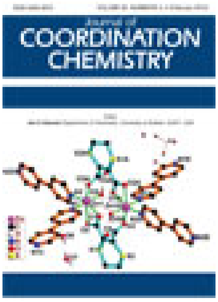
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:44
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

# Nanoparticle supported, magnetically separable vanadium complex as catalyst for selective oxidation of sulfides

Mojtaba Bagherzadeh [a], Mohammad Mehdi Haghdoost [a] & Ayoob Shahbazirad [a]

[a] Chemistry Department, Sharif University of Technology, P.O. Box 11155-3615, Tehran, Iran

Published online: 02 Feb 2012.

To cite this article: Mojtaba Bagherzadeh, Mohammad Mehdi Haghdoost & Ayoob Shahbazirad (2012) Nanoparticle supported, magnetically separable vanadium complex as catalyst for selective oxidation of sulfides, Journal of Coordination Chemistry, 65:4, 591-601, DOI: 10.1080/00958972.2012.657188

To link to this article: http://dx.doi.org/10.1080/00958972.2012.657188

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

*Journal of Coordination Chemistry*
Vol. 65, No. 4, 20 February 2012, 591–601

# Nanoparticle supported, magnetically separable vanadium complex as catalyst for selective oxidation of sulfides

MOJTABA BAGHERZADEH*, MOHAMMAD MEHDI HAGHDOOST and AYOOB SHAHBAZIRAD

Chemistry Department, Sharif University of Technology,
P.O. Box 11155-3615, Tehran, Iran

(*Received 20 October 2011; in final form 23 December 2011*)

A magnetically recyclable vanadium(V) catalyst was synthesized by covalent anchoring of VO(salen)Cl on silica-coated $Fe_3O_4$ nanoparticles. This straightforward preparation yields magnetically separable $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles with high vanadium loading. These nanoparticles were efficient catalysts for selective oxidation of sulfides to corresponding sulfoxides with urea hydrogen peroxide in excellent yields. Leaching and recycling experiments revealed that the nanocatalyst can be applied for nearly complete oxidation of sulfides for at least five successive cycles.

*Keywords*: Magnetic separation; Nanocatalyst; Vanadium(V); Oxidation of sulfides; Surface functionalization

## 1. Introduction

In many cases, application of the homogeneous catalysts on industrial scale has been prevented due to difficult separation and regeneration of the catalyst from the reaction mixture. Using heterogenized homogeneous catalysts is an attractive option to facile separation of catalyst, simplified product work-up and continuity of catalytic system [1–3]. However, immobilization of a homogeneous catalyst on solid supports somewhat facilitates its separation but normally results in a decrease in the active surface area and the reactivity of the catalyst [4]. Rational improvement of the catalytic systems will require advanced materials that have a high reactivity toward the chemical reactions and can be recycled and reused through simple separation and regeneration methods [5]. Homogeneous catalysts immobilized on magnetic nanoparticles (MNPs) surface occupy a unique position among these advanced materials due to combining the advantages of both homogeneous and heterogeneous catalysts [4–10]. Because of large surface area, nanoparticles can carry a very large payload of catalytically active species and therefore exhibit high catalytic activity and selectivity [5]. In addition, superparamagnetic nature of MNPs enable very simple separation of the immobilized

---

*Corresponding author. Email: bagherzadeh@sharif.edu

*Journal of Coordination Chemistry*
ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2012.657188

catalysts from the reaction mixture using an external magnet, which is typically more effective than filtration or centrifugation [8].

For this purpose and also to continue our study on the catalytic activity of metal complexes for synthesis of organic compounds [11–15] we herein report that an $Fe_3O_4$ nanoparticle-supported vanadium(V) catalyst ($Fe_3O_4$@$SiO_2$@VO(salen)) efficiently catalyzes selective oxidation of sulfides to sulfoxides using urea hydrogen peroxide (UHP) as oxidant. This catalytic system features two major novelties: (1) this is the first time that a magnetically recyclable nanocatalyst has been used in catalytic oxidation of sulfides and (2) this is the first report of a magnetically separable vanadium complex. The present catalyst also was easily recovered and reused for more than five times without any loss of catalytic activity or selectivity.

## 2. Experimental

### 2.1. *Methods*

Gas chromatographic (GC) analyses were performed on an Agilent Technologies 6890 N, 19019 J-413 HP-5, 5% phenyl methyl siloxane, capillary 60 m × 250 μm × 1 μm. $^1$H NMR and $^{13}$C NMR spectra were recorded at room temperature with a Bruker FT NMR 500 (500 MHZ) spectrophotometer using $CDCl_3$ as solvent and chemical shifts are reported in ppm with tetramethylsilane as an internal standard. Elemental analyses (C, H, and N) were performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elementar-Analysesysteme, GmbH). IR spectra were recorded as KBr pellets using an ABB FT-IR spectrophotometer. Measures of pH were carried out by a Mettler Toledo S40 SevenMulti$^{TM}$ pH-meter. Dynamic light scattering (DLS) analysis was conducted using a NanoZS (red badge)-ZEN3600 light scatter from Malvern instrument at 25°C. The chemical analysis of compounds was carried out in an ICP-AES Varian equipment. X-ray diffraction (XRD) pattern was obtained by a D4 ENDEAVOR diffractometer (Bruker AXS Inc.) with Cu-K$\alpha$ as a radiation source; the scan range ($2\theta$) was from 5° to 70°.

