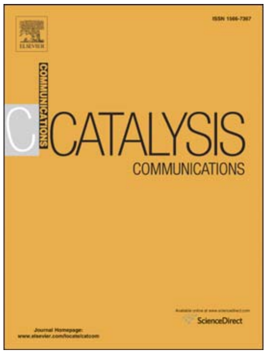

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Selective oxidation of sulfides to sulfoxides by a molybdate-based catalyst using 30% hydrogen peroxide

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Abstract

An efficient method is reported for selective oxidation of various types of sulfides to sulfoxides and sulfones in good to high yields using 30% H_2O_2 in the presence of catalytic amounts of molybdate-based catalyst in acetonitrile as solvent at room temperature. The catalyst can be easily recovered and reused for seven reaction cycles without considerable loss of activity.

Keyword: Selective oxidation, Magnetic nanoparticle, Molybdate anion, Highly reusable catalyst, Heterogeneous, Hydrogen peroxide

1. Introduction

The selective oxidation of sulfides to sulfoxides is an important transformation in organic chemistry [1,2], because sulfoxides are useful synthetic intermediates for the construction of various chemically and biologically active molecules [3-5] and also they play key role in activation of enzymes. Therefore, a large number of methods, procedures and oxidizing agents have been proposed for this type of transformation. Traditional synthesis is performed by using stoichiometric amounts of oxidants which are dangerous and can create a great quantity of waste [6-8]. Moreover, over-oxidation of the sulfoxides to sulfones is a common problem during the oxidation of sulfides [9]. From an economical and environmental viewpoint, an acceptable process involving the use of molecular oxygen or hydrogen peroxide as a primary oxidant in the presence of a catalyst is particularly attractive. Hydrogen peroxide produces water as by-product and controlled partial oxidation is easier to achieve than with molecular oxygen and air [10]. This feature has stimulated the development of useful procedures for H_2O_2 oxidation with various types of catalyst systems including transition metal complexes [11-14].

In recent years, various types of molybdenum based catalyst systems have been used in selective oxidation of sulfides to sulfoxides or sulfones. For example, $Na_2MoO_4.2H_2O$ is widely used as catalyst for hydrodesulfurization from petroleum [15-18]. This catalyst needs homogeneous reaction condition for hydrodesulfurization process and so it is difficult to recover and reuse the catalyst. Use of recycled catalysts is required for reducing the catalytic cost and the amount of used catalyst in the reactions. One way to attain this goal is to immobilize catalytic system onto a large surface area solid carrier.

In recent years, magnetic nanoparticles (MNPs) have attracted great interest as support materials in liquid phase reactions because they have unique physical properties and can be easily separated from reaction mixture by an external magnet [19,20]. Therefore, the recovery of catalysts is much easier than by filtration or centrifuge techniques. The Fe_3O_4 core trends to be oxidized or dissolved in acidic conditions during the treatment procedure. One of the materials can be used for coating of Fe_3O_4 is SiO_2. There are several advantages of using a silica shell as the stabilizer. Silica is chemically inert, and therefore does not affect the redox reaction at the core surface. The nonmagnetic shell can suppress the particle–particle magnetic bipolar interaction and prevent them from aggregating and agglomerating. Also, the silica shell acts as a stabilizer, limiting the effect of the outside environment on the core particles so that the Fe_3O_4 cores are not prone to oxidize as a response to the lowered magnetic performance γ–Fe_2O_3. In the present work, we report our results about Fe_3O_4@SiO_2 functionalized with ammonium molybdate as a recoverable heterogeneous catalyst for selective oxidation of sulfides to sulfoxides in the presence of 30% H_2O_2.

2. Experimental

2.1 Reagents and analysis

All chemicals and solvents were purchased from Sigma-Aldrich and used without further purification. Molybdenum content of the catalyst samples were determined by X-ray fluorescence (XRF ARL8410). A TGA-Q5 thermogravimetric analyzer was used to study the thermal properties of the compounds under an inert N_2 atmosphere (at 20 mL min^{-1}) and heating at a rate of 10 °C min^{-1}. X-ray diffraction (XRD) patterns of prepared catalyst were recorded with a APD 2000, using Cu Kα radiation (50 kV, 150 mA) in the range 2θ=10-120°. The SEM analysis was done with a KYKY-EM3200 with maximum acceleration voltage of the primary electron between 20 and 25 kV. Energy-dispersive X-ray spectroscopy (EDX) on the catalyst *I* was performed by Sirus SD. FT-IR spectra were recorded with ABB Bomem MB100 Fourier Transform Analyzer.

2.2 Preparation of magnetic nanoparticles (MNPs)

The MNPs were prepared as reported [21]. Briefly, $FeCl_3.6H_2O$ (4.8 g, 0.018mol) and $FeCl_2.4H_2O$ (1.8 g, 0.0089 mol) were added to 100 mL deionized water and vigorously stirred (700 rpm) under N_2 atmosphere until the salts dissolved completely. Then, 10mL of 25% NH_4OH was added quickly into the reaction mixture in one portion, which MNP black precipitate was formed immediately. After continuously stirring by mechanical stirrer for 1h, the precipitate was separated by external magnet and washed with the double distilled water (five times), then vacuum-dried at 50 °C for overnight.

2.3 Fe_3O_4 magnetic nanoparticles (MNPs) coated by silica (Fe_3O_4@SiO_2)

The prepared MNPs (1g) were homogeneously dispersed in the mixture of ethanol (80mL), deionized water (20mL) and pH of solution was adjusted to 10 by adding aqueous ammonia. Tetraethoxysilane (TEOS, 4.2 mmol) was added to the solution and stirred at 50 °C for 6 h to obtain Fe_3O_4@SiO_2 MNPs. After washing with ethanol and water for several times, Fe_3O_4@SiO_2 MNPs were dried at 60 °C for overnight.

2.4 Preparation of Fe_3O_4@SiO_2 coated by 3-aminpropyltriethoxysilane (Fe_3O_4@SiO_2-APTES)

The functionalization of Fe3O4@SiO2 (1g) were performed with 3-aminpropyltriethoxysilane (4.4 mmol, 1mL) in dry toluene for 24 h. The solid material was washed with toluene, methanol and ethanol and then dried overnight in an oven at 60 °C. This product will be referred as Fe_3O_4@SiO_2-APTES.

2.5 Preparation of catalyst *I*

The resulting Fe_3O_4@SiO_2-APTES (1g) was reacted with excess of HCl (1M, 5mL) solution for 4 h and then separated by magnet, washed with water and ethanol, and then dried in vacuum desicator at 60 °C for overnight to afford surface bound ammonium chloride. Finally, the prepared material (1g) was ultrasonically dispersed in water (15mL) and then Ag_2MoO_4 (0.15g, 0.4mmol) was added to the dispersed material in water at room temperature. The mixture was stirred for 1 h and then was magnetically separated and washed several times with water and ethanol and then dried to afford the catalyst *I* (Scheme 1).

(Scheme 1)

2.6 General procedure for the oxidation of sulfides to sulfoxides

To a solution of sulfide (1 mmol) and 30% H_2O_2 (3 equivalent) in CH_3CN (10 mL), catalyst *I* (0.189 g, 3 mol% Mo) was added and the mixture was stirred at room temperature for the time specified. Completion of the reaction was indicated by Thin Layer Chromatography (TLC) (n-hexane/ethylacetate 3.5:1) and GC. After completion of the reaction, Et_2O was added and the catalyst was separated by a small magnet placed at the bottom of the flask. Finally, the excess of solvent was removed under reduced pressure to give the corresponding pure sulfoxide. Further purification was achieved by chromatography on silica gel with n-hexane/ethylacetate. All reaction products were identified by GC chromatogram, IR spectra and melting point as compared with authentic samples.

3. Results and discussion

3.1 Catalyst characterization

The IR spectrum of catalyst *I* shows peaks which are characteristic of MoO_4^{2-} anion, which clearly differs from that of Fe_3O_4@SiO_2-APTES. The absorption peaks in 884 and 939 cm^{-1} (Fig. 1), were attributed to the M-O stretching frequency in MoO_4^{2-} species [22]. Also, peaks at 577 and 1101cm^{-1} were attributed to stretching frequency of Fe-O and Si-O, respectively [23].

The FT-IR spectrum of catalyst *I* also shows C-H stretching vibrations of APTES in around 2928 cm^{-1} and 2850 cm^{-1}. Therefore, the presence of the organic groups on the surface of catalyst *I* was confirmed by FT-IR spectroscopy (Fig. 1).

(Fig. 1)

Thermal analysis of the samples gives information about the thermal stability of catalyst *I*. In the TGA curve of catalyst (Fig. S1 of supporting information), the weight loss below 100°C (<1.57%) is attributed to residual physisorbed water and /or organic solvents, which was applied during the catalyst *I* prepared. Analysis of TGA diagram strongly suggests that catalyst *I* is stable and no further weight loss occurs below 200°C. The largest weight loss was occurred between 200 °C and 500 °C which is corresponding to 4.63% of the initial sample weight. This is due to the decomposition of the grafted APTES organic molecule on surface which is consistent with covalently bonded the aminopropyl group to the surface of MNPs.

Typical loading of surface-bound amino group was determined by TGA analysis which shows a loading 0.33 mmol g^{-1}. However, from the simultaneous XRF analysis of the catalyst *I* for molybdenum it was calculated that the loading molybdenum in catalyst *I* was 0.16 mmol g^{-1}. From this result, it was concluded that ratio between MoO_4^{2-} anion and the surface-bound ammonium group is 1:2 (Scheme 1).

The XRD pattern of catalyst match completely with the standard Fe_3O_4 sample (Fig. S2 in supporting information). The XRD spectrum of Fe_3O_4 clearly matches with the literature data from JCPDS PDF-2 Data Base (Card number 89-43191, 19-0629, 79-0419). Presence of diffraction peaks in XRD spectra of the catalyst I at $2\theta=30.2, 35.8, 43.4, 53.2, 57.2, 62.6$ were in good agreement with the corresponding (220), (311), (400), (422), (551) and (440) diffraction planes of Fe_3O_4 MNPs.

SEM image showed that the encapsulated nanoparticles were present as uniform particles (Fig. 2).

(Fig. 2)

From EDX analysis, the molybdenium peak clearly confirms the presence of a molybdate anion on catalyst I (Fig. 2). As seen from XRF and EDX analyses, there is a trace of Ag element on the catalyst because the ratio of Mo and ammonium group on the surface is not 1:2 exactly. Magnetic measurement of Fe_3O_4, $Fe_3O_4@SiO_2$ and catalyst I was investigated with a Quantum Design vibrating sample magnetometer (VSM) at room temperature in an applied magnetic field sweeping from −10 to 10 kOe. All of the magnetic particles exhibited superparamagnetic behavior and had little hysteresis, remanence and coercivity. The coat of silica resulted in the decrease in the magnetic strength of the composite because of the weight contribution from the nonmagnetic portion. The saturation magnetization of catalyst *I* was 21.5emu g^{-1} (Fig. S3), which was sufficient for magnetic separation with a conventional magnet.

3.2 Oxidation of sulfides to sulfoxides using catalyst *I*

In order to optimize the reaction conditions and test the activity of catalyst *I*, we examined the oxidation reaction of methyl phenyl sulfide as a model compound using 30% H_2O_2 under various reaction conditions in terms of time and product yield (Table 1). As seen in Table 1, no significant amount of sulfoxide was produced in absence of catalyst *I*.

(Table 1)

The results show (Table 1) that the optimize conditions for the complete conversion of methyl phenyl sulfide to methyl phenyl sulfoxides is in the presence of 30% H_2O_2 (3 equiv.) and catalyst *I* (3 mol % Mo, 189 mg) with CH_3CN as solvent at room temperature. Also, at a higher temperature and higher concentration of H_2O_2, the reaction took place at a shorter time with over oxidation and sulfone was formed. To assess generality and efficiency of the method, different aromatic, linear and benzylic sulfides were reacted using 30% H_2O_2 in the presence of catalyst *I* and CH_3CN as solvent under optimized reaction conditions (Table 2). As seen in Table 2, various types of sulfoxides were obtained in good to excellent yields. Therefore, these results show that the protocol was general and efficient.

(Table 2)

The chemoselectivity of the presented protocol was investigated in the selective oxidation of sulfides containing groups such as OH, $COOCH_3$ and double bond. These functional groups remained intact during the conversion of sulfide to sulfoxides (Table 2. entries 7-10)

The reusability of the catalyst *I* was evaluated in methyl phenyl sulfide oxidation at room temperature employing aqueous 30% H_2O_2 for 1 mmol of substrate. The catalyst was separated by external magnet after each cycle, washed with CH_2Cl_2 and then placed into a fresh reaction mixture. As shown in Fig. 3, the catalyst was reused seven times and no significant loss of activity was observed.

(Fig. 3)

To explore the catalyst leaching, we completely terminated the reaction by a removal of catalyst from the reaction mixture at 50% yield of methyl phenyl sulfoxide and the solution was kept back for oxidation under the same conditions did not increase the product yield. Inductively coupled plasma-atom emission spectrometer (ICP-AES) analysis of the liquid phase confirmed that the content of molebdenuim in the solution was 1.5% that this amount is acceptable. These results confirm that the reaction is attributed to the heterogeneous catalyst and leaching is low.

The efficiency of this method is demonstrated by compassion our results on the oxidation of methyl phenyl sulfide with data from the literature (Table 3). These results clearly point out the efficiency of the proposed methodology (Table 3, last entry) in both activity and recyclability of catalyst *I* as compared to literature reports involving several heterogeneous systems under various conditions (Table 3, entries 1-6) [9, 24-28].

(Table 3)

A plausible catalytic mechanism for the oxidation of sulfides to sulfoxides, which is the first stage of the oxidation process, is depicted in Scheme 2. In the first step, peroxo-molybdate species is formed and then the subsequent nucleophilic attack of the sulfur atom in the sulfide is performed on the peroxo species. As known, the role of the metal atom is to form peroxo-metal species which are able to activate the H_2O_2 molecule [18,6,29].

(Scheme 2)

4. Conclusion

We have developed efficient magnetic catalyst for the oxidation of sulfides to sulfoxides using H_2O_2 as oxidant at room temperature. This catalyst can be easily prepared from commercially available starting materials. Also, the catalyst *I* can be considered as heterogeneous version of Na_2MoO_4. Therefore, it is possible to recover and reuse the catalyst for several reaction cycles without considerable loss of activity. The main advantages of the present synthetic protocol are mild conditions and easy magnetic separation of the catalyst.

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Figure Caption

Scheme 1. Preparation of Catalyst *I*

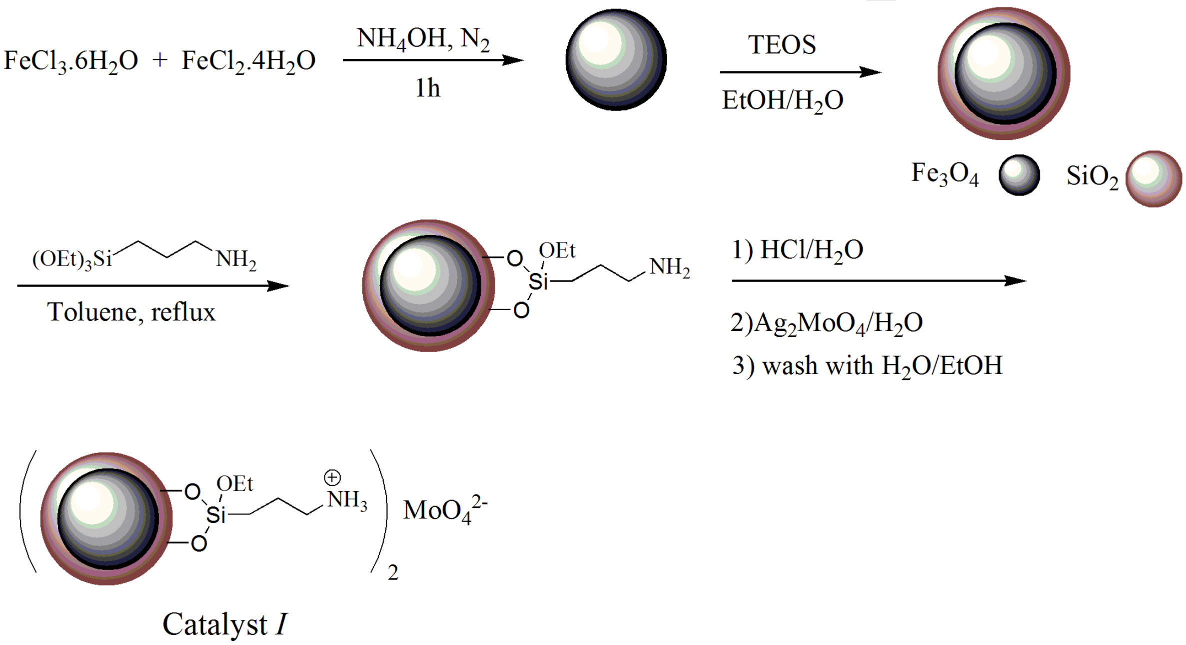
Scheme 2. Proposed mechanism for the sulfide oxidation with H_2O_2 in the presence of molybdate anion

Fig. 1 (a) FT-IR spectra of Fe_3O_4@SiO_2-APTES and (b) the catalyst *I*

Fig. 2 (a) SEM image and (b) EDX analysis of the catalyst *I*

Fig. 3 Catalyst reusability

Scheme 1.



$FeCl_3.6H_2O$ + $FeCl_2.4H_2O$
NH_4OH, N_2
1h
TEOS
$EtOH/H_2O$
Fe_3O_4
SiO_2
$(OEt)_3Si$
NH_2
Toluene, reflux
O
OEt
Si
O
NH_2
1) HCl/H_2O
2)Ag_2MoO_4/H_2O
3) wash with $H_2O/EtOH$
O
OEt
Si
O
$\oplus$
NH_3
2
MoO_4^{2-}
Catalyst *I*

Scheme 2.

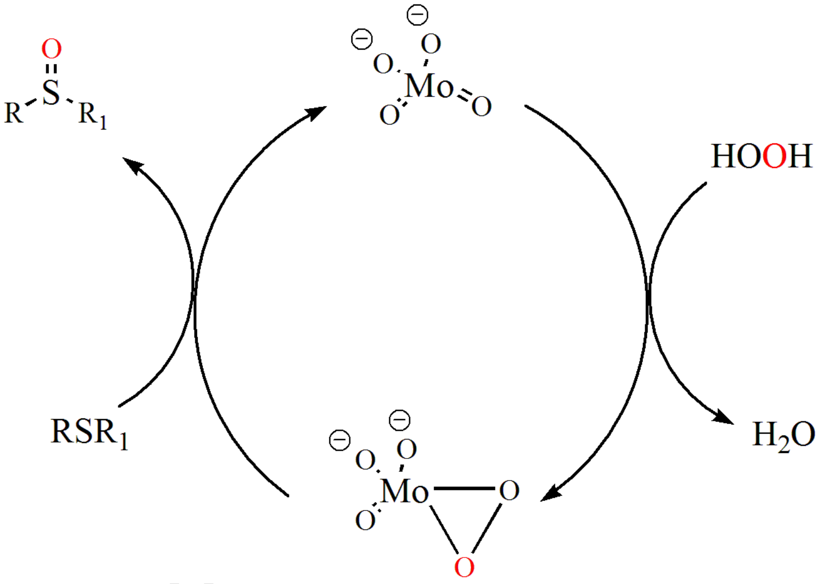
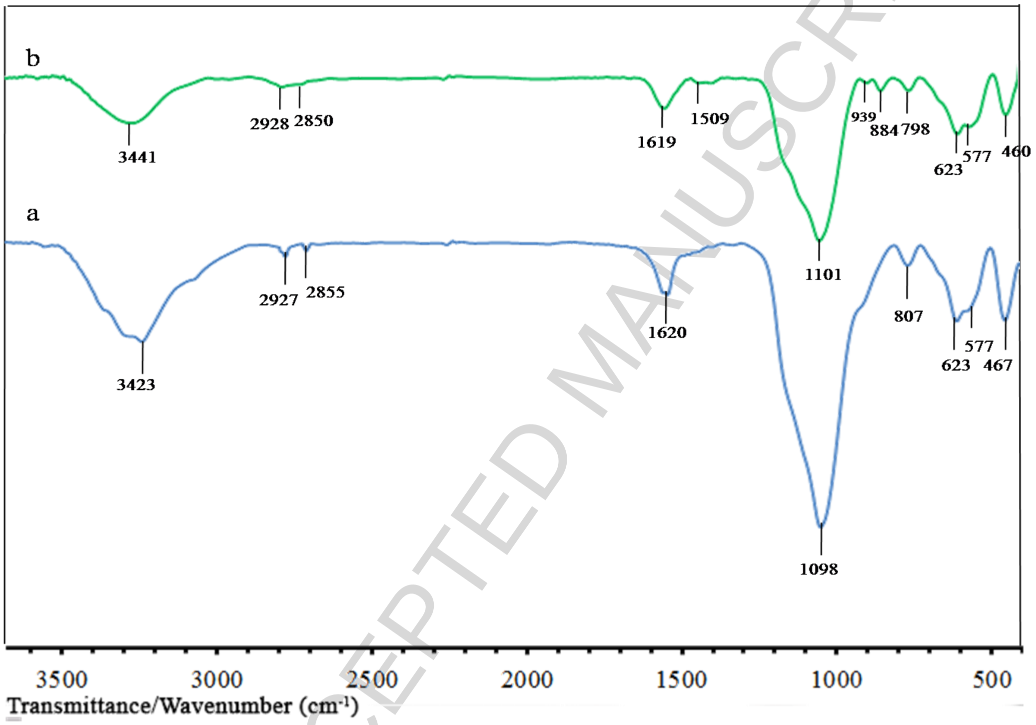


Fig. 1


b
3441
2928
2850
1619
1509
939
884
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623
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460
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a
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2927
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1620
807
623
577
467
1098
3500
3000
2500
2000
1500
1000
500
Transmittance/Wavenumber (cm-1)

Fig. 2

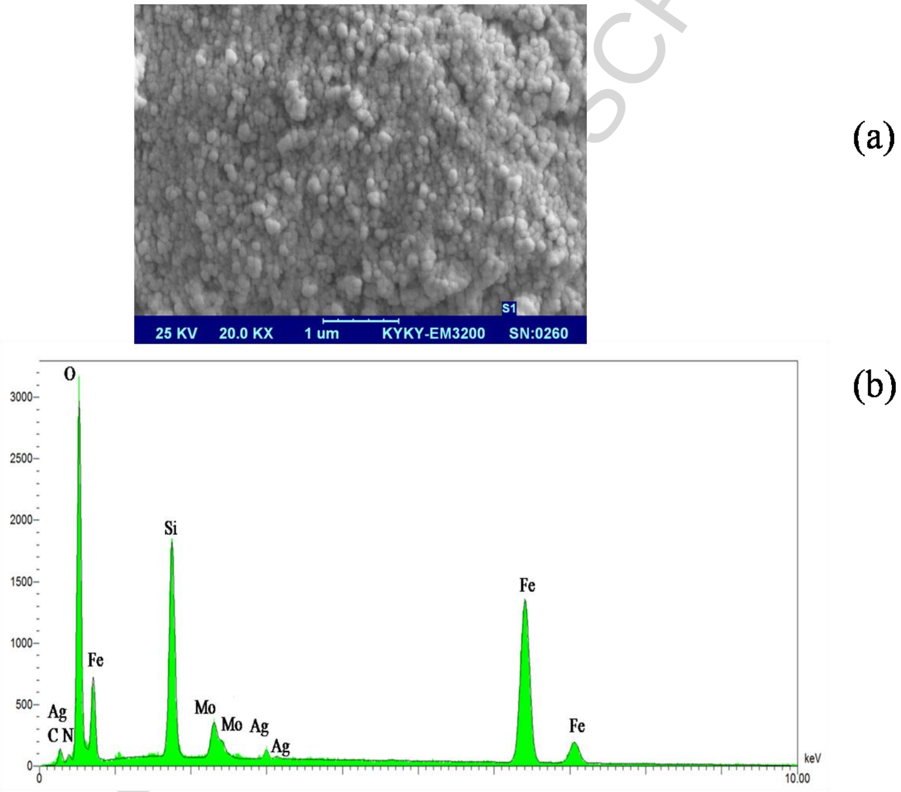
S1
25 KV
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Fig. 3

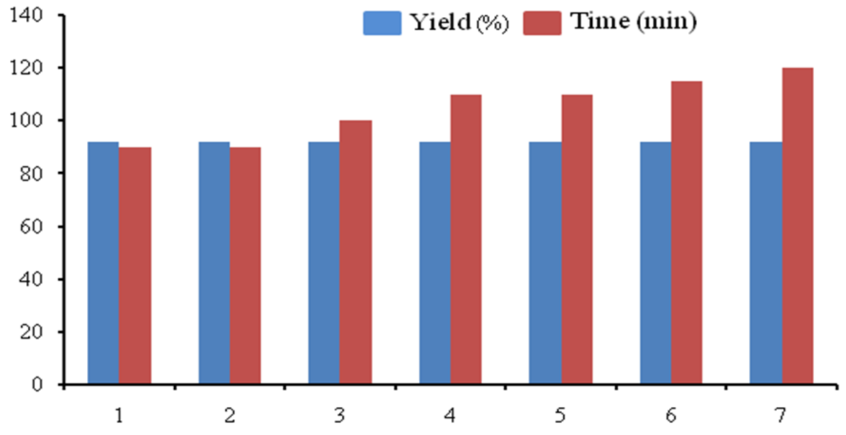
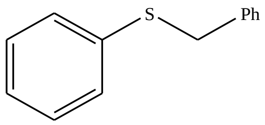
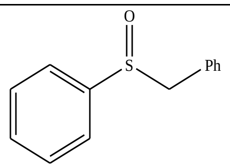
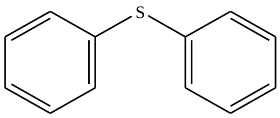
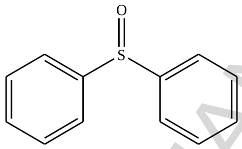
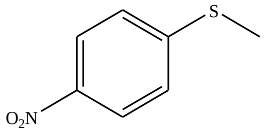
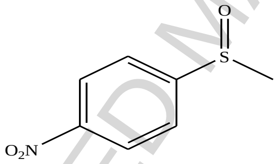
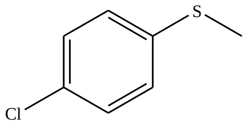
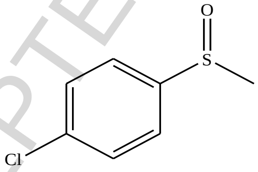
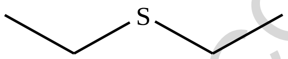
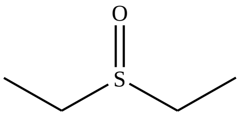
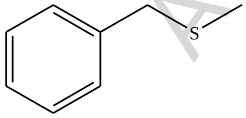
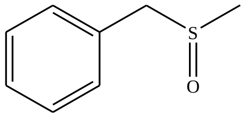
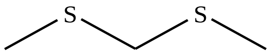
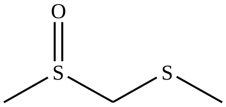
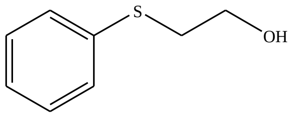
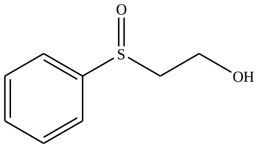
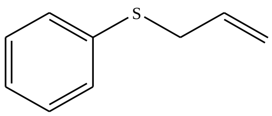
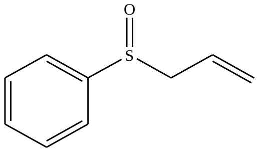


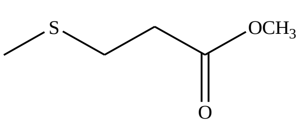
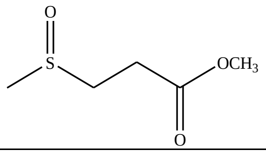
Table 1. Optimization of the reaction conditions for selective oxidation of methyl phenyl sulfide (1mmol) to methyl phenyl sulfoxide in the presence of H_2O_2 (3 equiv) and the catalyst *I* at room temperature.

Entry	Catalyst *I* %(g)	Solvent	Time (h)	Con. (%)	Yield (%)[a]	Sel. (%)[b]
1	-	CH_3CN	24	9	9	100
2	1mol%(0.063)	Water	5	59	55	93
3	1mol%(0.063)	CH_2Cl_2	5	71	70	98
4	1mol%(0.063)	CH_3CN	5	84	82	97
5	1.5mol%(0.093)	CH_3CN	3	88	84	95
6	2mol%(0.125)	CH_3CN	1.5	94	91	96
7	3mol%(0.189)	CH_3CN	1.5	96	92	95
8	3mol%(0.189)	CH_3CN	40 min	100[c]	75	75
9	3mol%(0.189)	CH_3CN	50 min	100[d]	78	78
10	1mol%(0.063)	CH_2Cl_2/MeOH	5	79	78	98
11	1mol%(0.063)	n-Hexane	5	51	50	98

[a]Sulfoxide yield, [b] Sulfoxide selectivity, [c]Temperature is 60 °C, [d]Temperature is 40 °C and the amount of 30% H_2O_2 is 5 equiv.

Table 2. Oxidation of sulfides to the corresponding sulfoxides using 30% H_2O_2 and catalyst *I*[a].

Entry	Substrate	Product	Time (h)	Con. (%)[b]	Yield (%)	Sel. (%)[b]
1			4	90	85	94
2			4	83	79	95
3			6	85	83	98
4			4.5	92	88	96
5			50 min	96	88	92
6			1.5	100	91	91
7			1	100	94	94
8			2	97	90	93
9			4	93	89	96

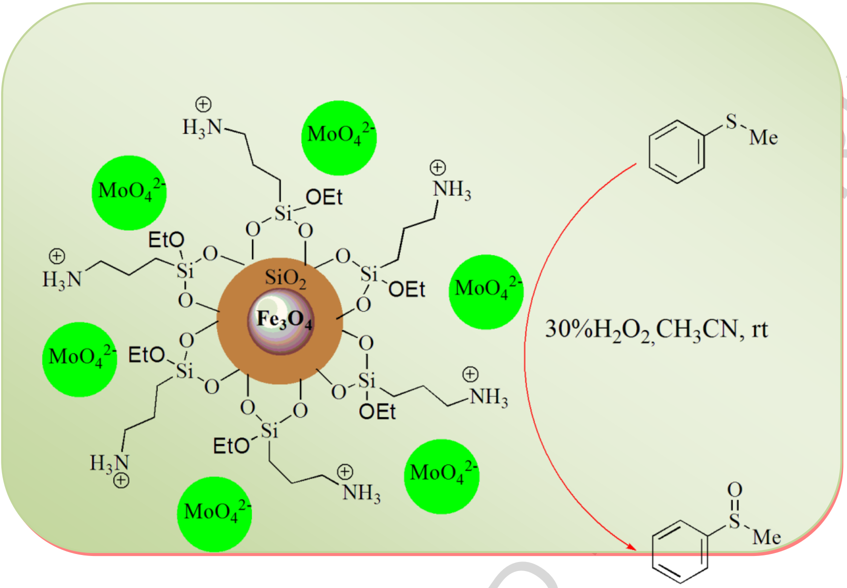
10			1	94	82	87

[a] Reaction conditions: sulfide (1 mmol), H_2O_2 (3 equiv.), catalyst *I* (3 mol%, 0.189 g) in acetonitrile as solvent at room temperature, stir.

[b] Determined by GC

Table 3. Comparison of the activity of various catalysts in the oxidation of methyl phenyl sulfide using H_2O_2.

Ref	Catalyst	Solvent	Temperature (°C)	Time (min)	Yield %	Reusability
9	Nanomagnetic-based N-propylsulfamic acid	Solvent-free	25	80	87	10
24	MCM-Mo	CH_3CN	40	60	> 99	4
25	Silica-based tungstate interphase	CH_2Cl_2/MeOH	25	90	82	8
26	Peroxotungstate supported on silica	CH_2Cl_2/MeOH	8	2.5h	91.9	6
27	Tungstate-exchanged Mg-Al-LDH catalyst	H_2O	25	30	88	6
28	VO(acac) 2-resin	H_2O	25	15	> 99	5
This work	Fe_3O_4@SiO_2/Mo	CH_3CN	25	90	92	7



Graphical abstract

Highlights

- An efficient magnetic catalyst is synthesized.
- The catalyst recovery is carried out by applying an external magnet device.
- Various types of aromatic and aliphatic sulfides are selectively oxidized to sulfoxides