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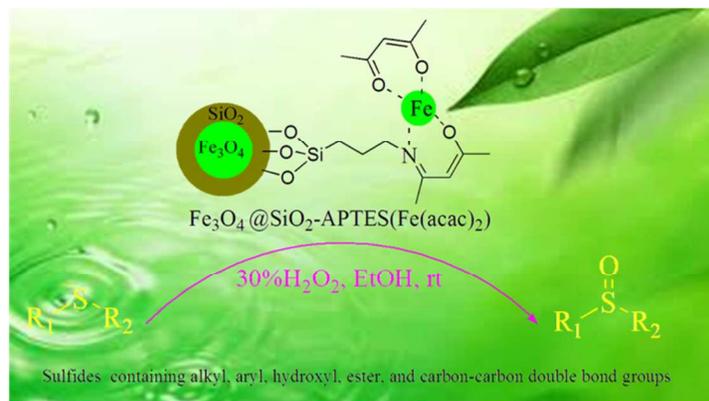
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## Graphical Abstract



Selective oxidation of sulfides to corresponding sulfoxides using  $\text{H}_2\text{O}_2$  as green oxidant at room temperature have been investigated by a magnetic supported iron (iron(II) acetylacetonate) as an efficient and recyclable heterogeneous catalyst with excellent sulfide conversion and good sulfoxide selectivity.

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ARTICLE TYPE

# The Magnetic Supported Iron Complex for Selective Oxidation of Sulfides to Sulfoxides Using 30% Hydrogen Peroxide at Room Temperature

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A magnetic supported iron (iron(II) acetylacetonate) was synthesized to be used as an efficient and recyclable heterogeneous catalyst for the selective oxidation of sulfides to corresponding sulfoxides using H<sub>2</sub>O<sub>2</sub> as green oxidant at room temperature. The synthesized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES(Fe(acac)<sub>2</sub>) catalyst presented excellent sulfide conversion and good sulfoxide selectivity. It can be easily recovered and reused for 8 reaction cycles without considerable loss of activity. The facile recovery of the catalyst is carried out by applying an external magnet device. The catalyst was fully characterized by techniques of TEM, SEM, XRD, EDS, FTIR, TGA, ICP-AES, VSM and elemental analysis (CHN).

## Introduction

The integration of nanotechnology with green chemistry offers innovative prospects to meet stringent demands for ecological and economical sustainability. The significant advancement in nanotechnology over the past decades has led to potential applications of magnetic nanoparticles (MNPs) in numerous scientific fields, including catalysis, biomedicine, environmental protection and energy storage [1-4]. Magnetic nanoparticles (MNPs) as catalyst supports have been attracting more and more attention because they are readily dispersed in reaction solution with intrinsically high surface area rendering the efficient accessibility of substrates to the surface. In addition, they are super-paramagnetic and can be easily recovered from the reaction mixture using an external magnet [5-7].

Unprotected MNPs are often unstable and tend to aggregate during the catalytic transformations. Therefore, MNPs are coated by silica which acts as a stabilizer, limiting the effect of the outside environment on the core particles. Encapsulation of MNPs with amorphous silica not only contributes to the amelioration of chemical stability and dispersibility but also combines the advantageous properties of the magnetically responsive core and possible further surface-functionalized silica shell [8-9]. At this time, silica-coated MNPs have appeared as versatile supports for the immobilization of active sites to form magnetically recyclable heterogeneous catalysts [6].

Magnetically recoverable heterogeneous catalysts have been developed and applied in versatile organic synthesis for a wide range of catalytic reactions, including coupling reactions [10-12], Friedlander reaction [13], hydrogenation, hydroformylation, epoxidation reactions [14], selective oxidation of sulfides to sulfoxides [15].

The selective oxidation of sulfides to sulfoxides is a great important in synthesis of chemically useful and biologically active molecules such as drugs [16-18]. A stoichiometric amount of organic or inorganic oxidizing agents are required to affect this oxidation process and thus are dangerous and a large amount of toxic waste would be generated [19-20]. In recent years, the procedures employing molecular oxygen or hydrogen peroxide as a primary oxidant in the presence of a catalyst have been found to be promising. Hydrogen peroxide is a non-toxic, cheap and effective oxidizer reagent. In addition, the oxidation reaction by hydrogen peroxide can be controlled easier than molecular oxygen and air [21-23].