### 2.2. *Synthesis of VO(salen)Cl complex*

$H_2$salen (bis(*N*,*N*′-disalicylalethylenediamine)) was prepared according to the reported procedure [16]. 1.73 g (4 mmol) of $H_2$Salen was loaded into a 100 mL Schlenk flask and filled with 20 mL dry $CH_2Cl_2$. To this stirring solution, 0.20 mL (0.70 g, 4 mmol) of freshly prepared $VOCl_3$ was added *via* syringe. After stirring under argon at room temperature for 2 h, the solvent was removed under vacuum, yielding dark green powder of VO(salen)Cl.

**$H_2$salen**: Yield: 97%; Anal. Calcd for $C_{16}H_{16}N_2O_2$ (%): C, 71.62; H, 6.01; N, 10.44. Found: C, 71.52; H, 5.97; N, 10.49. IR (KBr, cm$^{-1}$): 1634, 3141, 1196, 739, 1583; $^1$H NMR (500 MHz, $CDCl_3$, 21°C): 3.9 ppm (s, 2H, $CH_2$), 6.9 ppm (d, 1H, CH), 7.2 ppm (d, 1H, CH), 7.3 ppm (m, 2H, CH), 7.4 ppm (m, 2H, CH), 8.6 ppm (s, 1H, N(CH)), 13.4 ppm (s, 1H, OH); $^{13}$C NMR (500 MHz, $CDCl_3$, 21°C): 69.6, 117.3, 119.4, 132.5, 133.2, 161.4, 167.8 ppm; Melting point: 128°C; Mol. Wt.: 268.31.

**VO(salen)Cl**: Yield: 80%; Anal. Calcd for $C_{16}H_{14}ClN_2O_3V$ (%): C, 52.12; H, 3.83; N, 7.60. Found: C, 52.24; H, 3.83; N, 7.57. IR (KBr, $cm^{-1}$): 654, 763, 1619, 970, 1264, 1550; $^1H$ NMR (500 MHz, $CDCl_3$, 21°C): 4.4 ppm (s, 2H, $CH_2$), 6.9 ppm (d, 1H, CH), 7.2 ppm (d, 2H, CH), 7.6 ppm (m, 2H, CH), 8.6 ppm (s, 2H, N(CH)); $^{13}C$ NMR (500 MHz, $CDCl_3$, 21°C): 166, 165.4, 137.9, 135.5, 123.2, 122.2, 115.3, 61.41 ppm; Mol. Wt.: 368.69.

### 2.3. *Synthesis of $Fe_3O_4$ nanoparticles*

$Fe_3O_4$ nanoparticles were synthesized according to the procedure described previously [17]. In brief, under $N_2$ atmosphere, 5.2 g (19.3 mmol) of $FeCl_3 \cdot 6H_2O$, 2 g (10.0 mmol) of $FeCl_2 \cdot 4H_2O$ and 0.85 mL concentrated HCl were dissolved in 25 mL degassed water. This solution was added dropwise at room temperature to 250 mL of NaOH solution (1.5 mol $L^{-1}$) under $N_2$. The reaction mixture was vigorously stirred for 30 min (1300 rpm). The formed black precipitates were separated using a strong magnetic field (0.5 T magnet) and washed several times with degassed water. Finally, for storage, $Fe_3O_4$ nanoparticles were dispersed in 200 mL degassed water under $N_2$. The density of the resulting solution was found to be approximately 11.2 mg $mL^{-1}$.

### 2.4. *Synthesis of $Fe_3O_4$@$SiO_2$ nanoparticles*

In the next step, $Fe_3O_4$ MNPs were coated with a thin layer of silica [18]. One gram of freshly prepared $Fe_3O_4$ nanoparticles was added into 30 mL of an aqueous solution of citric acid (0.02 g $mL^{-1}$), then the pH was adjusted to 5.2 using ammonia, and the mixture was heated to 80–90°C for 1.5 h. After heating, the pH of the reaction mixture was increased with ammonia to pH = 11 and 1.25 mL of tetraethylorthosilicate (TEOS) dissolved in ethanol (12.5 mL) was added dropwise into the suspension of particles. The mixture was stirred at room temperature for 24 h to let the base-catalyzed hydrolysis and condensation of TEOS monomers on the nanoparticle surface go to completion. Finally, the dark brown $Fe_3O_4$@$SiO_2$ nanoparticles were separated using a 0.5 T magnet and were washed with distilled (not degassed) water (5 times, 150 mL) and ethanol (5 times, 150 mL).

