of ethanol (25 mL) and deionized water (7 mL) for 10 min under ultrasonic. Then 0.8 mL of  $NH_3$  was added followed by the addition of tetraethoxysilane (TEOS) (0.5 mL) drop by drop. This solution was stirred for 24 h at room temperature. The  $CoFe_2O_4@SiO_2$  product was separated by an external magnet and was washed with deionized water and ethanol three times and dried at 80 °C for 12 h to obtain  $CoFe_2O_4@SiO_2$  nanoparticle [45].

### 2.4. preparation of 4-[(E)-{(2-[(E)-2-hydroxybenzylidene)amino]phenyl}imino)methyl]benzene-1,3-diol

2,4- di hydroxyl 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 were 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 condition under  $N_2$  atmosphere. Upon completion, the product was filtered and was dried at 80 °C for 12 h to obtain 4-[(E)-{(2-[(E)-2-hydroxybenzylidene)amino]phenyl}imino)methyl]benzene-1,3-diol [46].

### 2.5. Procedure for the synthesis of Co(III) salen complex

Cobalt(II) acetate tetrahydrate (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 was stirred for 1 h. 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 [47].

## 2.6. Procedure for the synthesis and preparation of $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$ salen complex

$\text{CoFe}_2\text{O}_4@\text{SiO}_2$  (1.5 g) was suspended in dry toluene (100 mL) for 2 h under ultrasonic. To a mixture, Co(III) salen complex was added and heated under reflux with stirring for 48 h.  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen complex MNPs were isolated by an external magnet and was washed using toluene and ethanol. The product was dried under vacuum at 80 °C for 10 h to produce  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen complex [48].

## 2.7. General experimental procedure for the synthesis of di-indolyloxindole

A mixture of indole (2 mmol), isatin compounds (1 mmol), water (3 mL) and  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen complex (0.2 g) was stirred at 80 °C. The progress of the reaction was monitored by TLC. After the reaction was completed, the mixture was dissolved in acetone, and  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen complex was separated using an external magnet. Then, the solvent was removed from the solution under reduced pressure, and the resulting product was purified by recrystallization from methanol to afford the pure product and identified by IR,  $^1\text{H}$  and  $^{13}\text{C}$ NMR spectral data. Di-indolyloxindole was achieved with excellent yield (95%), using 0.2 g catalyst within 2 h in water as the solvent.

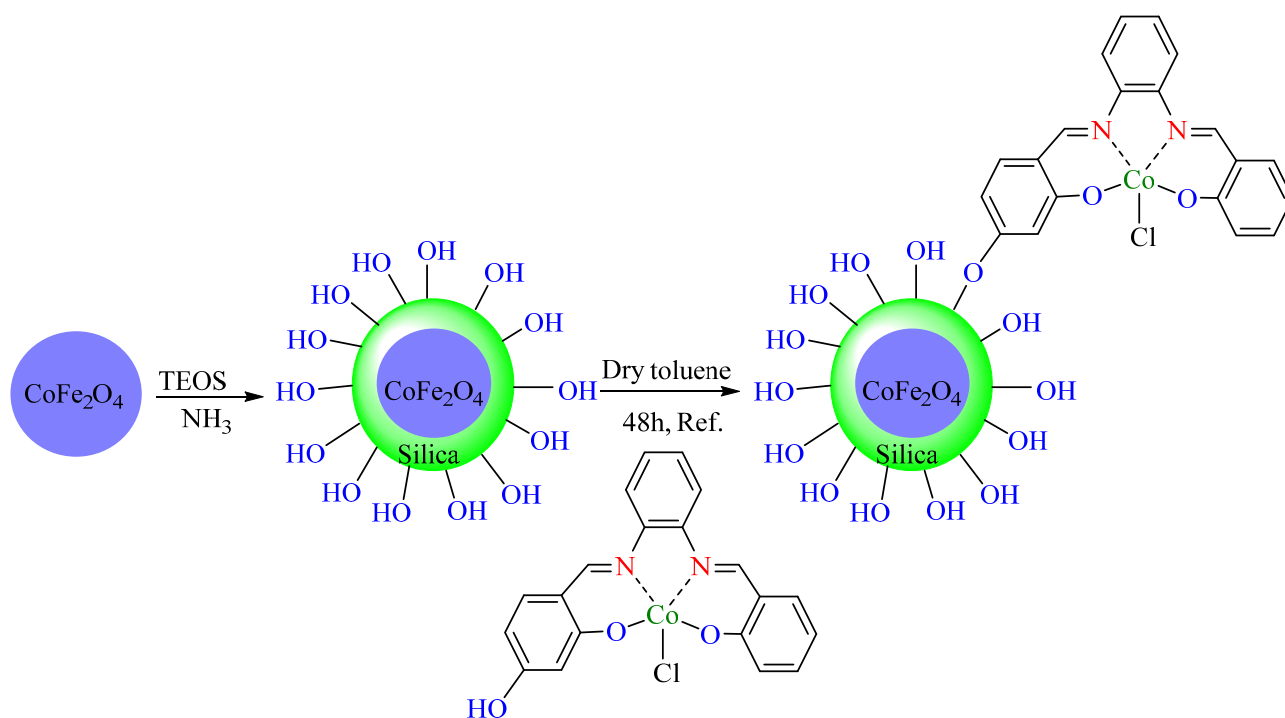
## 3. Results and Discussion

### 3.1. Characterization of the catalyst

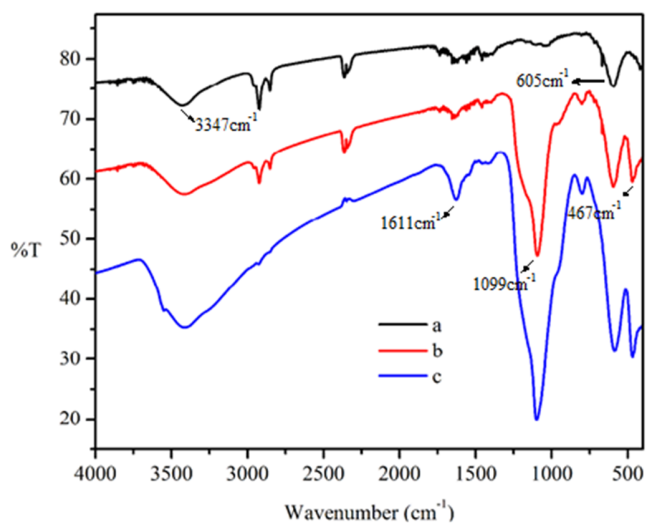
In this article, we report the synthesis of the more effective and magnetically separable catalyst by the immobilization of Cobalt (III) salen complex on the surface of silica-coated  $\text{CoFe}_2\text{O}_4$  (Scheme 1). The corresponding heterogeneous nanocatalyst was characterized by XRD, FT-IR, and SEM. The magnetic properties of nanocatalyst were investigated by VSM.

The FT-IR spectra of catalyst are presented (a)  $\text{CoFe}_2\text{O}_4$  (b)  $\text{CoFe}_2\text{O}_4@\text{SiO}_2$  and (c)  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen complex nanoparticles were studied by FT-IR spectroscopy, and the results are shown in Fig. 2. The broadening absorption peak at  $3347\text{ cm}^{-1}$  belongs to OH-stretching of absorbed water molecules. The peak located at  $605\text{ cm}^{-1}$  is attributed to the bending mode of Co-O and Fe-O [49]. In spectrum "b", the absorption band present at about  $1099\text{ cm}^{-1}$  is due to the stretching band vibrations of Si-O-Si. The absorption band present at about  $467\text{ cm}^{-1}$  is due to the bending of Si-O-Si [50,51]. In spectrum "c", the absorption peak at  $1611\text{ cm}^{-1}$  belongs to C=N stretching band vibrations in  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen complex [52].

The grain size of the (a)  $\text{CoFe}_2\text{O}_4$  (b)  $\text{CoFe}_2\text{O}_4@\text{SiO}_2$  and (c)  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen nanoparticles were investigated by TEM. They have a narrow distribution of sizes, from 18-30 nm (Fig. 3, 4).



**Scheme 1.** Preparation of catalyst ( $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen complex).



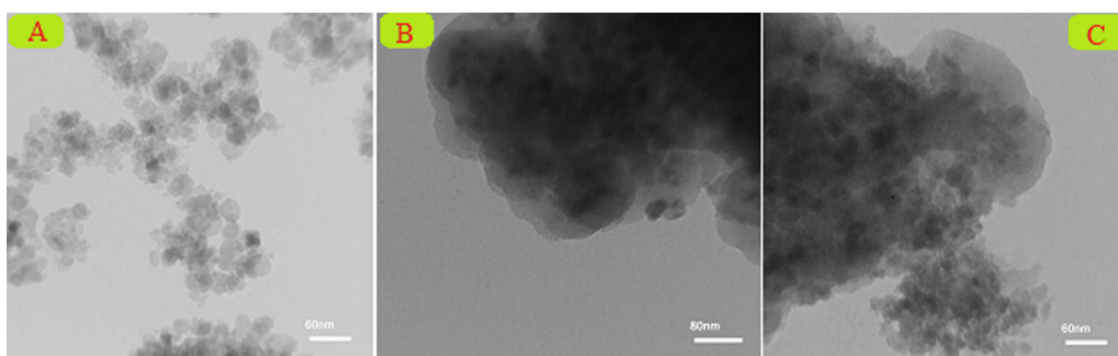
**Fig. 2.** FT-IR spectra of CoFe<sub>2</sub>O<sub>4</sub> (a) CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub> (b) and CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co(III) salen complex (c).

XRD patterns CoFe<sub>2</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub> in the 2θ range between 10° and 80° are shown in Fig. 5. The diffraction peaks of all samples at 18.14°, 30.27°,

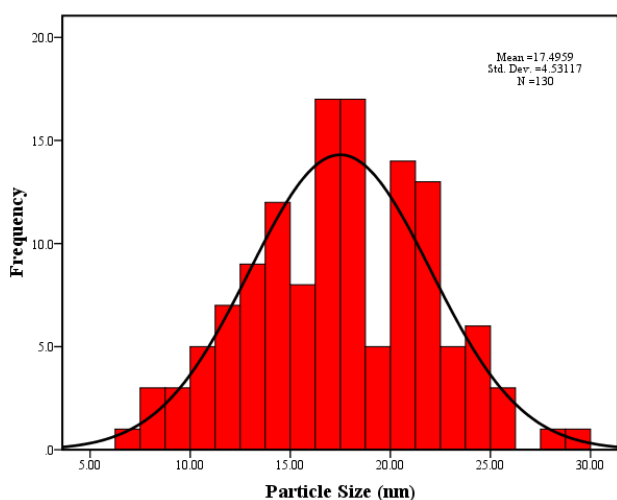
35.76°, 43.47°, 53.91°, 57.17° and 63.71° could be indexed to the (111), (220), (311), (400), (422), (511) and (440) planes of the inverse spinel CoFe<sub>2</sub>O<sub>4</sub>, respectively. The XRD pattern of the CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub> spheres has a broader peak in the 2θ range of 20-30°, this results from the amorphous CoFe<sub>2</sub>O<sub>4</sub>. It is found that all the peaks in the three patterns could be indexed to a cubic inverse spinel structure of CoFe<sub>2</sub>O<sub>4</sub> NPs, which are consistent with the standard data of ferrite phase (JCPDS Card No 22-1086) [53,54]. The average grain size of the samples is calculated using the Debye–Scherrer formula. From the well-known Scherrer formula the average crystallite size, L, is:

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

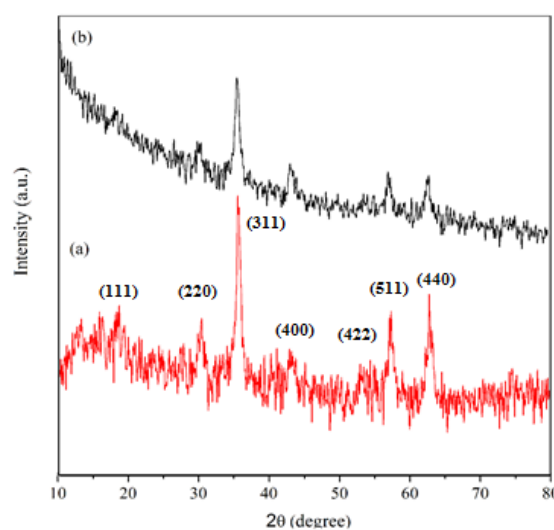
Where λ is the X-ray wavelength (nm), θ is the Bragg's angle, K is a constant related to crystallite shape, normally taken as 0.9, and β is the full width of the diffraction line at the half maximum intensity. The average crystallite size of synthesized products was thus calculated at about 14.5 and 17.2 nm.



**Fig. 3.** TEM image of CoFe<sub>2</sub>O<sub>4</sub> (a) CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub> (b) and CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co(III) salen complex (c).



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



**Fig. 5.** XRD pattern of CoFe<sub>2</sub>O<sub>4</sub> (a) CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub> (b).

The magnetic properties of (a)  $\text{CoFe}_2\text{O}_4$  (b)  $\text{CoFe}_2\text{O}_4@\text{SiO}_2$  and (c)  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen complex nanoparticles were studied by a vibrating sample magnetometer (VSM) at 300 K (Fig. 6). Fig. 6 shows the absence of the hysteresis phenomenon and indicates the product has superparamagnetism at room temperature. The saturation magnetization values for  $\text{CoFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4@\text{SiO}_2$  and  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen nanoparticles were 39.124, 30.387 and 27.348 emu/g, respectively.

Fig. 7 shows energy-dispersive X-ray spectroscopy (EDX) of  $\text{CoFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4@\text{SiO}_2$  and  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen complex nanoparticles; it is recorded to investigate the elemental composition of nanoparticles. The results demonstrate that Co, Fe and O appear in  $\text{CoFe}_2\text{O}_4$  sample and Co, Fe, Si, and O appear in  $\text{CoFe}_2\text{O}_4@\text{SiO}_2$  sample.

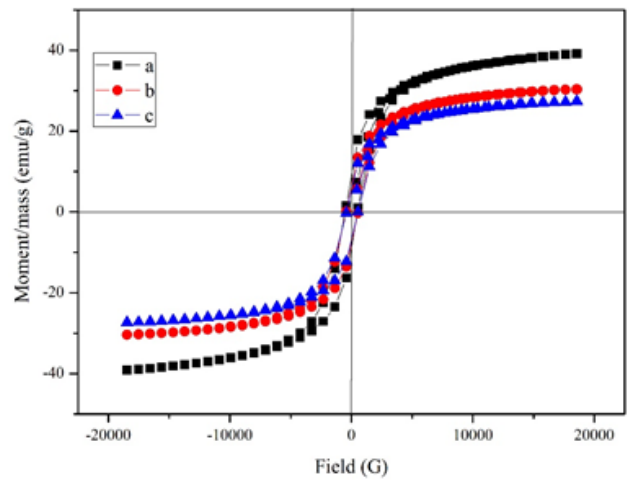


Fig. 6. VSM pattern  $\text{CoFe}_2\text{O}_4$  (a)  $\text{CoFe}_2\text{O}_4@\text{SiO}_2$  (b) and  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen complex (c).

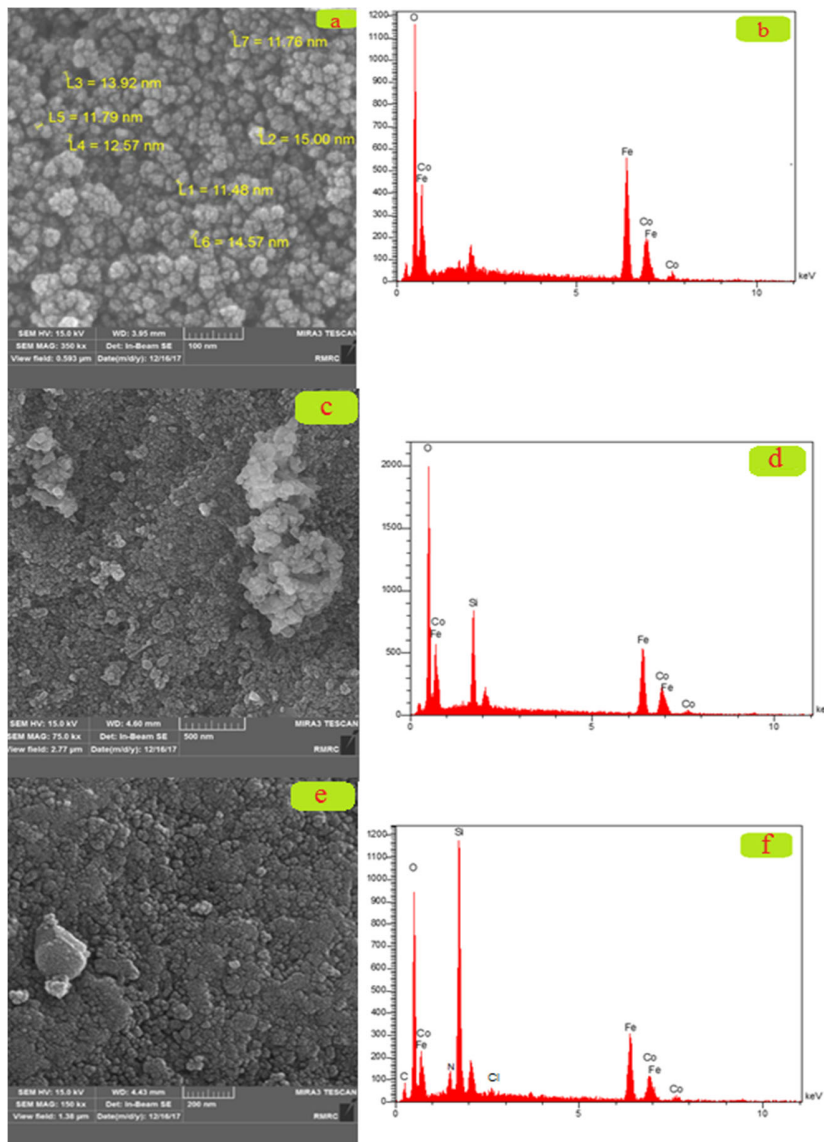


Fig. 7. SEM-EDX of  $\text{CoFe}_2\text{O}_4$  (a,b),  $\text{CoFe}_2\text{O}_4@\text{SiO}_2$  (c,d) and  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen complex (e,f).



Also, the results demonstrate that Co, Fe, Si, O, N and C appear in  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen nanoparticles. SEM analysis of the products (Figs. 7) provided information on the size and morphology of  $\text{CoFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ , and  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen nanoparticles.

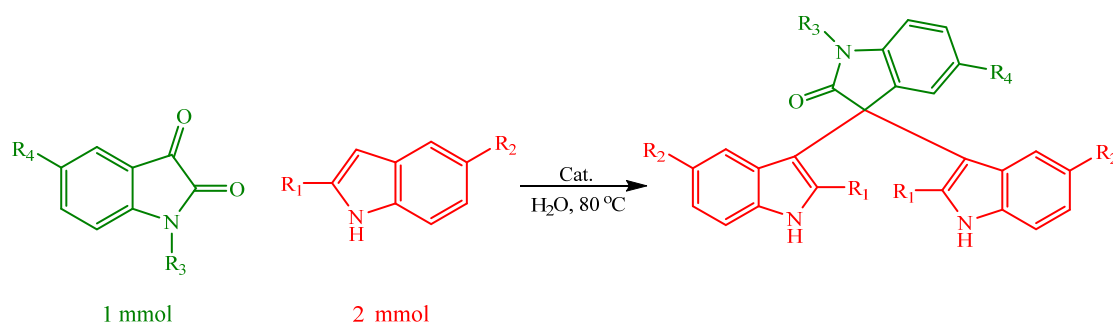
The metal content was determined by ICP-AES, this revealed the existence of  $0.33 \text{ mmol g}^{-1}$  cobalt in the prepared complex.

### 3.2. The catalytic activity of $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$ salen complex

In the initial experiment, the reaction of indole (2 mmol) and isatin (1 mmol) in the water at  $80^\circ\text{C}$  was performed for the synthesis of corresponding di-indolyloxindole in the presence of  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen complex as the catalyst in  $\text{H}_2\text{O}$  at  $80^\circ\text{C}$  (Scheme 2).

To determine the optimized amount of catalyst, we changed the amount of catalyst. As shown in Table 1, 0.2 g of  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen complex was the optimum amount of catalyst. Increasing the amount of  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen complex did not exhibit any effect on efficiency. Decreasing the catalyst concentration resulted in lower yields under the same conditions. In order to study the catalytic activity of  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen complex, this coupling was carried out in the absence of the catalyst. In this case, the reaction proceeded in low yield (12%) in 2 h.

After that, the reaction was carried out in different temperatures, the yield of the product was improved by raising the temperature, and the best result was obtained at  $80^\circ\text{C}$  (Table 2).



**Scheme 2.** Schematic illustration for the synthesis of di-indolyloxindole derivatives in the presence of Co(III) salen complex.

**Table 1.** The effect of  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co}$ -Salen complex on the reaction.<sup>a</sup>

Entry	$\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co}$ -Salen complex (g)	Time (h)	Yield (%)
1	-	2	12
2	0.05	2	40
3	0.1	2	75
4	<b>0.2</b>	<b>2</b>	<b>95</b>
5	0.3	2	96

<sup>a</sup>Reaction conditions: Isatin (1.0 mmol), Indole (2.0 mmol) in  $\text{H}_2\text{O}$  (3 mL), at  $80^\circ\text{C}$ .

**Table 2.** The Effect of temperatures on the synthesis of di-indolyloxindole.<sup>a</sup>

Entry	Temp. ( $^\circ\text{C}$ )	Time (h)	Yield (%)
1	25	2	25
2	50	2	60
3	<b>80</b>	<b>2</b>	<b>95</b>

<sup>a</sup>Reaction conditions: Isatin (1.0 mmol), Indole (2.0 mmol) in  $\text{H}_2\text{O}$  (3 mL).

Furthermore, the utilization of different solvents such as  $\text{H}_2\text{O}$ , EtOH, DMF,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CHCl}_3$  was investigated in the presence of 0.2 gr of  $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{Co(III)}$  salen complex. Acetonitrile, chloroform, and dichloromethane afforded low yields, while the use of solvents such as ethanol could improve the yields. Finally, when water was used, the yield increased to 95% which is better than any other solvents being examined here. In the absence of the solvent, the yield of model reaction decreased to 25%. (Table 3).

**Table 3.** Effect of different solvents on the reaction yield.<sup>a</sup>

Entry	Solvent	Yield (%)
1	H <sub>2</sub> O	95
2	EtOH	70
3	CH <sub>3</sub> CN	60
4	CH <sub>2</sub> Cl <sub>2</sub>	35
5	CHCl <sub>3</sub>	20
6	THF	25
7	DMF	15
8	Solvent-free	25

<sup>a</sup>Reaction conditions: Isatin (1.0 mmol), Indole (2.0 mmol) in H<sub>2</sub>O (3 mL), at 80 °C.

Under the optimized conditions (0.2 gr catalyst (0.6 mol%) in H<sub>2</sub>O (3 mL) at 80 °C), several reactions between substituted indole and isatin were examined (Table 4). Numerous indole and isatin derivatives containing an electron-deficient and electron-releasing groups pushed the reactions forward to give corresponding oxindole derivatives with satisfactory yields (Table 4, 65-95%).

Electron-withdrawing groups in the R<sub>2</sub> position of the indole led to low yields due to the decreased nucleophilicity of the indole (Table 4, Entry 2) and electron-donating groups in the R<sub>1</sub> position of the indole led to high yields due to the increased nucleophilicity of the indole (Table 4, Entry 3). However, an electron-withdrawing halogen as R<sub>4</sub> was found to speed up the reactions. In addition, isatin with N-benzyl as an electron-releasing group gave lower yields (65–82%) in 2 h (Table 4, entries 7-9).

**Table 4.** Synthesis of di-indolyloxindoles catalyzed by Co(III) salen complex.

Entry	Reactant				Time (h)	Yield (%)	TON	TOF (h <sup>-1</sup> )	m.p. (°C)		Ref.
	Indole		Isatin						Found	Reported	
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>							
1	H	H	H	H	2	95	158.33	79.17	313-315	312-314	[55]
2	H	Br	H	H	4.30	80	133.33	29.63	299-301	298-300	[56]
3	Me	H	H	H	1.30	93	155	103.33	296-298	300-303	[57]
4	H	H	H	Cl	2	90	150	75	302-303	305-307	[58]
5	H	Br	H	Cl	6	80	133.33	22.22	310-313	>300	[56]
6	H	H	H	NO <sub>2</sub>	3	95	158.33	52.78	298-300	297-298	[59]
7	H	H	PhCH <sub>2</sub>	H	2	70	116.66	58.33	283-285	288-289	[60]
8	Me	H	PhCH <sub>2</sub>	H	2	82	136.66	68.33	209-211	212-214	[60]
9	H	Br	PhCH <sub>2</sub>	H	2	65	108.33	54.16	288-290	289-291	[61]
10	H	Me	H	H	2	85	141.66	70.83	275-277	272-273	[60]
11	Me	H	Me	H	2	91	151.66	75.83	268-270	271-273	[62]

<sup>a</sup>Reaction conditions: CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co(III) salen complex (0.2 g), indole derivatives (2 mmol), isatin derivatives (1.0 mmol), and H<sub>2</sub>O (3 mL), 80 °C.

Scheme 3 proposes a mechanism for the reaction. As shown in Scheme 3, the interaction of Co(III) in Co(III) salen complex with the carbonyl groups of isatin activated them and the activated group was attacked by the nucleophilic addition of indole producing the intermediate (A). Further nucleophilic attack on the intermediate (A) afforded di-indolyloxindole derivatives [63].

To show advantages of the present method, the catalyst CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co(III) salen complex was compared with the previously reported catalyst for the preparation of di-indolyloxindole (Table 5).

At the end of the reaction, CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co(III) salen complex could be recovered by an external permanent magnet. The recycled catalyst was washed with ethanol twice and subjected to a second reaction process. The results showed that the yield of the product after 6 runs was only slightly reduced.

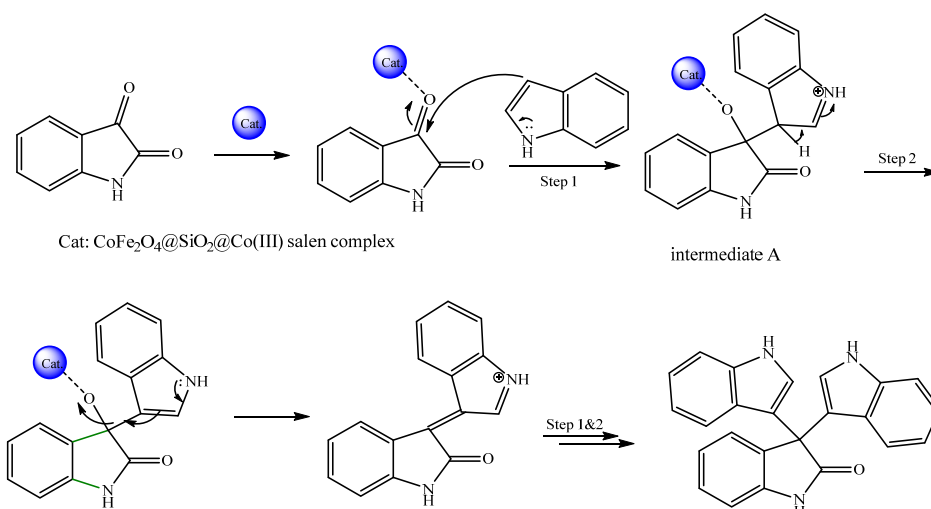
#### 4. Conclusions

In conclusion, the Co(III) salen complex was immobilized on the CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticle. The corresponding nanocatalyst was characterized by different techniques including XRD, VSM, FT-IR, SEM-EDX, and TEM. Then, the synthesis of di-indolyloxindole derivatives was investigated in the presence of the catalytic amount of Co(III) salen complex (0.6 mol%) using isatin (1 mmol) and indole (2 mmol) at 80 °C temperature in water as the solvent. The reaction was completed in a short period of time with small amounts of the catalyst. Also, it is easy to separate and recover the catalyst for another catalytic recycling.

**Table 5.** Comparison of the efficiency of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co(III) salen complex with different catalysts.<sup>a</sup>

Entry	Catalyst	Solvent/Temp. (°C)	Time (min)	Yield (%)	Ref.
1	GO (0.05 g)	H <sub>2</sub> O/r.t.	150	95	[64]
2	CSA (5 mol %)	Solv-free/r.t.	120	88	[65]
3	Tungstic acid (10 mol %)	EtOH/r.t.	360	92	[66]
4	I <sub>2</sub> (10 mol %)	CH <sub>2</sub> Cl <sub>2</sub> /r.t.	840	82	[67]
5	LiClO <sub>4</sub> (10 mol %)	EtOH/60 °C	240	93	[68]
6	SiO <sub>2</sub> -OSO <sub>3</sub> H (0.2 g)	CH <sub>2</sub> Cl <sub>2</sub> /r.t.	120	94	[56]
7	Bi (OTf) <sub>3</sub>	CH <sub>3</sub> CN/r.t.	180	92	[69]
8	CAN	EtOH/U.S.	180	95	[70]
9	PEG/OSO <sub>3</sub> H	CH <sub>3</sub> CN/r.t.	150	93	[71]
10	CoFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> @Co(III) salen complex	Water/80 °C	120	95	This work

<sup>a</sup>Reaction conditions: Indole (2.0 mmol), isatin (1 mmol).

**Scheme 3.** Plausible mechanism for the synthesis of di-indolyloxindole catalyzed by CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Co(III) salen complex.

### Acknowledgments

We gratefully acknowledge the support of this work by the University of Birjand.

### References

- [1] E.N. Jacobsen, W. Zhang, M.L. Guller, *J. Am. Chem. Soc.* 113 (1991) 6703-6704.
- [2] J. Long, *Front. Chem.* 7 (2019) 63-69.
- [3] Z. Li, K.R. Conser, E.N. Jacobsen, *J. Am. Chem. Soc.* 115 (1993) 5326-5327.
- [4] T. Katsuki, *Chem. Rev.* 140 (1995) 189-214.
- [5] P. Jain, G. Pandey, D. Kumar, S. Chandra, *Adv. Sci. Eng. Med.* 11 (2019) 144-154.
- [6] Y. Kohmura, T. Katsuki *Tetrahedron Lett.* 42 (2001) 3339-3342.
- [7] W. Sun, H. Wang, C. Xia, J. Li, P. Zhao *Angew. Chem. Int. Ed.* 42 (2003) 1042-1044.
- [8] W. Sun, E. Herdtweck, F.E. Kuhn. *New J. Chem.* 29 (2005) 1577-1580.
- [9] E.M. McGarrigle, D.M. Murphy, D.G. Gilheany, *Tetrahedron: Asymmetry* 15 (2004) 1343-1354.
- [10] J.A. Gladysz, *Chem. Rev.* 102 (2002) 3215-3216.
- [11] J.A. Gladysz, *Pure Appl. Chem.* 73 (2001) 1319-1324.
- [12] D.E. De Vos, M. Dams, B.F. Sels, P.A. Jacobs, *Chem. Rev.* 102 (2002) 3615- 3640.
- [13] C.E. Song, S. Lee, *Chem. Rev.* 102 (2002) 3495-3524.
- [14] Q.H. Fan, Y.M. Li, A.S.C. Chan, *Chem. Rev.* 102 (2002) 3385-3466.
- [15] R. Ferreira, M. Silva, C. Freire, B. de Castro, J.L. Figueiredo, *Microporous Mesoporous Mater.* 38 (2000) 391-401.
- [16] R. Ferreira, C. Freire, B. de Castro, A.P. Carvalho, J. Pires, M. Brotas de Carvalho, *Eur. J. Inorg. Chem.* 11 (2002) 3032-3038.
- [17] V. Ramaswamy, M. Sivarama Kirshnan, A.V. Ramaswamy, *J. Mol. Catal. A: Chem.* 181 (2002) 81-89.
- [18] A.R. Silva, C. Freire, B. de Castro, M.M.A. Freitas, J.L. Figueiredo, *Microporous Mesoporous Mater.* 46 (2001) 211-221.



- [19] J. Tong, Z. Li, C. Xia, *J. Mol. Catal. A: Chem.* 231 (2005) 197-203.
- [20] J. Tong, Y. Zhang, Z. Li, C. Xia, *J. Mol. Catal. A: Chem.* 249 (2006) 47-52.
- [21] V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J.M. Basset, *Chem. Rev.* 111 (2011) 3036-3075.
- [22] L. Hamidipour, F. Farzaneh, M. Ghandi, *React. Kinet. Mech. Catal.* 107 (2012) 421-433.
- [23] H. Zeng, J. Li, J. P. Liu, Z.L. Wang, S. H. Sun, *Nature* 420 (2002) 395-398.
- [24] J. Park, K. An, Y. Hwang, J.G. Park, H.J. Noh, J.Y. Kim, J.H. Park, N.M. Hwang, T. Hyeon, *Nat. Mater.* 3 (2004) 891-895.
- [25] G.C.P. Leite, E.F. Chagas, R. Pereira, R.J. Prado, A.J. Terezo, M. Alzamora, E. Baggio-Saitovitch, *J. Magn. Magn. Mater.* 324 (2012) 2711-2716.
- [26] Q.A. Pankhurst, J. Connolly, S.K. Jones, J. Dobson, *J. Phys. D Appl. Phys.* 36 (2003) 167-181.
- [27] G.V.M. Jacintho, A.G. Brolo, P. Corio, P.A.Z. Suarez, J.C. Rubim, *J. Phys. Chem. C* 113 (2009) 7684-7691.
- [28] K. Gandha, K. Elkins, N. Poudyal, X. Liu, J.P. Liu, *Sci. Rep.* 4 (2014) 5345-5349.
- [29] K. Gandha, N. Poudyal, Q. Zhang, J.P. Liu, *IEEE Trans. Magn.* 49 (2013) 3273-3281.
- [30] Y. Cedeno-Mattei, O. Perales-Perez, *Microelectr. J.* 40 (2009) 673-676.
- [31] B.H. Liu, J. Ding, Z.L. Dong, C.B. Bothroyd, J.H. Yin, J.B. Yi, *Phys. Rev. B* 74 (2006) 184427-184436.
- [32] Q. Song, Z. John Zhang, *J. Am. Chem. Soc.* 126 (2004) 6164-6168.
- [33] Z. F. Zi, Y.P. Sun, X.B. Zhu, Z.R. Yang, J.M. Dai, W.H. Song, *J. Magn. Magn. Mater.* 321 (2009) 1251-1255.
- [34] Y. Yu, A. Mendoza-Garcia, B. Ning, S. Sun, *Adv. Mater.* 25 (2013) 3090-3094.
- [35] Y. Lee, J. Lee, C.J. Bae, J.G. Park, H.J. Noh, J.H. Park, T. Hyeon, *Adv. Funct. Mater.* 15 (2005) 503-509.
- [36] N. Hanh, O.K. Quy, N.P. Thuy, L.D. Tung, L. Spinu, *Physica B* 327 (2003) 382-384.
- [37] R.P. Chaudhary, S.K. Mohanty, A.R. Koymen, *Carbon* 79 (2014) 67-73.
- [38] B.S. Jursic, E.D. Stevens, *Tetrahedron Lett.* 43 (2002) 5681-5683.
- [39] A.M.Sh. El-Sharief, Y.A. Ammar, A. Belal, M.A.M. Sh. El-Sharief, Y.A. Mohamed, A.B.M. Mehany, G.A.M.E. Ali, A. Ragab, *Bioorg. Chem.* 85 (2019) 399-412.
- [40] G. Brahmachari, B. Banerjee, *ACS Sustainable Chem. Eng.* 2 (2014) 2802-2812.
- [41] F.X. Felpin, O. Ibarguren, L. Nassar-Hardy, E. Fouquet, *J. Org. Chem.* 74 (2009) 1349-1352.
- [42] I. Sharma, A. Saxena, C.K. Ojha, C.K.P. Paradasani, R.T. Paradasani, T. Mukherjee, *Proc. Indian Acad. Sci.* 114 (2002) 523-531.
- [43] J. Kothandapani, A. Ganesan, G.K. Mani, A.J. Kulandaisamy, J.B. Balaguru Rayappan, S.S. Ganesan, *Tetrahedron Lett.* 57 (2016) 3472-3475.
- [44] J. Saffari, D. Ghanbari, N. Mir, K. Khandan-Barani, *J. Ind. Eng. Chem.* 20 (2014) 4119-4123.
- [45] E. Rafiee, N. Rahpeyma, *Chin. J. Catal.* 36 (2015) 1342-1349.
- [46] L.J. Chen, F.M. Mei, G.X. Li, *React. Kinet. Catal. Lett.* 98 (2009) 99-105.
- [47] J. Yu, Y. Luan, Y. Qi, J. Hou, W. Dong, M. Yang, G. Wang, *RSC Adv.* 4 (2014) 55028-55035.
- [48] A. Allahresani, M.A. Nasser, *J. Chem. Sci.* 129 (2017) 343-352.
- [49] M. Ma, Y. Zhang, W. Yu, H.Y. Shen, H.Q. Zhang, N. Gu, *Colloids Surf. A* 212 (2003) 219-226.
- [50] C.Y. Haw, C.H. Chia, S. Zakaria, F. Mohamed, S. Radiman, C.H. Teh, P.S. Khiew, W.S. Chiu, N.M. Huang, *Ceram. Int.* 37 (2011) 451-464.
- [51] P.C. Morais, R.L. Santos, A.C.M. Pimenta, R.B. Azevedo, E.C.D. Lima, *Thin Solid Films* 515 (2006) 266-270.
- [52] T. Abou Khalil, S. Boujday, J. Blanchard, L. Bergaoui, *Chem. Africa* 2 (2019) 77-87.
- [53] M.K. Surendra, D. Kannan, M.S. Ramachandra Rao, *Mater. Res. Soc. Symp. Proc.* 1368 (2011) 1368-1373.
- [54] C. Ren, X. Ding, H. Fu, C. Meng, W. Li, H. Hang, *RSC Adv.* 6 (2016) 72479-72486.
- [55] J. Bergman, N. Eklund, *Tetrahedron* 36 (1980) 1445-1450.
- [56] M. Nikpasand, M. Mamaghani, K. Tabatabaeian, H.A. Samimi, *Synth. Commun.* 40 (2010) 3552-3560.
- [57] M. Haghghi, K. Nikoofar, *J. Saudi Chem. Soc.* 20 (2016) 101-106.
- [58] G. Mohammadi Ziarani, R. Moradi, A. Badiei, N. Lashgari, B. Moradi, A. Abolhassani Soorki, *J. Taibah Univ. Sci.* 9 (2015) 555-563.
- [59] K. Alimohammadi, Y. Sarrafi, M. Tajbakhsh, *Monatsh. Chem.* 139 (2008) 1037-1039.
- [60] J. Azizian, A.A. Mohammadi, N. Karimi, M.R. Mohammadzadeh, A.R. Karimi, *Catal. Commun.* 7 (2006) 752-755.
- [61] K. Nikoofar, Z. Khalili, *Z. Naturforsch. B* 71 (2016) 31-36.
- [62] N. Karimi, H. Oskooi, M.M. Heravi, M. Saeedi, M. Zakeri, N. Tavakoli, *Chin. J. Chem.* 29 (2011) 321-323.
- [63] A. Allahresani, B. Taheri, M.A. Nasser, *Res. Chem. Intermed.* 44 (2018) 6741-6751.
- [64] A. Allahresani, M.A. Nasser, A. Akbari, B. Zakerinasab, *React. Kinet. Mech. Catal.* 116 (2015) 249-259.
- [65] H. Alinezhad, A.H. Haghghi, F. Salehian, *Chin. Chem. Lett.* 21 (2010) 183-186.
- [66] G.M. Patel, P.T. Deota, *Heterocycl. Commun.* 19 (2013) 421-424.
- [67] B.V. Subba Reddy, N. Rajeswari, M. Sarangapani, Y. Prashanthi, R.J. Ganji, A. Addlagatta, *Bioorg. Med. Chem. Lett.* 22 (2012) 2460-2463.
- [68] K. Rad-Moghadam, S. Gholizadeh, *Iran. J. Catal.* 4 (2014) 41-47.
- [69] J.S. Yadav, B.V. Subba Reddy, K.U. Gayathri, S. Meraj, A.R. Prasad, *Synthesis* 24 (2006) 4121-4123.
- [70] S.Y. Wang, S.J. Ji, *Tetrahedron.* 62 (2006) 1527-1535.
- [71] M.A. Nasser, B. Zakerinasab, *Iran. J. Org. Chem.* 5 (2013) 1021-1025.