So far, some interesting transition metal catalysts have been reported for the sulfide oxidation, including Cu [24], Mo [16], Ti [25], V [26] and Fe [27] in the presence of a suitable oxidant such as hydrogen peroxide. Owing to low price and low toxicity of iron, Fe complexes have been widely used as homogenous catalysis. Very recently, the elegant work of Liang-Nian and co-workers [28] has shown that Fe(acac)<sub>2</sub> can be effectively applied for selective oxidation of sulfide to sulfoxide using oxygen in poly ethylene glycol (PEG 1000) as solvent.

Although this protocol has shown remarkable properties such as high activity and selectivity in oxidation of sulfide to sulfoxide, but its use has been limited due to the solubility of catalyst in the liquid phase along with reactants. Therefore, the catalyst separation from the reaction products, recycling and reuse is difficult.

One way to solve this drawback is to immobilize catalytic system onto a large surface area solid carrier. One of the solid carriers is magnetic nanoparticles. The use of magnetic nanoparticles enables the separation from reaction mixture by an external magnet and reuse of the catalyst itself. In this study, we report our results about the preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES(Fe(acac)<sub>2</sub>)

composite as a recoverable heterogeneous nanocatalyst for selective oxidation of sulfides to sulfoxides using 30% hydrogen peroxide as oxidant under mild reaction conditions in ethanol as green solvent.

## Experimental Materials and methods

All chemicals were purchased from Sigma-Aldrich and used without further purification. X-ray diffraction (XRD) patterns were obtained with a APD 2000, using Cu K $\alpha$  radiation (50 kV, 150 mA). Fourier transform infrared (FT-IR) spectra of KBr powder-pressed pellets were recorded on a ABB Bomem MB100 spectrometer. A TGA-Q5 thermogravimetric analyzer was used to study the thermal properties of the compounds under an inert N<sub>2</sub> atmosphere (at 20 mL min<sup>-1</sup>) and heating at a rate of 10 °C min<sup>-1</sup>. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed on KYKY-EM3200 and Philips CM30, respectively. An energy dispersive detector (EDS) coupled to the microscope was used to identify chemical elements of the prepared catalyst.

The room-temperature magnetization in the applied magnetic field was performed by a homemade vibrating sample magnetometer (Meghnatis Daghigh Kavir Company, Iran) from -10000 to +10000 Oersted. The immobilized iron content on the catalyst was measured by inductively coupled plasma atomic emission analysis (ICP-AES, Perkin-Elmer Optima 3300 DV). Elemental analysis (CHN analysis) was carried out on Perkin Elmer, USA (2400, Series II).

### Synthesis of Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (MNPs)

The Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles were prepared as reported in literature [29]. Briefly, FeCl<sub>3</sub>·6H<sub>2</sub>O (4.8 g, 0.018 mol) and FeCl<sub>2</sub>·4H<sub>2</sub>O (1.8 g, 0.0089 mol) were added to 100 mL deionized water and vigorously stirred (700 rpm) under Ar atmosphere for 1 h until the salts dissolved completely (Scheme 1). Then, 10 mL of 25% NH<sub>4</sub>OH was added dropwise into the reaction mixture in 10 min and MNP black precipitate was formed immediately. After continuously mechanical stirring for 1 h, the precipitate was separated by an external magnet and washed with the double distilled water in five times, and then vacuum-dried at 50 °C overnight.

### Synthesis of silica coated Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>)

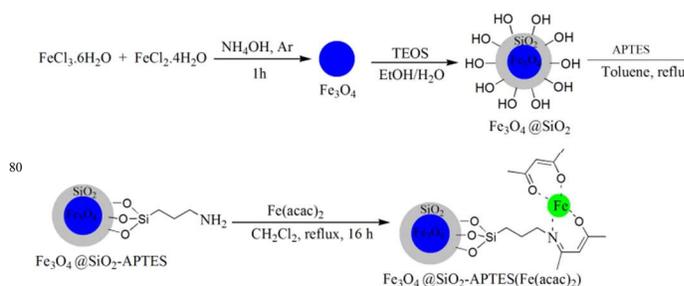
1g of Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles was ultrasonically dispersed in a solution containing 40 ml ethanol and 10 ml water, and then loaded into a three-necked bottle. The pH value was adjusted to 10 with an ammonia solution and 0.5 ml TEOS was dropwise added and stirred at 50 °C for 6 h to obtain magnetic nanoparticles of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>. After washing with ethanol and water for several times, magnetic nanoparticles of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> were dried at 60 °C overnight.

### Synthesis of amino-functionalized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>

3-aminopropyltriethoxysilane (APTES) (1 ml) was added to a suspension of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (1 g) in dry toluene (25 ml) and refluxed for 24 h under N<sub>2</sub> atmosphere. Afterwards, the sample was collected by magnetic separation, washed with toluene and anhydrous ethanol several times, and then dried under vacuum in an oven at 60 °C overnight. The resulting material was denoted as Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES.

### Immobilization of [Fe(acac)<sub>2</sub>] onto Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES (1 g) was dispersed into 20 ml dry dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) under mechanical stirring. [Fe(acac)<sub>2</sub>] (1 mmol) was then added into the above mixture and then refluxed for 16 h. The resulting nanocomposites (nominated as Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES(Fe(acac)<sub>2</sub>)) were magnetically collected, washed with dichloromethane, ethanol and water and dried under vacuum (Scheme 1).



**Scheme 1** Preparation of magnetically recoverable heterogeneous nanocatalysts Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES(Fe(acac)<sub>2</sub>).

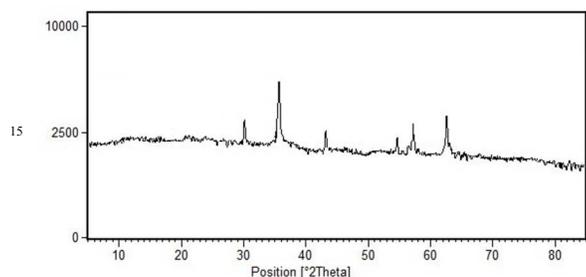
### General procedure for the oxidation of sulfides to sulfoxides

A mixture of sulfide (1 mmol), 30% H<sub>2</sub>O<sub>2</sub> (1.5 equiv), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES(Fe(acac)<sub>2</sub>) catalyst in ethanol (3 mL) was stirred at 25 °C. Completion of the reaction was indicated by TLC (n-hexane/ethylacetate 10:1) and gas chromatography (GC). After completion of the reaction, the catalyst was separated by an external magnet and then water (10 mL) was added to the mixture and extracted by ethyl acetate (3 × 5 mL). After drying with anhydrous sodium sulfate, the organic residue was analyzed by GC and then purified by column chromatography on silica gel with ethyl acetate/hexane (1:10) to afford the desired product. The separated catalyst was washed with EtOH and used directly for a subsequent round of reaction without further purification. All reaction products were identified by GC chromatogram, IR spectra and melting point as compared with authentic samples.

## Results and discussion

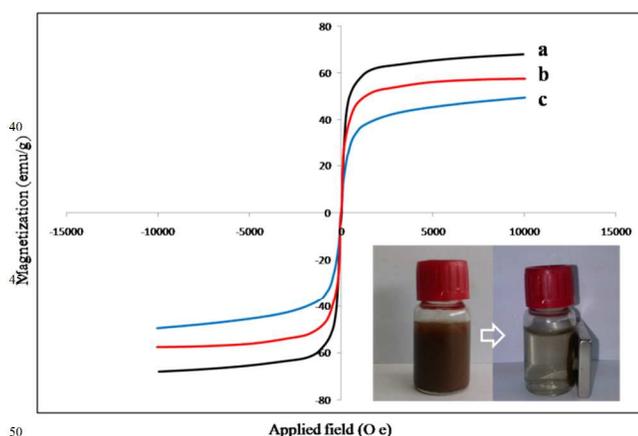
### Catalyst characterization

The crystalline structure of the synthesized  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES(Fe(acac)}_2)$  catalyst was identified by wide angle XRD. As shown in Fig. 1, six characteristic peaks ( $2\theta = 30.8, 35.4, 43.6, 53.5, 57.7,$  and  $62.4$ ) corresponding to (220), (311), (400), (422), (551) and (440) diffraction planes of  $\text{Fe}_3\text{O}_4$  MNPs are in good agreement with the standard XRD data for the cubic  $\text{Fe}_3\text{O}_4$  phase of inverse spinel crystal structure (JCPDS Card numbers 89-43191, 19-0629, 79-0419) [30-31].



**Fig. 1** The wide-angle XRD pattern of the  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES(Fe(acac)}_2)$  catalyst.

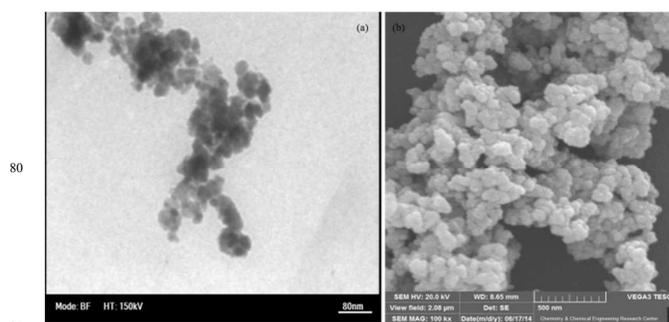
Typical magnetization curves as a function of the applied field at room temperature are shown in Fig. 2. As seen from Fig. 2, all of the samples exhibit superparamagnetic behavior and had little hysteresis, remanence and coercivity. Low decreasing of saturation magnetization of  $\text{Fe}_3\text{O}_4$  from about 70 emu/g (a) to almost above 59 emu/g (b) for  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  illustrated that the coated silica on  $\text{Fe}_3\text{O}_4$  is thin layer and then the weight contribution from nonmagnetic portion is low. Also, the  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES(Fe(acac)}_2)$  catalyst could be easily separated by applying an external magnet (Fig. 2). This property provides an easy and efficient way to separate and recycle the catalyst from heterogeneous systems, which minimizes the loss of catalyst during the separation stage.



**Fig. 2** Magnetization curves of  $\text{Fe}_3\text{O}_4$  (a),  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  (b), and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES(Fe(acac)}_2)$  catalyst (c). The inset is a photograph of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES(Fe(acac)}_2)$  catalyst under an external magnetic field.

The transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images for the  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES(Fe(acac)}_2)$  catalyst are shown in Fig. 3. Both the TEM and SEM showed that the  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES(Fe(acac)}_2)$  nanoparticles were present as spherical and uniform particles and the size of nanoparticles was less than 50 nm. The EDS analysis also confirms the presence of C, N, O, Si, and Fe atoms in the structure of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES(Fe(acac)}_2)$  catalyst (Fig. S1, see Supporting information).

In order to confirm the existence of organic groups on the surface of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ , FTIR spectra of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES}$  and the  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES(Fe(acac)}_2)$  catalyst are shown in Fig. 4. As shown in Fig. 4a, there are two characteristic absorption bands at  $623\text{ cm}^{-1}$  and  $1098\text{ cm}^{-1}$  which correspond to the stretching vibration of Fe-O and Si-O, respectively [32]. The bands at  $807\text{ cm}^{-1}$  and  $467\text{ cm}^{-1}$  are due to the deformation of Si-O bond [33]. Fig. 4a also exhibits absorption bands in the  $2855\text{ cm}^{-1}$  and  $2927\text{ cm}^{-1}$  which are assigned to the stretching of C-H bonds and the broad peak at  $3423\text{ cm}^{-1}$  is due to the O-H and N-H vibrations. The band around  $1620\text{ cm}^{-1}$  is due to the bending vibration of water molecules adsorbed on the surface.



**Fig. 3** Transmission electron microscopy (TEM) image (a), scanning electron microscopy (SEM) image (b).

The FT-IR spectrum of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES(Fe(acac)}_2)$  catalyst shows peaks which are clearly different from those of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES}$ . The FT-IR spectrum of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES(Fe(acac)}_2)$  catalyst (Fig. 4b) shows several new sharp bands in the range of  $1300\text{-}1600\text{ cm}^{-1}$  which don't exist in the spectrum of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES}$  [34].

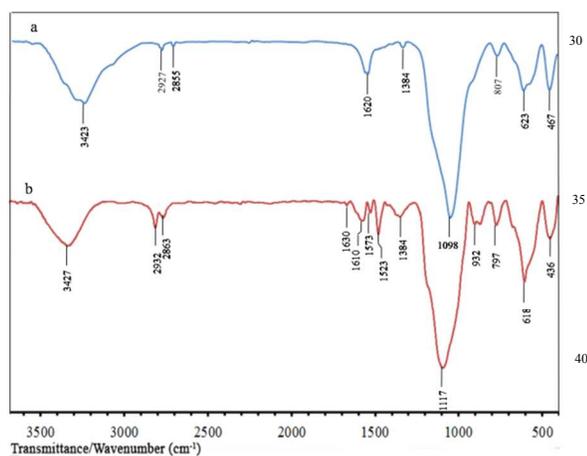
The peaks at  $1523\text{ cm}^{-1}$  and  $1573\text{ cm}^{-1}$  correspond to the double bond of C=C and carbonyl group, respectively. The peak at  $932\text{ cm}^{-1}$  and relatively small peak at  $1630\text{ cm}^{-1}$  are also corresponding to stretching vibrations of C-O and C=N bonds, respectively. By going from  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES}$  to  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES(Fe(acac)}_2)$  catalyst, the intensity of stretching vibration of C-H bonds at  $2863\text{ cm}^{-1}$ ,  $2932\text{ cm}^{-1}$  and also the bending vibration of H-C-H bond at  $1384\text{ cm}^{-1}$  increases [34-35]. Thus, it can be confirmed that surface modification of the  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES}$  by anchoring of  $\text{Fe(acac)}_2$  was successful.

Thermogravimetric analysis (TGA) of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES}$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES(Fe(acac)}_2)$  catalyst, is seen in Fig. S2. The first weight loss curve below  $200\text{ }^\circ\text{C}$  in thermogravimetric analysis (TGA) of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES}$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}$

APTES( $\text{Fe}(\text{acac})_2$ ) catalyst is attributed to residual physisorbed water and/or organic solvents, which was applied during their preparation. TGA diagrams of  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES and  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES( $\text{Fe}(\text{acac})_2$ ) show that the largest weight loss occurs between 200 °C and 600 °C. This is due to the decomposition of the grafted organic molecule on the surface which is consistent with covalently bonded organic groups to the surface of MNPs.

The largest weight loss is corresponding to 2.6% and 5.5% of the initial sample weight for  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES and  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES( $\text{Fe}(\text{acac})_2$ ), respectively. The small amount of 5.5% weight loss in the range of 200-600 °C indicates that the  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES( $\text{Fe}(\text{acac})_2$ ) catalyst have a good thermal stability up to 200 °C.

The difference between the largest weight loss for  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES and  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES( $\text{Fe}(\text{acac})_2$ ) could be attributed to the amount of iron acetylacetonate grafted on the surface. A loading 0.114 mmol.g<sup>-1</sup> for Fe grafted on the  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES obtains from this difference. The Fe content was also measured by elemental analysis (CHN analysis) which indicated a loading of 0.1 mmol.g<sup>-1</sup>. In order to obtain an insight into the accurate amount of Fe grafted on the  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES, inductively coupled plasma atomic emission analysis (ICP-AES) was applied on the  $\text{Fe}(\text{acac})_2$  solution before and after grafting on the  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES. The Fe content grafted on the  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES was measured about 0.11 mmol.g<sup>-1</sup>. The loading of APTES on the  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$  was measured by TGA (Fig. S2a) and CHN analysis about 0.44 and 0.38 mmol.g<sup>-1</sup>, respectively.



**Fig. 4** The FTIR spectra of  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES (a) and  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES( $\text{Fe}(\text{acac})_2$ ) catalyst (b)

### Oxidation of sulfides to sulfoxides by using $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES( $\text{Fe}(\text{acac})_2$ ) catalyst

To investigate the catalyst activity of  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES( $\text{Fe}(\text{acac})_2$ ), we have chosen the oxidation of sulfides to sulfoxide. In order to get an insight into the optimum catalytic conditions for the selective oxidation of sulfides to sulfoxides, the oxidation reaction of methyl phenyl sulfide by 30%  $\text{H}_2\text{O}_2$  hydrogen peroxide and in the presence of  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES( $\text{Fe}(\text{acac})_2$ ) catalyst as a model experiment was

investigated. In this study the effect of solvent, temperature and the amount of  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES( $\text{Fe}(\text{acac})_2$ ) catalyst on the conversion and selectivity toward sulfoxide was examined. The results of the solvent effect on the oxidation reaction are summarized in Table 1. It was found that conversion of sulfide in

**Table 1** Optimization of the reaction conditions for selective oxidation of methyl phenyl sulfide (1 mmol) to methyl phenyl sulfoxide in the presence of  $\text{H}_2\text{O}_2$  (1.5 equiv) and  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES( $\text{Fe}(\text{acac})_2$ ) (1 mol%) catalyst at room temperature.

Sel. (%) <sup>b</sup>	Yield(%) <sup>a</sup>	Con. (%) <sup>a</sup>	Time (h)	Solvent	Entry
92	34	37	6	EtOAc	1
98	20.5	21	6	Toluene	2
54	36	67	6	$\text{H}_2\text{O}$	3
87	61	70	6	$\text{CH}_2\text{Cl}_2$	4
97	85	88	6	EtOH	5
90	73	81	6	MeOH	6
94	72.4	77	6	THF	7
94	74	79	6	$\text{CH}_3\text{CN}$	8
88	15	17	6	n-Hexane	9

<sup>a</sup>Determined by GC with area normalization, <sup>b</sup>Sulfoxide selectivity

less-polar solvents (Entries 2, 9) is low. In addition, selectivity to the corresponding sulfoxide was decreased to 54% in high-polar solvent (water). Among different solvents, EtOH (Entry 5) was found to be the best solvent in terms of conversion and selectivity toward sulfoxide. The amount of  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES( $\text{Fe}(\text{acac})_2$ ) catalyst and the effect of temperature was also investigated after choosing EtOH as the best solvent for the oxidation reaction.

The amount of catalyst was also considered. It was found that the amount of catalyst could remarkably promote conversion of sulfide to sulfoxide. As shown in Table 2, no significant amount of sulfoxide was produced in absence of  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES( $\text{Fe}(\text{acac})_2$ ) catalyst (Entry 1). The conversion of sulfide was 72% when the catalyst amount was 0.5 mol% (45 mg). With the increase of the catalyst amount from 0.5 mol% to 2 mol% (180 mg), conversion value was increased from 72% to 97%. When more amounts of catalyst (3 mol% and 4 mol%) were used, the conversion of sulfide and selectivity for sulfoxide did not change remarkably. These results show that 2 mol% of the catalyst was sufficient for oxidation of sulfides to corresponding sulfoxides.

In the next step, we examined the effect of temperature on the oxidation reaction. At room temperature, the obtained conversion and selectivity toward sulfoxide were 97% and 96%, respectively. However, a quantitative conversion was generally observed with the increase of temperature to 40 and 60 °C but over-oxidation of the sulfoxide product to sulfone occurred which reduced the selectivity of the target product (Table 2, entries 7,8). Therefore, the best selectivity was obtained in room temperature.

### Catalytic activity of $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTES( $\text{Fe}(\text{acac})_2$ ) for the oxidation of sulfides to sulfoxides

The applicability of this protocol was studied by oxidation of several types of sulfides with different electronic and steric effects to corresponding sulfoxides under the optimized conditions. As shown in Table 3, the sulfides with less steric hindrance were

**Table 2** Optimization of the reaction conditions in EtOH<sup>a</sup>.

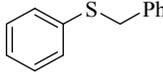
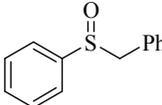
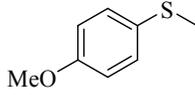
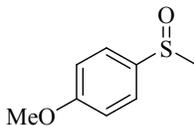
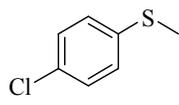
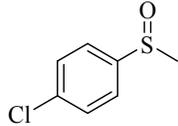
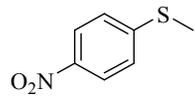
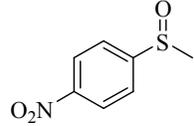
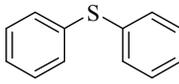
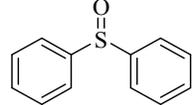
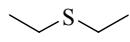
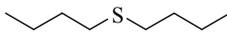
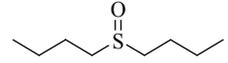
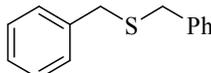
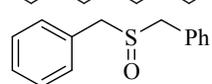
Entry	Catalyst (mol%)	Time (h)	T (°C)	Con. (%) <sup>b</sup>	Yield (%) <sup>b</sup>	Sel. (%) <sup>b</sup>
1	-	24	25	14	13.6	97
2	0.5	9	25	72	69	96
3	1	6	25	88	85	97
4	2	2	25	97	94	96
5	3	2	25	97.7	91.8	94
6	4	2	25	97	92	95
7	2	2	40	99	73	74
8	2	2	60	>99	47.5	48

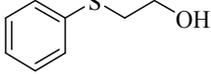
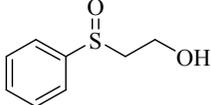
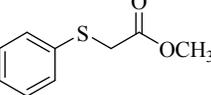
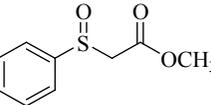
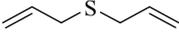
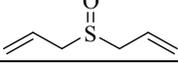
<sup>a</sup>Reaction conditions: methyl phenyl sulfide (1 mmol), 30% H<sub>2</sub>O<sub>2</sub> (1.5 equiv), indicated amount of catalyst, ethanol (3 mL) as solvent at reaction temperature; the amount of Fe grafted on the surface was determined by ICP-AES analysis (loading = 0.11 mmol.g<sup>-1</sup>). <sup>b</sup>Determined by GC with area normalization.

converted to the corresponding sulfoxides in good to excellent yields. Also, the influence of electronic effect was found in the case of 4-nitrophenyl sulfide, which has a negative effect on the reaction time. The chemoselectivity of the presented protocol was also investigated in the selective oxidation of sulfides containing hydroxyl, ester, and carbon-carbon double bond groups. These substrates selectively underwent oxidation at the sulfur atom without undergoing further structural changes in their functional

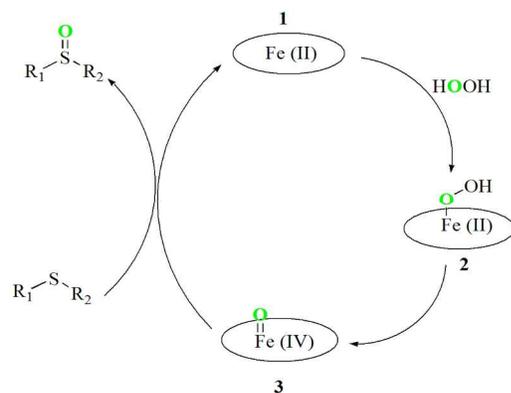
group. For example, in the case of allylic sulfides, no over oxidation to the sulfone or epoxidation of the double bond was observed and only the corresponding sulfoxide were obtained in excellent yields (Table 3, entries 11). Also, the presence of ester group did not interfere with the oxidation process of the sulfide, and desired sulfoxides were obtained in excellent yield (Table 3, entry 10). It is clear that these kinds of sulfides are completely unaffected under the reaction conditions, indicating the good ability of this protocol in oxidation of different types of sulfides. It would be interesting to know that there is not a clear mechanism for iron-catalyzed sulfoxidation at the present stage. An electrophilic Fe(IV)=O (one redox equivalent above the Fe(III) state) has been proposed to be the active oxidizing species involved in oxidation by Fe complexes and O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>. Therefore, the presence of Fe(IV)=O complex (high-valent iron oxo complex) is essential in oxidation reactions. The first stage for the formation of Fe(IV)=O complex is performed in situ by the reaction of Fe (II) complex (**1**) with H<sub>2</sub>O<sub>2</sub> as oxidizing agent to form compound **2** (Scheme 2). Then, O–O bond homolysis/heterolysis of compound **2** results in the generation of compound **3**, which is involved in oxygen atom transfer reaction for the oxidation of sulfides to sulfoxides [28,36-37].

**Table 3** Oxidation of sulfides to the corresponding sulfoxides by using 30% H<sub>2</sub>O<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES(Fe(acac)<sub>2</sub>) catalyst<sup>a</sup>.

Entry	Substrate	Product	Time (h)	Con. (%) <sup>b</sup>	Yield (%) <sup>b</sup>	Sel. (%) <sup>b</sup>
1			2.7	96	91	95
2			2.5	98	96	98
3			2.5	95	93	98
4			8	84	80	95
5			6	86	80	93
6			4	>99	96	97
7			4.5	96	92	96
8			3	95	90	95

9			3	97	88	90
10			3.5	96	92	96
11			4	86	76	89

<sup>a</sup>Reaction conditions: sulfide (1 mmol), 30% H<sub>2</sub>O<sub>2</sub> (1.5 equiv.), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES(Fe(acac)<sub>2</sub>) catalyst (2 mol%, 180 mg), ethanol (3 ml) as solvent at room temperature. <sup>b</sup>Determined by GC with area normalization.



**Scheme 1** Proposed mechanism for the oxidation of sulfides to sulfoxide using 30% H<sub>2</sub>O<sub>2</sub> in the presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES(Fe(acac)<sub>2</sub>) catalyst.

In order to show the efficiency of our methodology, our results in oxidation of methyl phenyl sulfide was compared to literature reports (Table 4). Table 4 clearly point out the efficiency of the proposed methodology (Table 4, last entry) in both activity and reusability of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES(Fe(acac)<sub>2</sub>) catalyst as compared to literature reports involving several homogeneous and heterogeneous systems under various conditions (Table 4, entries 1-7).

Entry 5 indicates that heterogeneous system (Fe/SBA-15) have higher catalytic activity, better reusability than Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES(Fe(acac)<sub>2</sub>) catalyst but these kinds of heterogeneous catalysts have a problem in recovery in such a way that most heterogeneous systems require a filtration or centrifugation step or

a tedious workup of the final reaction mixture to recover the catalyst, although Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES(Fe(acac)<sub>2</sub>) catalyst can be easily recovered from the reaction mixture only using an external magnet.

A comparison between Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES(Fe(acac)<sub>2</sub>) catalyst (this work) and molybdate-based Fe<sub>3</sub>O<sub>4</sub> catalyst (entry 7) which are recyclable heterogeneous catalysts by external magnet indicates that the oxidation of sulfides to sulfoxides in EtOH as a green solvent gives almost better results in yield and reusability of the catalyst. On the other hand, less amounts of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES(Fe(acac)<sub>2</sub>) catalyst (2 mol%) and H<sub>2</sub>O<sub>2</sub> (1.5 equiv.) as oxidizing agent are used in this work. In addition, the results in Table 4 indicate that the amount of yield and reusability of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES(Fe(acac)<sub>2</sub>) catalyst is comparable with the other results summarized in Table 4.

### Catalyst recycling

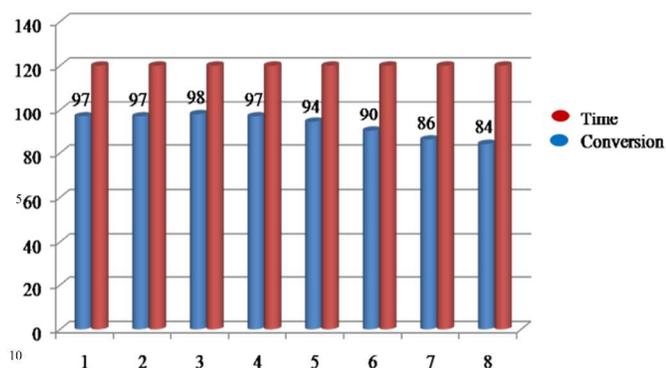
The recycling properties of catalyst were investigated in methyl phenyl sulfide oxidation at room temperature employing aqueous 30% H<sub>2</sub>O<sub>2</sub> for 1 mmol of substrate. After the completion of first oxidation reaction of methyl phenyl sulfide to afford the methyl phenyl sulfoxide under optimized condition, the catalyst was magnetically isolated after each cycle, washed with EtOH, and then placed into a fresh reaction mixture. Under the described conditions, the catalyst exhibited high activity but the yield of reaction in 8 run decreased with respect to 1 run at the time of 120 min (Fig. 4).

**Table 4** Comparison of the activity of various catalysts in oxidation of methyl phenyl sulfide using 30% H<sub>2</sub>O<sub>2</sub>.

Entry	Catalyst	Solvent	Temp (°C)	Time (min)	Yield %	Reusability [ref]
1	polymer anchored Cu(II) complex	CH <sub>3</sub> CN	25	180	83	5 [38]
2	Ionic liquid-based polyoxometalate salts	MeOH	25	30	94.7	5 [39]
3	silica-based tungstate interphase	CH <sub>2</sub> Cl <sub>2</sub> :MeOH	25	90	82	8 [23]
4	Peroxtungstate supported on silica	CH <sub>2</sub> Cl <sub>2</sub> :MeOH	8	150	91.9	6 [40]
5	Fe/SBA-15	H <sub>2</sub> O	25	120	99	10 [41]
6	bis-[N-(propyl-1-sulfoacid)-pyridinium] hexafluorotitanate	[BPy][BF <sub>4</sub> ]	25	120	95	6 [25]
7	molybdate-based Fe <sub>3</sub> O <sub>4</sub> catalyst	CH <sub>3</sub> CN	25	90	91	7 [15]
This work	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -APTES(Fe(acac) <sub>2</sub> )	EtOH	25	120	92	8

<sup>a</sup>The amounts of catalyst and oxidizing agent (H<sub>2</sub>O<sub>2</sub>) are 3 mol% and (3 equiv.), respectively.

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**Fig. 5** The recycling experiment of catalyst in the oxidation reaction of methyl phenyl sulfide to methyl phenyl sulfoxide under optimized condition; the oxidation reaction was quenched after 120 min at each step.

## Conclusion

We have prepared recyclable catalyst of iron(II) acetylacetonate immobilized on amine-modified magnetic nanoparticles ( $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES}(\text{Fe}(\text{acac})_2)$ ) for sulfide oxidation using  $\text{H}_2\text{O}_2$  as oxidant at room temperature. Under the mild conditions, a wide range of sulfides with different steric/electronic effects and containing the oxidation-sensitive groups (such as OH or C=C double bond) could be converted into their corresponding sulfoxide with high chemoselectivity in ethanol as green solvent. This catalyst can be considered as heterogeneous version of  $\text{Fe}(\text{acac})_2$  and easily prepared from commercially available starting materials. The properties of high activity, high stability, easy recoverability, and reusability of the catalyst render it potentially valuable catalyst in industrial applications.

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## Supporting Information

The EDS analysis and thermogravimetric analyses (TGA) of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES}$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES}(\text{Fe}(\text{acac})_2)$  catalyst. This material is available free of charge on the web at <http://pubs.rsc.org/en/Journals/Issues/CY#!issueid=cy004007&type=current&issnprint=2044-4753>.

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