### 2.5. *Synthesis of $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles*

In a subsequent process, $Fe_3O_4$@$SiO_2$ nanoparticles were functionalized with a vanadium(V) complex. A total of 0.7 g of the $Fe_3O_4$@$SiO_2$ nanoparticles was suspended in 100 mL of dry dichloromethane (DCM) and then 0.1 g (0.27 mmol) of VO(salen)Cl was added to the suspension of nanoparticles and the reaction mixture was refluxed for 10 h. After cooling, nanoparticles were separated using a strong magnet, washed with dry DCM several times, and then dried in an oven for 24 h, yielding a green-brown powder.

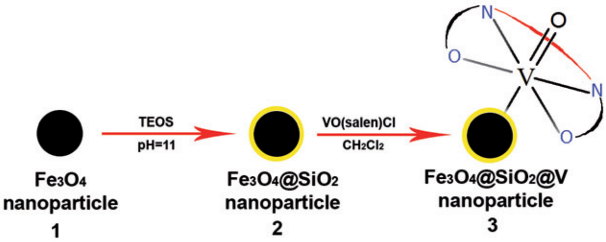
### 2.6. *General conditions for catalytic oxidation of sulfides*

A typical reaction using the $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles as catalyst and sulfides as substrate is described as follows. To a solution of sulfide (0.4 mmol), chlorobenzene (40 µL, 0.4 mmol) as the internal standard and catalyst (0.01 g, containing 0.031 mmol of vanadium complex) in a (1 : 1) mixture of $CH_3OH$–$CH_2Cl_2$ (1 mL), was added UHP (0.042 g, 0.45 mmol) as the oxidant. The mixture was stirred at room temperature for 6 h. The catalyst particles were then collected at the bottom of the test tube using a magnet, supernatant carefully decanted and formation of products was monitored by GC. To establish the identity of the products clearly, the retention times and spectral data of products were compared with those of commercially available sulfoxides and sulfones. After separation of catalyst nanoparticles, the supernatant was dried under vacuum at 40°C to yield the corresponding sulfoxide compound. Isolated products were weighted and also analyzed by $^1$H NMR. Washing several times with methanol and DCM, the catalyst particles were dried in vacuum and could be reused.

## 3. Results and discussion

Magnetically separable vanadium(V) catalyst was synthesized by the route schematically demonstrated in scheme 1. In the first step, $Fe_3O_4$ nanoparticles were prepared using the co-precipitation method and characterized with XRD (figure 1). Six characteristic peaks for $Fe_3O_4$ ($2\theta = 32.1$, 35.3, 43.1, 51.0, 54.9, and 64.1°), which correspond to (220), (311), (400), (422), (511), and (440) Bragg reflections, respectively, were observed. These peaks are consistent with the database in JCPDS file (PCPDFWIN v.2.02, PDF No. 85-1436) and reveal that the resultant nanoparticles were pure $Fe_3O_4$ with a cubic spinel structure without impurity phases.

The silica-coated nanoparticles (**2**) were prepared by hydrolysis and condensation of TEOS on the surface of the $Fe_3O_4$ nanoparticles (**1**). Figure 2 shows FT-IR spectra of the $Fe_3O_4$ MNP before and after being supported with a silica layer. The FT-IR spectrum of $Fe_3O_4$ nanoparticles exhibits significant absorption band at 597 cm$^{-1}$, while absorption band at 1055 cm$^{-1}$ was observed for the silica-coated nanoparticles which could be assigned to vibration of Si–O–Si bond [19]. As a result, FT-IR spectrum indicates that the surface of $Fe_3O_4$ nanoparticles has been coated by a silica layer. FT-IR spectrum of $Fe_3O_4$ MNP shows the presence of trace amount of water.



Scheme 1. Step-by-step synthesis of the $Fe_3O_4$@$SiO_2$@VO(salen) catalyst.

The results of the previous experiments show that base-catalyzed hydrolysis and condensation of TEOS provides the resulting particles with negative surface charges due to the surface formation of ($\equiv$SiO$^-$) [20]. It is expected that surface negative oxygen atoms (hard base) could replace the chloride at the axial position of VO(salen)Cl complex and link to the hard vanadium(V) cation. An interesting example of grafting vanadium(V) complex onto the silica surface *via* displacement of the chloride by free surface SiO$^-$ groups was recently reported [21]. With this idea in mind, we treated $Fe_3O_4$@$SiO_2$ nanoparticles with VO(salen)Cl in $CH_2Cl_2$ solvent to synthesize $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles (**3**). During optimization of this reaction, we observed that the $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles synthesis does not proceed in methanol and acetonitrile solvents. Comparing FT-IR spectra of **2** and **3** (figure 3), IR spectrum of $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles shows new peaks at 659, 765, 916, 971, 1013, 1039, 1087, 1255, 1277, 1402, and 1509 $cm^{-1}$, also observed in FT-IR spectrum of VO(salen)Cl. CHN analysis of the $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles gave the percentages of C, H, and N to be 7.52%, 2.24%, and 4.45%, respectively.

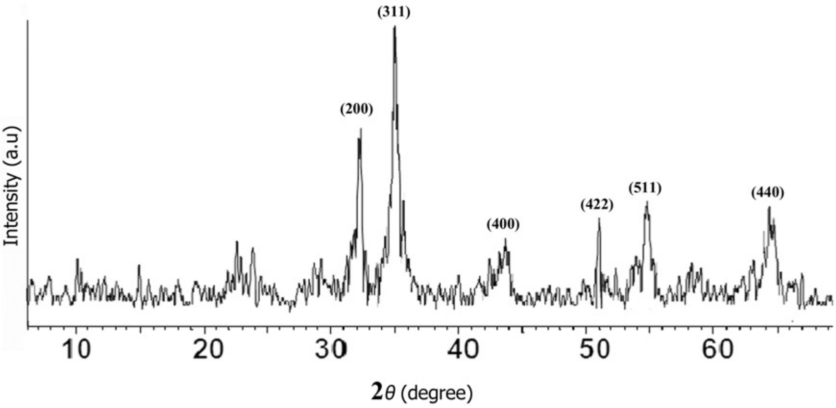


Figure 1. XRD patterns of the as-synthesized $Fe_3O_4$ nanoparticles.

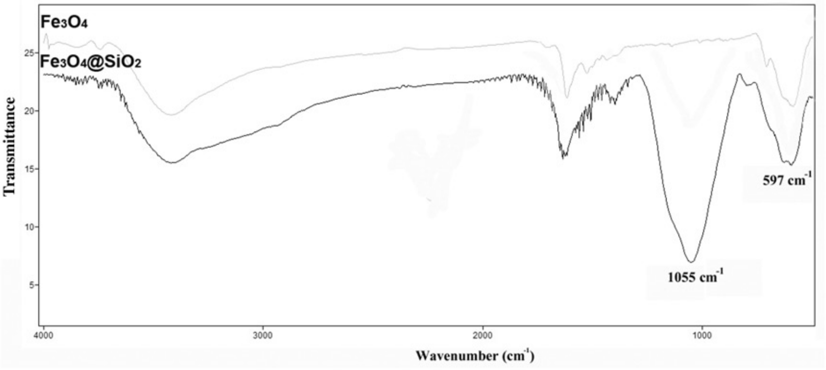


Figure 2. IR spectra of $Fe_3O_4$ (up) and $Fe_3O_4$@$SiO_2$ (down) nanoparticles.

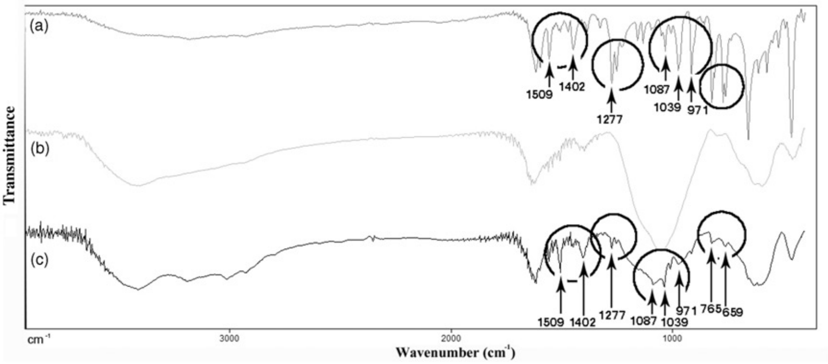


Figure 3. IR spectra of (a) VO(salen)Cl complex, (b) $Fe_3O_4$@$SiO_2$ nanoparticles, and (c) $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles.

The FT-IR spectrum, coupled with the elemental analyses, provide evidence for anchoring of vanadium(V) complex on silica-coated $Fe_3O_4$ nanoparticles. The loading of vanadium(V)-salen complex was 3.1 mmol $g^{-1}$, determined by ICP-AES test of vanadium after acid digestion. To the best of our knowledge, this loading value is much higher than that previously reported for similar systems [7, 10].

The average size and the size distribution of nanoparticles have been determined using DLS measurements. As can be seen in figure 4, for the synthesis of $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles (**3**), we started with $Fe_3O_4$ nanoparticles (**1**) of approximately 25 nm average diameter. These nanoparticles have narrow size distribution (12–32 nm). However, the DLS study of $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles (figure 4b) confirmed that the size distributions lie in the range 14–50 nm with 30 nm average diameters and 50–115 nm with 103 nm average sizes, corresponding to the uncoated and coated particles, respectively. These results also demonstrate that the $Fe_3O_4$@$SiO_2$@VO(salen) catalyst has particles well in the nanosize range.

Oxidation of sulfides to sulfoxides or sulfones is a fundamental chemical reaction and has been intensively studied due to economic and environmental benefits [11, 22–25]. The capability of $d^0$ metal complexes to activate peroxides led us to test the $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles as a heterogeneous catalyst for selective oxidation of sulfides (table 1). During the optimization of the catalytic conditions, it was observed that stirring $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles and **4** in $CH_2Cl_2$/MeOH solvent in the presence of UHP for 6 h afforded **5** in >99% yield and 95% selectivity (table 1, entry 5). To evaluate the effect of solvent, oxidation of sulfide **4** also was carried out in methanol, DCM, and acetonitrile (table 1, entries 6–8). Sulfoxide **5** was obtained in 93% conversion in methanol, but in DCM and acetonitrile, the reaction proceeded slowly and afforded lower conversion of **4**. Compared with other oxidants tested, UHP exhibited the highest conversion and selectivity; *tert*-butyl hydroperoxide (TBHP) also resulted in relatively high yield of product (table 1, entries 9–10) and cumene hydroperoxide (CHP) showed low activity (table 1, entry 11). In the presence of a radical scavenger such as 2,6-di-*tert*-butyl-*p*-cresol, the conversion reduced to 47% and remained almost constant (table 1, entries 12–13), suggesting a radical pathway. Control experiments indicated that no oxidation of sulfide **4** occurred in the absence of either $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles or oxidants (table 1, entries 1–2). In addition,

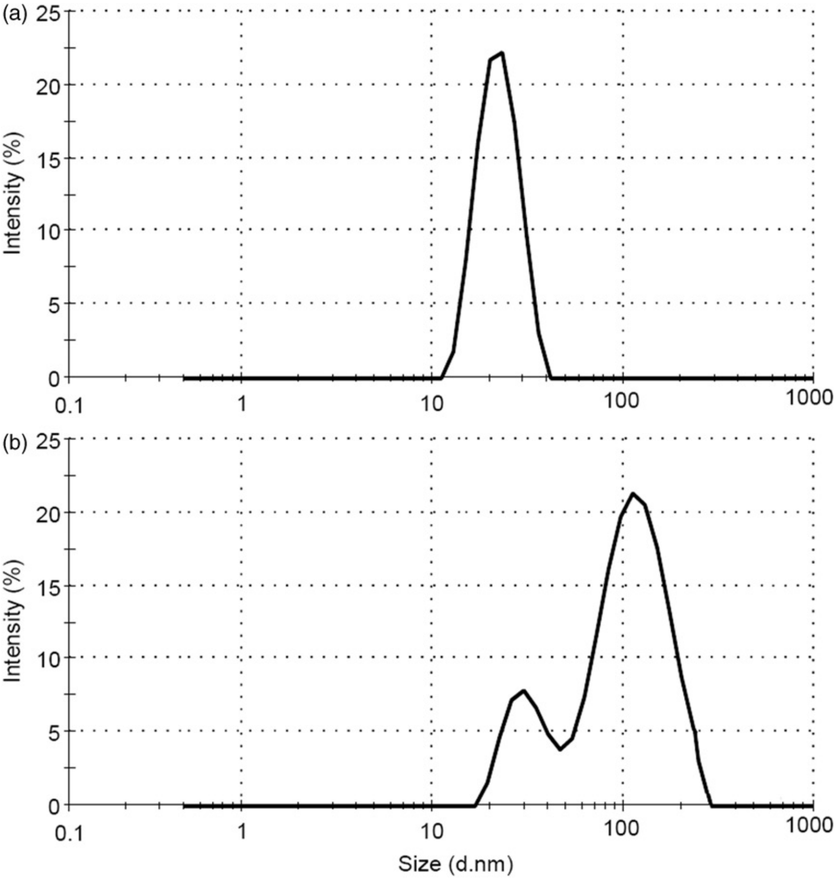


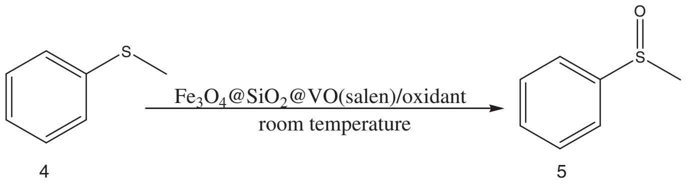
Figure 4. Size distribution of (a) bare $Fe_3O_4$ nanoparticles and (b) $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles.

the use of $Fe_3O_4$ or $Fe_3O_4$@$SiO_2$ nanoparticles in place of $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles did not promote oxidation (table 1, entries 3–4).

The reaction scope for $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles in the selective oxidation of sulfides is summarized in table 2. $Fe_3O_4$@$SiO_2$@VO(salen)/UHP system could oxygenate a wide range of sulfides, affording the corresponding sulfoxides in excellent conversion and selectivity. For example, arylalkyl sulfides (table 2, entries 1–2), diaryl sulfides (table 2, entries 3–5), and dialkyl sulfides (table 2, entries 6–7) were successfully employed. Conversions of diaryl sulfides (table 1, entries 3–5) were lower than others, as a result of the electronic and steric effect of the aryl groups. The highest yields were obtained for methylphenyl (table 2, entry 1) and diethyl (table 2, entry 7) sulfides. In the case of dioctyl sulfide (table 2, entry 6), the conversion of the substrate was also reduced by the steric effect of two octyl groups.

Catalyst stability and reusability are equally important issues for industrial applications of heterogeneous catalyst systems. The $Fe_3O_4$@$SiO_2$@VO(salen) nanocatalyst can be reused more than five times, by simple magnetic separation (figure 5), without significant loss in selectivity and activity (table 3). $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles retained their magnetic properties even after six successive usages.

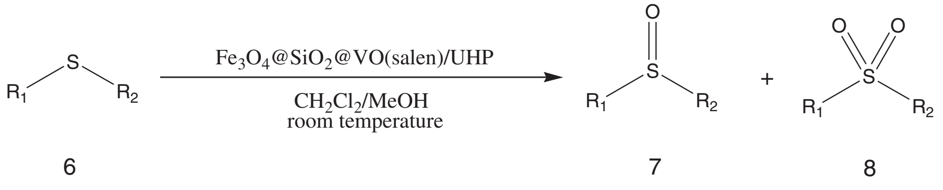
Table 1. Oxidation of methylphenylsulfide by $Fe_3O_4@SiO_2@VO(salen)$ catalyst.[a]



| Entry | Catalyst | Oxidant | Solvent | *t* (h) | Conversion[b,c] (%) | Selectivity to **5**[d] (%) |
|---|---|---|---|---|---|---|
| 1 | – | UHP | $CH_2Cl_2$/MeOH | 24 | Trace | – |
| 2 | $Fe_3O_4@SiO_2@VO(salen)$ | – | $CH_2Cl_2$/MeOH | 24 | Trace | – |
| 3 | $Fe_3O_4$ | UHP | $CH_2Cl_2$/MeOH | 24 | Trace | – |
| 4 | $Fe_3O_4@SiO_2$ | UHP | $CH_2Cl_2$/MeOH | 24 | Trace | – |
| 5 | $Fe_3O_4@SiO_2@VO(salen)$ | UHP | $CH_2Cl_2$/MeOH | 6 | >99 (83) | 95 |
| 6 | $Fe_3O_4@SiO_2@VO(salen)$ | UHP | MeOH | 6 | >99 (81) | 93 |
| 7 | $Fe_3O_4@SiO_2@VO(salen)$ | UHP | $CH_3CN$ | 6 | 64 | 75 |
| 8 | $Fe_3O_4@SiO_2@VO(salen)$ | UHP | $CH_2Cl_2$ | 6 | 13 | 100 |
| 9 | $Fe_3O_4@SiO_2@VO(salen)$ | TBHP | $CH_2Cl_2$/MeOH | 6 | 91 | 91 |
| 10 | $Fe_3O_4@SiO_2@VO(salen)$ | TBHP | $CH_3CN$ | 6 | 75 | 100 |
| 11 | $Fe_3O_4@SiO_2@VO(salen)$ | CHP | $CH_2Cl_2$/MeOH | 6 | 42 | 90 |
| 12 | $Fe_3O_4@SiO_2@VO(salen)$ | UHP | $CH_2Cl_2$/MeOH | 6 | 47[e] | 92 |
| 13 | $Fe_3O_4@SiO_2@VO(salen)$ | UHP | $CH_2Cl_2$/MeOH | 24 | 48[e] | 91 |
| 14 | VO(salen)Cl | UHP | $CH_2Cl_2$/MeOH | 1 | >99 | 100 |

[a] Reaction condition: sulfide (0.4 mmol), UHP (0.45 mmol), $Fe_3O_4@SiO_2@VO(salen)$ nanoparticles (0.01 g), 1 mL solvent, room temperature.
[b] Determined by GC using chlorobenzene as an internal standard.
[c] Values in parentheses are the isolated yields.
[d] Determined by GC, selectivity to sulfoxide = [sulfoxide %/(sulfoxide % + sulfone %)] × 100.
[e] In the presence of 2,6-di-*tert*-butyl-*p*-cresol (0.25 equiv.).

Table 2. Oxidation of sulfides by $Fe_3O_4@SiO_2@VO(salen)$ nanoparticles in the presence of UHP.[a]



| Entry | Substrate | Time (h) | Conversion[b,c] (%) | Selectivity to **7**[d] (%) |
|---|---|---|---|---|
| 1 | Methylphenyl sulfide | 6 | >99 (83) | 95 |
| 2 | Ethylphenyl sulfide | 6 | 84 | 89 |
| 3 | Diphenyl sulfide | 6 | 9 | 100 |
| 4 | Diphenyl sulfide | 30 | 37 | 100 |
| 5 | Diphenyl sulfide | 24 | 80 (54)[e] | 76 |
| 6 | Dioctyl sulfide | 6 | 60 | 100 |
| 7 | Diethyl sulfide | 4 | >99 (91) | 100 |

[a] Reaction condition: sulfide (0.4 mmol), UHP (0.45 mmol), $Fe_3O_4@SiO_2@VO(salen)$ nanoparticles (0.01 g), 0.5 mL $CH_2Cl_2$, 0.5 mL MeOH, room temperature.
[b] Determined by GC using chlorobenzene as an internal standard.
[c] Values in parentheses are the isolated yields.
[d] Determined by GC, selectivity to sulfoxide = [sulfoxide %/(sulfoxide % + sulfone %)] × 100.
[e] 8 mmol of UHP were employed.

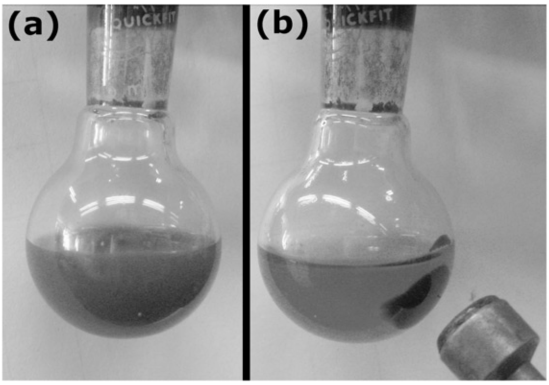
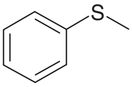
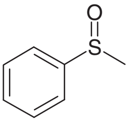
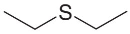
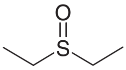
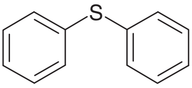
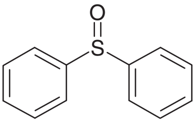


Figure 5. (a) $Fe_3O_4$@$SiO_2$@VO(salen) nanocatalyst dispersion in reaction mixture and (b) $Fe_3O_4$@$SiO_2$@VO(salen) nanocatalyst adsorbed on the magnet.

Table 3. Results of catalyst reuse experiments in the oxidation of various sulfides.[a]

| Entry | Substrate | Product | Cycles | Conversion[b,c] | Selectivity[d] |
|---|---|---|---|---|---|
| 1 |  |  | 1 | >99 (83) | 95 |
| 2 | | | 2 | >99 | 92 |
| 3 | | | 3 | >99 | 97 |
| 4 | | | 4 | >99 (93) | 93 |
| 5 | | | 5 | >99 | 97 |
| 6 | | | 6 | >99 (89) | 91 |
| 7 |  |  | 1 | >99 (91) | 100 |
| 8 | | | 2 | >99 | 100 |
| 9 | | | 3 | >99 (90) | 100 |
| 10 |  |  | 1 | 80 (54)[e] | 76 |
| 11 | | | 2 | 78[e] | 77 |

[a] Reaction condition: sulfide (0.4 mmol), UHP (0.45 mmol), $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles (0.01 g), 0.5 mL $CH_2Cl_2$, 0.5 mL MeOH, room temperature.

[b] Determined by GC using chlorobenzene as an internal standard.

[c] Values in parentheses are the isolated yields.

[d] Determined by GC, selectivity to sulfoxide = [sulfoxide%/(sulfoxide% + sulfone%)] × 100.

[e] 8 mmol of UHP were employed.

After each catalytic reaction, the catalyst particles were collected at the bottom of the test tube using a magnet, supernatant carefully decanted and analyzed by ICP-AES analysis to determine the amount of vanadium leaching. ICP-AES analysis did not show any leaching of vanadium species into the solution (< 0.01 ppm). In addition,

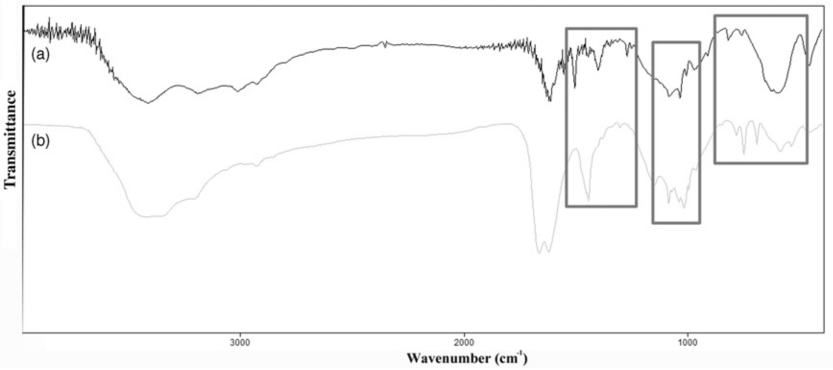


Figure 6. FT-IR spectrum of (a) freshly prepared $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles and (b) same catalyst after six reuses.

FT-IR pattern of catalyst was the same as freshly prepared $Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles (figure 6), which indicated that decomposition of surface vanadium complexes did not occur. These results imply high stability of the $Fe_3O_4$@$SiO_2$@VO(salen) catalyst.

## 4. Conclusion

$Fe_3O_4$@$SiO_2$@VO(salen) nanoparticles are efficient, easily recoverable catalysts for selective oxidation of sulfides. With this catalytic system, various sulfides were transformed to corresponding sulfoxide with the following advantages: (1) high conversions and selectivities; (2) applicability to a wide range of sulfides; (3) high loading value, and (4) successful recycle of catalyst by simple magnetic separation with stable conversion efficiency of 100%. We believe that such magnetically separable nanocatalysts for oxidation can be applied not only to sulfides but also to alkenes, alkanes, and alcohols. Further study on the wider applications of this efficient strategy is under exploration in our group.

## Supplementary material

Diphenyl sulfoxide: $^1$H NMR (500 MHz, $CDCl_3$, 21°C): 7.44–7.50 ppm (m, 3H), 7.67–7.69 ppm (m, 2H); Melting point: 68–70°C.

Methylphenyl sulfoxide: $^1$H NMR (500 MHz, $CDCl_3$, 21°C): 2.88 (d, 3H), 7.54 ppm (s, 5H); Melting point: 25–27°C.

Diethyl sulfoxide: $^1$H NMR (500 MHz, $CDCl_3$, 21°C): 1.46 ppm (t, 3H), 2.78 ppm (q, 2H).

## Acknowledgments

We acknowledge the Research Council of Sharif University of Technology for research funding of this project. We also thank Dr M.R. Hormozi-Nezhad for useful discussions.

## References

[1] E.D. Park, K.H. Lee, J.S. Lee. *Catal. Today*, **63**, 147 (2000).
[2] A.K. Kakkar. *Chem. Rev.*, **102**, 3579 (2002).
[3] N. End, K.-U. Schöning. *Top. Curr. Chem.*, **242**, 241 (2004).
[4] J. Zhang, W. Zhang, Y. Wang, M. Zhang. *Adv. Synth. Catal.*, **350**, 2065 (2008).
[5] C.W. Lim, I.S. Lee. *Nano Today*, **5**, 412 (2010).
[6] M.J. Jacinto, R. Landers, L.M. Rossi. *Catal. Commun.*, **10**, 1971 (2009).
[7] A.K. Tucker-Schwartz, R.L. Garrell. *Chem. Eur. J.*, **16**, 12718 (2010).
[8] F.-H. Lin, R.-A. Doong. *J. Phys. Chem. C*, **115**, 6591 (2011).
[9] Y. Sun, G. Liu, H. Gu, T. Huang, Y. Zhang, H. Li. *Chem. Commun.*, **47**, 2583 (2011).
[10] S. Shylesh, J. Schweizer, S. Demeshko, V. Schunemann, S. Ernst, W.R. Thiela. *Adv. Synth. Catal.*, **351**, 1789 (2009).
[11] M. Bagherzadeh, M. Amini, D.M. Boghaei, M.M. Najafpour, V. McKee. *Appl. Organomet. Chem.*, **25**, 559 (2011).
[12] M. Bagherzadeh, M. Amini. *J. Coord. Chem.*, **63**, 3849 (2010).
[13] M. Bagherzadeha, L. Tahsini, R. Latifi, V. Amani, A. Ellern, L.K. Woo. *Inorg. Chem. Commun.*, **12**, 476 (2009).
[14] M. Bagherzadeh, R. Latifi, L. Tahsini, M. Amini. *Catal. Commun.*, **10**, 196 (2008).
[15] M. Bagherzadeh, L. Tahsini, R. Latifi. *Catal. Commun.*, **9**, 1600 (2008).
[16] H. Diehl, C. Hach. *Inorg. Synth.*, **3**, 196 (1950).
[17] H. Bagheri, O. