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Co(III)@Fe₃O₄@SiO₂ salen complex as a highly selective and recoverable magneticnanocatalyst for the oxidation of sulfides and benzylic alcohols

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Abstract

In this study, Co(III) salen complex was synthesized and immobilized onto the surface of Fe_3O_4@SiO_2 magnetic nanoparticle. The heterogeneous nanocatalyst was characterized by different techniques including X-ray diffraction (XRD), Fourier transform infrared spectra (FT-IR), thermogravimetric analysis (TGA), transmission electron microscopy (TEM), nitrogen adsorption−desorption isotherm (BET), vibrating sample magnetometer (VSM) and atomic absorption spectroscopy (AAS). The oxidation reaction of sulfides to sulfoxide with hydrogen peroxide (30%) was investigated in the presence of catalytic amount of heterogeneous magnetic Co(III) salen complex at room temperature in water and corresponding products were achieved with excellent yields and selectivity. This catalyst was also used for the oxidation of benzyl alcohol derivatives with tert-butyl hydroperoxide (TBHP) as an oxidant in acetonitrile at reflux conditions. Accordingly, excellent yields and selectivity were observed. Magnetic Co(III) salen complex showed good stability and magnetic properties without significant loss in the activity and selectivity.

Keywords: Co (III) salen complex; sulfides; hydrogen peroxide; tert-butylhydroperoxide; sulfoxide; benzylic alcohols.

Introduction

Sulfoxide derivatives which are synthesized by selective oxidation of sulfide are the valuable building block for the synthesis of various useful compounds such as antibacterial, antifungal, and anti-hypertensive agents [1]. Carbonyl compounds such as benzaldehyde with a great application are valuable intermediates for many agrochemicals, vitamins, fragrances, and drugs in both laboratory and industry [2]. Alcohol oxidation is one of the most important reactions in organic synthesis [3]. The oxidation reactions have been extensively studied by metal and metal oxide nanoparticles [4-9]. Considering the environmental and economic aspects, the development of cheap, novel and efficient catalytic systems for the partial oxidation of sulfides and alcohols to the corresponding sulfoxide and carbonyl compounds is still of great attention in a laboratory and industrial chemistry. Metal Schiff-base complexes are an extremely versatile synthetic tool for the oxidation of organic compounds.

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These types of catalysts have been used in reactions such as the oxidation of alcohols and olefins [10-14]. Among them, Co(III) salen complexes are found to be good candidates for the oxidation of sulfides and alcohols. But, recovering of homogeneous Co(III) salen complex from solution possess a considerable challenge in a way that attaching the homogeneous Co(III) salen complex onto solid supports which is easy to recover and retain the activity of the homogeneous Co(III) salen complex would have numerous benefits in terms of process design and environmental factors. Considering this point of view, magnetic iron oxide nanoparticles, especially Fe_3O_4, has attracted extensive interest due to the ease of separation by external magnet,

high catalyst loading capacity- because of high surface area - and high dispersion. Fe_3O_4 has been extensively employed as a solid support for homogeneous catalysts [15,16]. Several types of modified Fe_3O_4 nanoparticles and also the studies on immobilization of organocatalysts and metal on silica coated Fe_3O_4 nanoparticles have been recently reported [17-19]. Now, in continuation of our research on the heterogeneous catalyst [20-24], herein, we synthesized Co(III) salen complex and grafted it onto the surface of $Fe_3O_4@SiO_2$ (CoFS). Then, the oxidation of sulfide and alcohol derivatives were investigated in the presence of CoFS in water media with H_2O_2 (30%) and TBHP, respectively (Scheme 1).
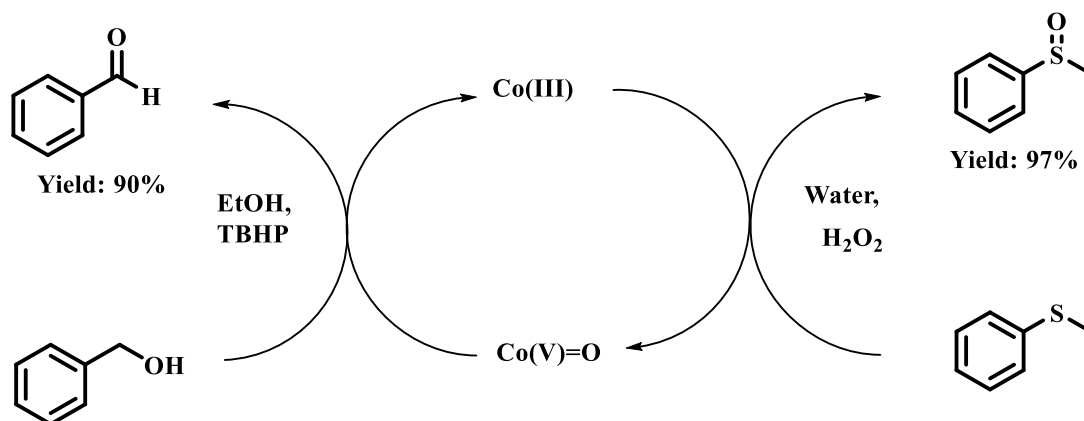
Scheme 1. Oxidation of sulfides and alcohols catalyzed by CoFs with H_2O_2 and TBHP, respectively

Experimental methods
Materials
All chemicals were purchased from Merck Company and used without further purification. The gas chromatograph (GC-17A, Shimadzu) equipped with a flame ionization detector and a capillary column (CBP-1, 30 m × 0.25 mm × 0.25 mm) was used for obtaining the Conversion, yields and selectivity of various sulfoxide. Perkin-Elmer 783 infrared

spectrophotometer was applied for obtaining the IR spectra in a KBr pellet, scanning from 4000 to 400 cm^{-1} at room temperature. The TEM images were also recorded using Philips CM10 instrument and XRD measurements were carried out using Bruker D$_8$-advance X-ray diffractometer with Cu K$_\alpha$ radiation (k = 1.5406A^0). TGA patterns were recorded, using Perkin–Elmer Diamond TG/DTA thermal analyzer, by heating the samples in an

Argon flow at a rate of 100 ml min⁻¹ with a heating rate of 10 ⁰C min⁻¹. Vibrating sample magnetometer (VSM Leak shore 7200) was applied for recording magnetization curve at 300 K.

Catalyst preparation

Synthesis of Fe₃O₄/SiO₂nanocatalyst
Black powder of Fe_3O_4 magnetic nanoparticles was synthesized as described in the literature [25]. $Fe_3O_4@SiO_2$ core-shell was synthesized using Stober method with some modification [26]. Briefly, Fe_3O_4 (0.5 gr, 2.1 mmol) was dispersed in ethanol/deionized water (80:20 mL) for 30 min. 3 mL of NH_3 and 1.5 mL of TEOS were added, in turn, to the mixture. The mixture was stirred mechanically for 20 h at room temperature. The $Fe_3O_4@SiO_2$ core-shell magnetic nanoparticles were separated by an external magnet, washed with de-ionized water and ethanol three times and dried at 80 ⁰C for 8 h.

Synthesis of CoFSnanocatalyst
Homogeneous Co(III) salen complex was synthesized as described in the literature [27,28]. Co(III) complex was chemically immobilized onto the surface of core-shell $Fe_3O_4@SiO_2$ NPs. Briefly, $Fe_3O_4@SiO_2$ NPs (2g) were dispersed in dry toluene (100 mL) followed by addition of 0.5 g of homogeneous Co(III) complex. The mixture was refluxed for 24 h under inert atmosphere. After that, the heterogeneous CoFS was separated by an external magnet, washed with dry toluene and EtOH (Scheme 2). The CoFS catalyst was dried at 70 ⁰C in a vacuum oven for 8 h and characterized by FT-IR, TEM, XRD, VSM, BET and TGA.
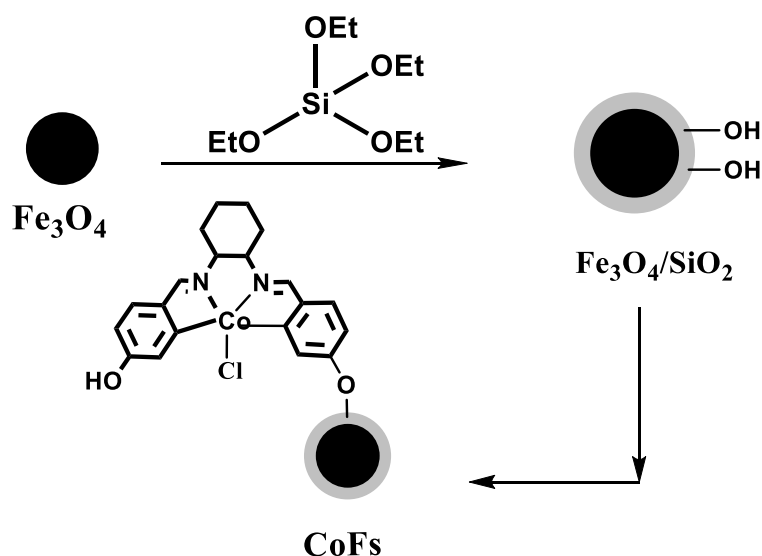
Scheme 2. Schematic illustration for the synthesis of CoFs catalyst

General procedure for the oxidation of sulfides to sulfoxides
0.004 mmol (0.0095 g) CoFS catalyst (based on Co element), 1 mmolemethyl phenyl sulfide (0.118 mL), 40 µl toluene (internal standard) and 2.0 mmol hydrogen peroxide (0.2 mL, 30%) as oxidant were added to the reaction vessel containing water (3 mL) and stirred for 40 min at room temperature. The progress of the reaction was monitored by thin layer chromatography. After the reaction was completed, the heterogeneous CoFS

catalyst was separated by an external magnet. Methyl phenyl sulfoxide was extracted with ethyl acetate from the aqueous water and dried over a hydrous Na_2SO_4. 1 μl of the corresponding product which was injected to the GC equipped with FID detector to determine the conversion, yield, and selectivity of the products. The heterogeneous CoFS catalyst was washed with EtOH, dried and used for the next runs.

General procedure for the oxidation of benzyl alcohols to carbonyl compounds
CoFS nanoparticles (0.005 mmol based on Co element, 0.0119 g) were dispersed in 3 mL of acetonitrile for 30 min followed by an addition of benzyl alcohol (1.0 mmol, 0.1 mL) and TBHP (2.0 mmol, 0.192 mL). Then, the reaction mixture was refluxed for 2.5 h. The progress of the reaction was monitored by TLC. By the end of the reaction, CoFS was separated by an external magnet and the product was extracted with ethyl acetate and dried over anhydrous Na_2SO_4. Finally, the conversion, yield, and selectivity of the products were determined by GC using toluene as the internal standard. The

heterogeneous catalyst was washed with EtOH, dried and used for the next runs.

Results and discussion
Characterizations of catalyst
The Fe_3O_4, $Fe_3O_4@SiO_2$ and CoFS NPs were characterized by different techniques (FT-IR, TEM, VSM, XRD, BET, AAS and TGA). IR spectrum of salen ligand showed the vibration band in 3450 cm^{-1} (O-H) and 2920 and 2880 cm^{-1} (aliphatic C-H bond) which are shown in Figure 1 a. The band shown at 1618 cm^{-1} is assigned to the C=N bond which shifts to the lower position (23 cm^{-1}) in homogeneous Co(III) salen complex, assigning the coordination of Co through C=N bond (Figure 1b). Figure 1c which belongs to CoFS showed several important vibration bands in 560–590, 954, 2920, 2880 and 3400 cm^{-1} which are assigned to the Fe-O, Si-OH, C-H and O-H, respectively. The vibration bands at 755 and 1100 cm^{-1} are due to Si-O-Si and the vibration bands at 1590, 2880 and 2920 cm^{-1} confirming the immobilization of homogeneous Co(III) salen complex on the $Fe_3O_4@SiO_2$ NPs.
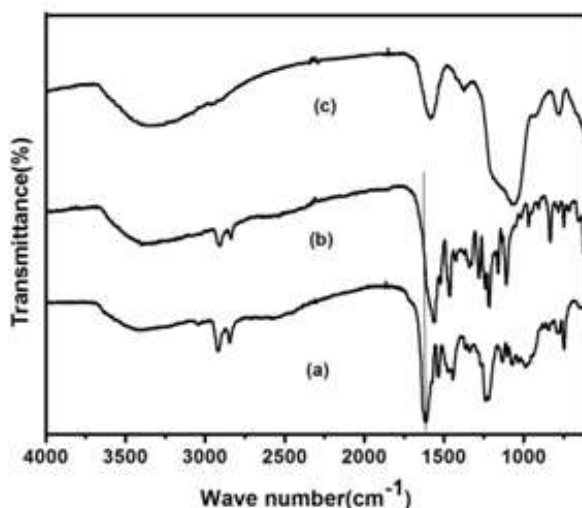

Figure 1. FT-IR spectra of (a) ligand salen (b) Co (III) salen complex (c) CoFS

Figure 2 shows the TG curve of $Fe_3O_4@SiO_2$ and CoFSNPs. The first step of weight loss is observed in the TG curve of $Fe_3O_4@SiO_2$NPs over the range of 90-165 ^{0}C (3%) which is attributed to the dehydroxylation of internal –OH groups and loss of adsorbing water. The second weight loss, over the range of 250-590 ^{0}C, is ascribed to even further decomposition of the materials. The total weight losses are approximately 10% (Figure 2 a). In Figure 2b, a decrease in the first step weight loss is observed, which indicated that the Co (III) salen complex has been successfully grafted onto the Fe_3O_4/SiO_2. In the TGA curve of CoFS, two weight losses over the range of 90-160 ^{0}C and 250-650 ^{0}C with total weightlosses, approximately 13%, are observed which are similar to the $Fe_3O_4@SiO_2$ (Figure 2 b). The loading of Co(III) salen complex onto the surface of $Fe_3O_4@SiO_2$ is estimated 0.40 mmol g $^{-1}$ based on the difference in the weight losses for the CoFS and Fe_3O_4/SiO_2.
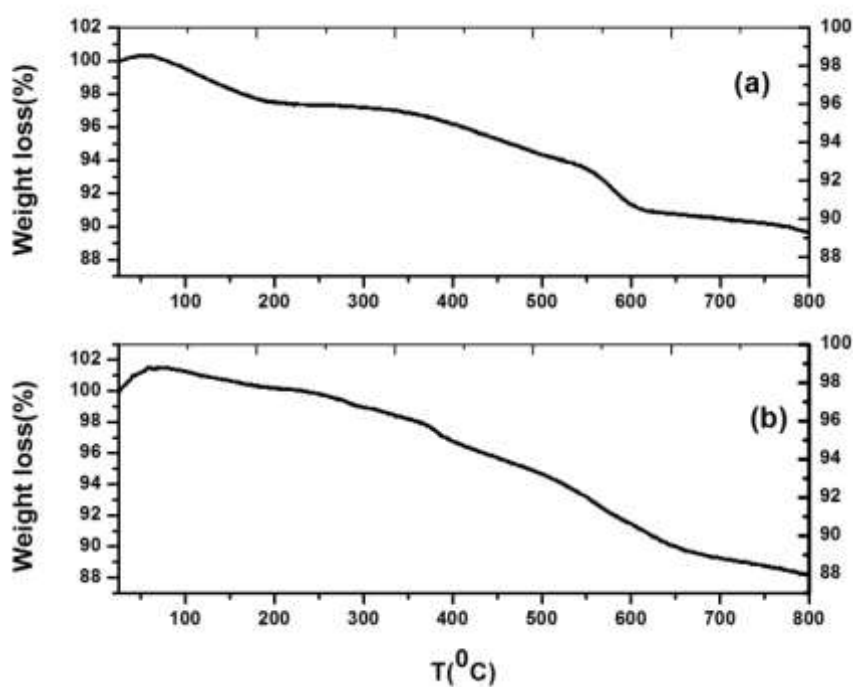

Figure 2. Thermogravimetric weight loss pattern of $Fe_3O_4@SiO_2$NPs (a) and CoFS (b) with temperature raised of 10 ^{0}C/min and initial sample weigh of 5 mg

Figure 3 shows the vibrating sample magnetometer (VSM) of three nanoparticles (Fe_3O_4, $Fe_3O_4@SiO_2$ NPs and CoFS). As it is clear in Figure 3, all the nanoparticles have no hysteresis phenomenon and superparamagnetism properties at 300 K. The values of saturation magnetization 70.495, 38.30 and 34.30 emu/g are observed for Fe_3O_4, $Fe_3O_4@SiO_2$ and CoFSNPs, respectively. Despite decreasing in the saturation magnetization values of $Fe_3O_4@SiO_2$ and CoFS catalyst, these nanoparticles can still be separated from the solution by using an external magnetic field on the sidewall of the reactor.

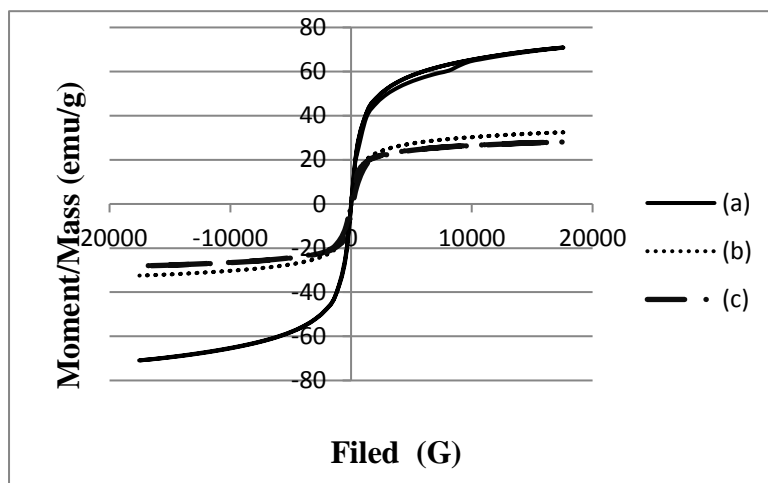**Figure 3.** Magnetization curves of (a) Fe_3O_4 (b) $Fe_3O_4@SiO_2$NPs (c) CoFS NPs at 300 K. All nanopartricles can be separated easily with external magnet.

The XRD pattern of Fe_3O_4, $Fe_3O_4@SiO_2$ and CoFSNPs are shown in Figure 4. The XRD pattern of Fe_3O_4 NPs indicates a crystallized structure at 2θ: 30.2°, 35.4°, 43.3°, 53.6°, 57.5° and 63.1° which are assigned to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) crystallographic faces of magnetite (Figure 4 a). A broad peak at 2θ = 15–27° in the XRD pattern of $Fe_3O_4@SiO_2$ and CoFSNPs shows the amorphous silica illustrated in Figure 4(b, c). The size of the particles is estimated by Debye–Scherrer equation (1).

$$D = \frac{k\lambda}{\beta cos\theta} \qquad (1)$$

where, D is the size of particles, λ is the wavelength of the X-ray, k is the Scherrer constant, β is the half width of the peak and θ is half of the Bragg angle. The average diameter of Fe_3O_4 NPs was 15 nm, while the diameter of $Fe_3O_4@SiO_2$ NPs was about 20 nm which is due to the agglomeration of Fe_3O_4 inside nanosphere and surface growth of silica on the shell.
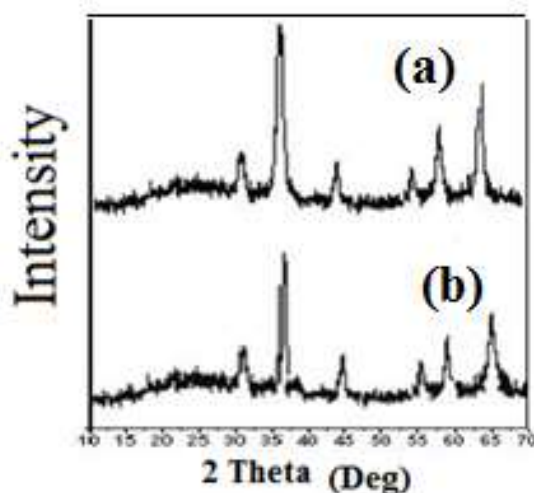

Figure 4. XRD pattern of (a) $Fe_3O_4@SiO_2$ NPs and (b) CoFSNPs which are in good agreement with the literature value (JCPDS Card No. 19-0629)

The TEM images of Fe_3O_4 and $Fe_3O_4@SiO_2$ NPs are shown in Figure 5 (a&b). As shown in the TEM of Fe_3O_4 and $Fe_3O_4@SiO_2$, the average

size of nanoparticles is 16 and 22 nm for Fe₃O₄ and Fe₃O₄@SiO₂, respectively. These results are similar to the results of XRD patterns. The TEM image of CoFS showed the successful immobilization of Co(III) salen complex on the Fe₃O₄@SiO₂ NPs.
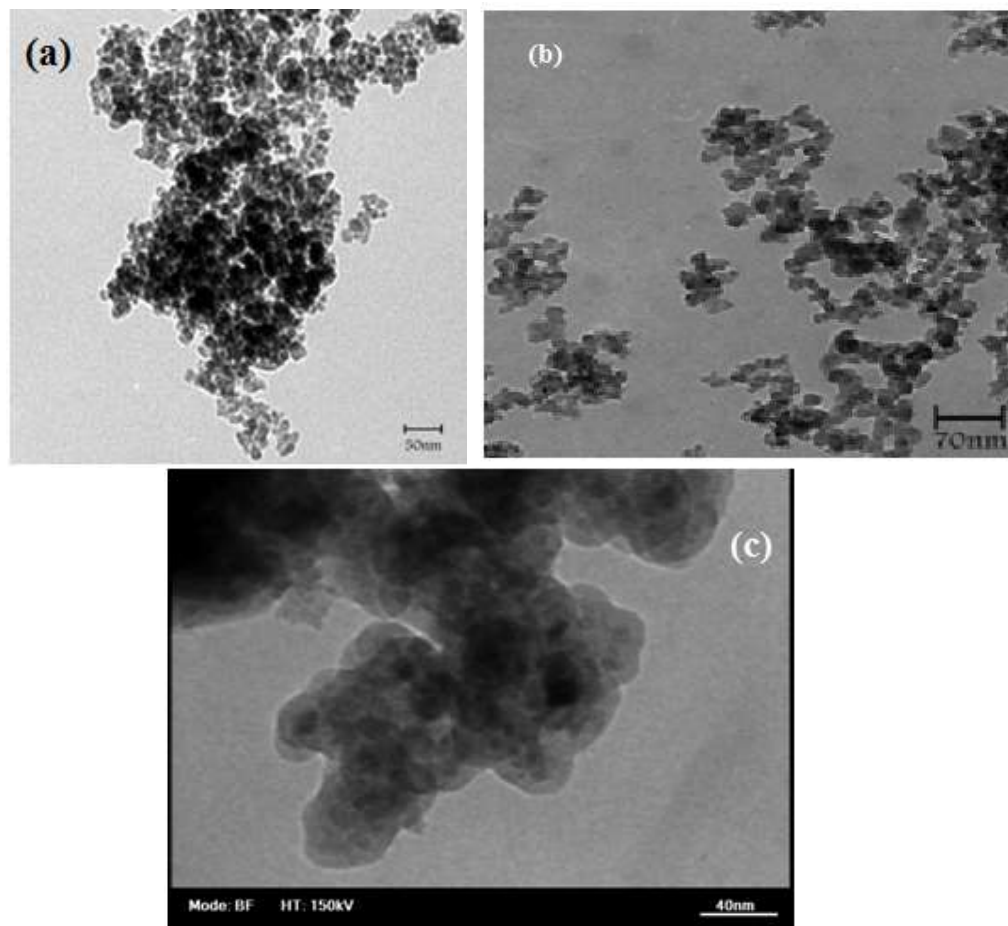

Figure 5. TEM image of Fe₃O₄ (a), TEM image of Fe₃O₄@SiO₂ (b) and TEM image of CoFS(c)

BET specific surface area of the CoFS was also obtained at room temperature by nitrogen physisorption and the surface area of 20 m^2/g was observed. Furthermore, the loading of Co (III) salen complex which is immobilized on the Fe₃O₄@SiO₂ was 0.42 mmol/g based on Co-element analysis by AAS.

Catalytic activity studies
Oxidation of sulfides to sulfoxides
The oxidation reaction of methyl phenyl sulfide (0.5 mmol) was initiated with hydrogen peroxide (1 mmol) in water. Initially, the oxidation reaction did not show considerable proceeding in the absence of CoFS at ambient as well as high temperatures. The above reaction was repeated with the addition of CoFS (0.001mmole based on Co element) and the conversion of methyl phenyl sulfide was 25 and 45 % within 20 and 40 min, respectively. The oxidation reaction conditions were optimized by studying the effect of catalyst loading, solvents, oxidant, time and temperature (Table 1).

Table 1. The effect of different amounts of CoFSon the oxidation reaction[a].

Entry	CoFS (mmol based on Co element)	Yield[b]	
		Sulfoxide %	Sulfone %
1	0.001	45	0
2	0.002	65	0
3	0.003	82	0
4	0.004	97	3
5	0.005	91	9
6	0.006	80	20
7	homogeneous Co (III) complex	97	3
8	------	8	0

[a]Reaction condition: methyl phenyl sulfide (1 mmol), H_2O_2 (2 mmol), water (3 mL), run at room temperature for 40 min. [b]GC yields based on the toluene as the internal standard.

By increasing the amount of CoFS from 0.001 to 0.004 mmole, the yield of methyl phenyl sulfoxide was obviously increased and reached to 97% (Table 1, Entries 1-4). Further, increase in the amount of catalyst leads to the over-oxidation of sulfoxide to sulfone (Table 1, Entries 5 and 6). Homogeneous Co(III) complex was also introduced into the reaction and corresponding sulfoxide was achieved in 24 min with

97% yield (Table 1, Entry 7). Different solvents with the range of polarity (nonpolar to polar solvents) such as (CHCl₃, DCM, THF, EtOAc, CH₃CN, EtOH, MeOH and water) were also applied for this reaction and the yield and selectivity of products were investigated. In this sense, water was selected as reaction medium (Table 2, Entry 8).

Table 2. The effect of different solvents on the oxidation reaction[a].

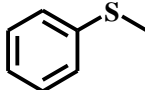| Entry	Solvent	Yield[b]	
		Sulfoxide %	Sulfone %
1	$CHCl_3$	40	0
2	DCM	45	0
3	THF	53	0
4	EtOAc	71	0
5	CH_3CN	74	0
6	EtOH	60	0
7	MeOH	63	0
8	Water	97	3

[a]Reaction condition: methyl phenyl sulfide (1 mmol), CoFs (0.004 mmol based on Co element), H_2O_2 (2 mmol), run under air at room temperature for 40 min
[b]GC yields based on the toluene as the internal standard

Oxidant is essential in the oxidation reaction. Therefore, the yield and selectivity of sulfoxide were investigated in the presence of different oxidant. As shown in Table 3, H_2O_2 was selected as a good oxygen source for the reactions. The reaction was also

investigated in the presence of various amounts of H_2O_2 and the best conversion and selectivity was achieved with 2 eq. H_2O_2 (Table 3, Entry 3). Further, increasing the molar ratio of hydrogen peroxide, decreased the selectivity of the products (Table 3, Entries 4 and 5).

Table 3. The effect of different amounts of H_2O_2 on the oxidation reaction[a].

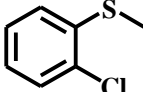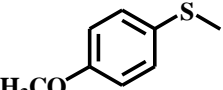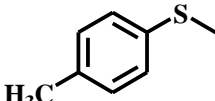| Entry	H_2O_2(mmol)	Yield[b]	
		Sulfoxide %	Sulfone %
1	1	55	0
2	1.5	80	0
3	2	97	3
4	2.5	87	13
5	3	65	35

[a]Reaction condition: methyl phenyl sulfide (1 mmol), CoFS (0.004 mmol based on Co element), water (3 ml) run under air at room temperature for 40 min.
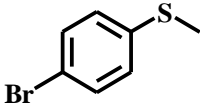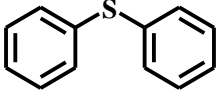[b]GC yields based on the toluene as the internal standard.

The generality of the oxidation reaction for the oxidation of different sulfides was investigated under optimum conditions (Table 4). As the results shown, different sulfides with electron-releasing and electron-withdrawing substituent undergo selective oxidation and produce the corresponding sulfoxides with 100% conversion and excellent yields (94-97%) (Table 4, Entries 3-6). In addition, TON (235-242.5) and TOF (352.5-363.75 h⁻¹) of the reactions confirmed the efficiency of the CoFS on the oxidation reactions.

Table 4. Oxidation of different sulfide with H_2O_2 in water[a]

Entry	Substrate	Sulfoxide[a]				
		Conv.[b] (%)	Yield (%)	Select.[c] %	TON[d]	TOF[e] (h⁻¹)
1		100	97	97	242.5	363.5
2		100	96	96	240	360
3		100	97	97	242.5	363.75
4		100	97	97	242.5	363.75
5		100	95	95	237.5	363.25

6		100	95	95	237.5	363.25
7		100	94	94	235	352.5
8		100	96	96	240	360

[a]Reaction conditions: sulfide (1 mmol), 30% H_2O_2 (2 equiv.), catalyst (0.004 mmol based on Co element), 40 min., rt. [b]Conversion and selectivity were determined by GC, Conversion= [(initial moles of substrate - final moles of substrate)/initial moles of substrate] × 100, [c]Selectivity to sulfoxide = [sulfoxide/(sulfoxide + sulfone)] × 100. [d]TON= number of moles of substrate converted per mole of catalyst. [e]TOF = number of moles of substrate converted per mole of catalyst per hour.

The oxidation of benzyl alcohols to carbonyl compounds

Oxidation of benzyl alcohol derivatives to corresponding carbonyl compounds was investigated in the presence of catalytic amount of CoFS. Initially, the oxidation of benzyl alcohol (Scheme 3) was studied as a representative substrate with TBHP in the presence of CoFS in CH_3CN media at reflux conditions which clarified that the catalyst and oxidant are essential for the promotion of the reaction at reflux conditions.
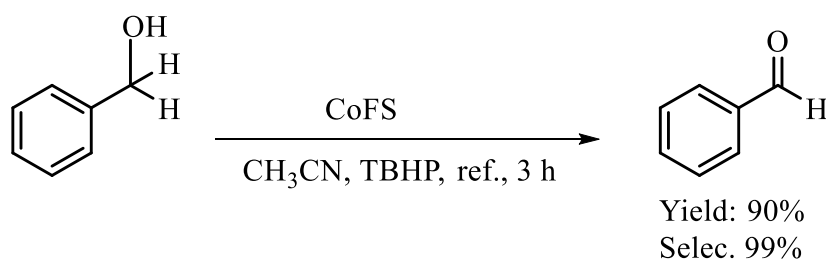
Scheme 3. Oxidation of benzyl alcohol in the presence of CoFS

The effect of parameters such as catalyst loading, solvent, time, oxidant and temperature were investigated on the model reaction obtained the optimum conditions.

The effect of catalyst loading

The effect of catalyst loading was studied on the model reaction (Table 5).

At first, the oxidation of benzyl alcohol was done in the absence of CoFS (blank reaction). The model reaction was investigated at different amount of catalyst (0.001-0.007 mmol based on Co element) and the best result was observed in the presence of 0.005 mmol of catalyst (Table 5, Entry 5). Further, increasing in the amount of catalyst did

not increase the yield of product (Table 5, Entry 6, 7). Moreover, Fe₃O₄@SiO₂ (0.1 g) was used in the oxidation reaction and benzaldehyde was produced in low yield (20 %) (Table 5, Entry 9). The selectivity of corresponding carbonyl compounds was (97-99%) in all experiments which shows the selectivity of the reactions are independent of the loading of Co.

Table 5. The effect of different amounts of catalyst on the oxidation of benzyl alcohol[a]

Entry	CoFS (mmol based on Co element)	Yield[b] (%)	Selectivity (%)
1	0.001	27	99
2	0.002	40	99
3	0.003	61	99
4	0.004	75	99
5	0.005	90	99
6	0.006	92	99
7	0.007	94	99
8	------	0	----
9	Fe₃O₄/SiO₂	20	99

[a]Reaction condition: benzyl alcohol (1 mmol), TBHP (2 mmol), acetoniyrile (3 mL), 2.5 h.
[b]Yields are based on the starting benzyl alcohol.

The effect of different solvents

To investigate the effect of different solvents, oxidation of benzyl alcohol was investigated in various solvents with different polarity and dielectric constant (Water, Acetonitrile, Tetrahydrofuran, Chloroform, Dichloromethane, Dioxane,Tuluene, *n*-Hexane) (Table 6). The results showed that the conversion (%) of substrate decreased in the order: acetonitrile >tetrahydrofuran > dioxane>dichloromethane > toluene > chloroform > n-hexane >water with 97-99 % selectivity to benzaldehyde.

Table 6. The effect of different solvents on oxidation of benzyl alcohol[a]

Entry	Solvents	Dielectric Constant	Yield[b] (%)	Selectivity (%)
1	water	80.1	20	99
2	Acetonitrile	37.5	90	99
3	Tetrahydrofuran	7.5	60	99
4	Chloroform	4.8	47	99
5	Dichlorometane	8.93	55	99
6	Tuluene	2.4	42	99
7	Dioxane	2.25	55	99
8	*n*-Hexane	----	22	99

[a]Reaction condition: Benzyl alcohol (1 mmol), TBHP (2 mmol), CoFS (0.005 mmol based on Co element) run under air at reflux condition for 2.5 h
[b]Yields are based on the starting benzyl alcohol.

Acetonitrile is a polar solvent with a high dielectric constant which can readily dissolve substrate (benzyl alcohol) and oxidant (TBHP) as well as facilitate the formation of active oxygen species and thereby increase the efficiency of the catalytic system (Table 6, Entry 6). The low conversion of benzyl alcohol in water may be

related to the low solubility of the substrate (Table 6, Entry 1).

The effects of temperature and reaction time

The effect of different temperature and time were investigated in the conversion (%) of benzyl alcohol in the presence of TBHP oxidant and CoFS catalyst and plotted with respect to time (Figure 6). As shown in Figure 6, increasing the time of the reaction increased the conversion of benzyl alcohol continuously up to 90 %. Furthermore, temperature has significant effects on the reaction rate. Increasing of the reaction temperature, strongly increased the catalytic activity and conversion of benzyl alcohol.
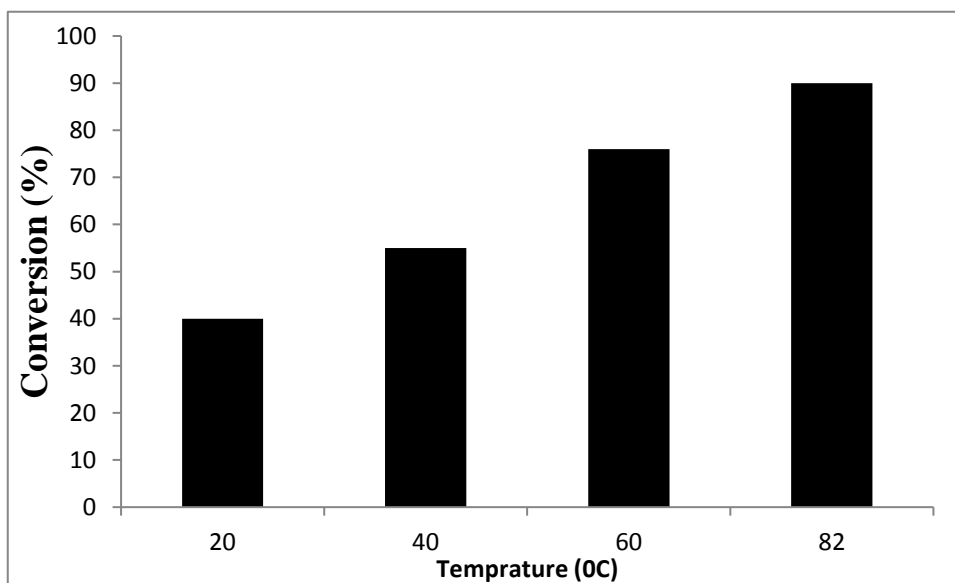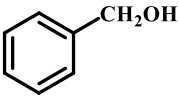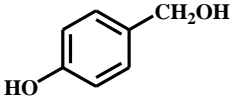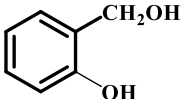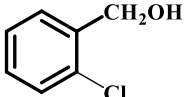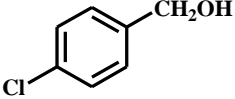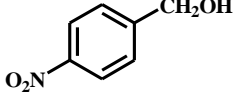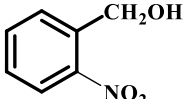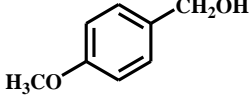

Figure 6. Conversion of benzyl alcohol as a function of time at 25, 40, 60 and 82 ^{0}C in the presence of TBHP oxidant and CoFS as catalyst
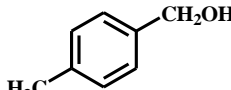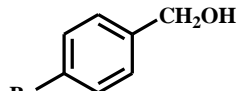
The effect of oxidant/alcohol molar ratio

The effect of different oxidants (TBHP, H_2O_2, and UHP) was studied on the oxidation of benzyl alcohol at reflux conditions and, consequently, TBHP was selected as the best oxidant. Furthermore, the different molar ratio of oxidant to benzyl alcohol were studied and the best conversion was achieved by the molar ratio of 2:1. To study the generality of the reaction under optimized conditions, various benzyl alcohols were oxidized with TBHP (Table 7). As shown in Table 7, Different benzyl alcohols were oxidized to the corresponding carbonyl compounds with good yield and excellent selectivity (Yields: 70-90 %, Selectivity: 97-99 %). Also, phenyl rings with electron-releasing groups such as OH, CH_3 and CH_3O have higher yields as compared to phenyl rings with electron-withdrawing groups (Table 7, Entries 2-3 and 8-9). Furthermore, TON and TOF of the oxidation reactions were 150-190 and 60-76 h^{-1}, respectively. The oxidation of aliphatic alcohol was also investigated. The results showed that aliphatic alcohols were reacted in longer time (4.5 h, Entries 11 and 12).

Table 7. Oxidation of different benzyl alcohol using TBHP catalyzed by CoFS[a]

Entry	Substrate	Products			
		Conv.[b] (%)	Select.[b] %	TON (h⁻¹)	TOF[c] (h⁻¹)
1	CH₂OH	90	99	180	72
2	CH₂OH, HO	92	98	184	73.6
3	CH₂OH, OH	91	99	182	72.8
4	CH₂OH, Cl	85	97	170	68
5	CH₂OH, Cl	87	98	174	69.6
6	CH₂OH, O₂N	78	97	156	62.4
7	CH₂OH, NO₂	75	98	150	60
8	CH₂OH, H₃CO	95	99	190	76

9 (4-methylbenzyl alcohol, CH₂OH with H₃C)	95	99	190	76
10 (4-bromobenzyl alcohol, CH₂OH with Br)	89	99	178	71.2

[a]Reaction conditions: Substrate (1 mmol), TBHP (2 equiv.), catalyst (0.005 mmol based on Co element), CH₃CN (3 ml), 3 h, reflux. [b]Conversion and selectivity were determined by GC, Conversion= [(initial moles of substrate - final moles of substrate)/initial moles of substrate] × 100, Selectivity to benzaldehyde = [benzaldehyde /(benzaldehyde + benzoic acid)] × 100. [c]TOF = number of moles of substrate converted per mole of catalyst per hour.

The oxidation reaction involved in hemolytic cleavage which proceeds through free radical pathway mechanism in Co(III) and Co (II) [29]. These ions react with TBHP to give peroxo and alkoxoradicals. Then, the benzylic hydrogen from the alcohol is abstracted by peroxo radical, giving the radical intermediate. The produced benzylic radical reacts with the *tert*-butyl alkoxo radical producing the desired product and *t*-butyl alcohol (Scheme 4).

$$t\text{-BuOOH} + Co^{3+} \longrightarrow Co^{2+} + t\text{-BuOO}^{\circ} + H^{+}$$

$$t\text{-BuOOH} + Co^{2+} \longrightarrow Co^{3+} + t\text{-BuO}^{\circ} + OH^{-}$$
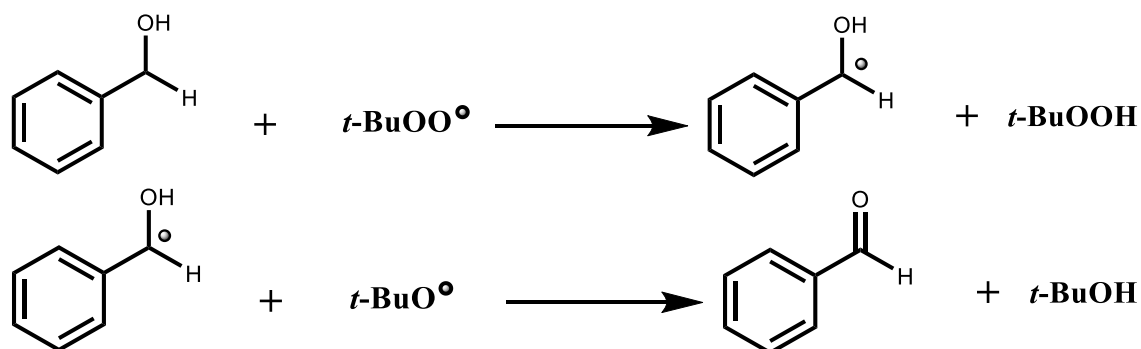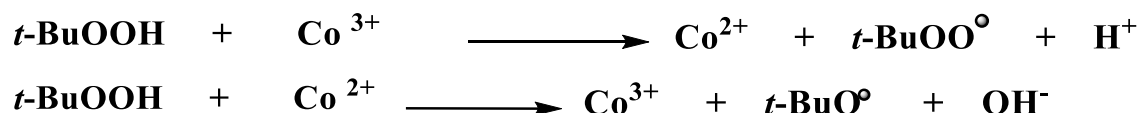
Scheme 4. Proposed mechanism for the oxidation of benzy alcohol derivatives

The efficiency of CoFs in the oxidation reaction of benzyl alcohol to corresponding benzaldehyde was also compared to earlier reports (Table 8). As shown in Table 7, this catalyst is comparable in term of yield and time of the reaction with other reports.

Table 8. Comparison of the CoFS catalyst with earlier reported ones for the oxidation of benzyl alcohol to benzaldehyde with TBHP

Entry	Catalyst	Condi.	Solvent	Time (min)	Yield (%)	Ref.
1	Y-Al_2O_3 supported copper	r.t.	Solv.-free	300	90	[30]
2	Mg–Al–hydrotalcite	Ref.	Solv.-free	300	99.98	[31]
3	[Mn(bipy)$_2$]$^{2+}$(86.5)/HMS	50 ^{0}C	Acetonitrile	30	40.21	[32]
4	U_3O_8/nano-gold	94 ^{0}C	Solv.-free	30	85	[33]
5	MgO/Nano gold	94^{0}C	Solv.-free	30	72.5	[34]
6	Mn(Salen) complexes/ SBA-15	Ref.	Acetonitrile	480	73.49	[35]
7	dicopper(II)-tetracarboxylates	65^{0}C	MeOH	180	83	[36]
8	Phosphonate-MOF	60^{0}C	EtOAC	120	58	[37]
9	CoFS	Ref.	Acetonitrile	180	90	This work

The reusability of the recovered CoFS catalyst was also investigated for new oxidation reactions. After each run, the separated CoFS catalyst was washed with ethanol, dried and reused for a subsequent round of reaction. The results showed that the catalyst worked well for the oxidation of sulfide and alcohol derivatives upto five cycles without a significant decrease in the reactivity and selectivity (Figures 7 and 8). In addition, the filtrates were analyzed by AAS and no leaching of Co metal was detected in it.
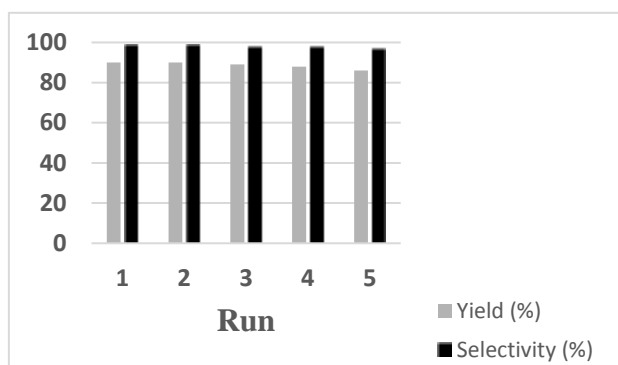
Figure 7. The reusability of the catalyst on the oxidation of benzyl alcohol
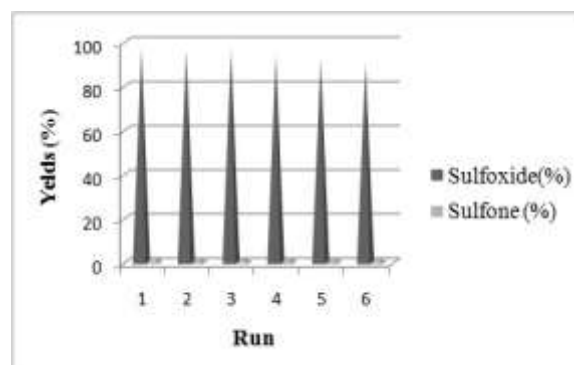
Figure 8. The effect of recycling of catalyst on the oxidation of sulfides

Conclusion

In conclusion, CoFS was synthesized by immobilization of Co(III) salen complex onto the surface of Fe₃O₄/SiO₂. The magnetic CoFS was characterized by different techniques (FT-IR, TEM, TGA, VSM, BET, XRD and AAS). Heterogeneous CoFS catalyst showed strong magnetic, responsively, due to a high saturation magnetization value (34.3 emu g^{-1}) which can be regarded as the possible separation of the catalyst with an external magnet. The heterogeneous CoFS was applied as a novel nanocatalyst for the oxidation of different sulfides using H_2O_2 as an oxidant in aqueous media. The reactions were carried out in mild conditions and excellent yields. Therefore, CoFS can be applied in a green system for the oxidation of various sulfides into sulfoxides at room temperature. In addition, the oxidation

of benzyl alcohol derivatives with TBHP was investigated in the presence of CoFS catalyst. The reactions were carried out in acetonitrile media at reflux conditions and benzyl alcohol derivatives oxidized to corresponding carbonyl compounds in excellent yields and selectivity. The advantages of this nanocatalyst are including simple workup, short reaction times, green conditions and excellent selectivity and yields.

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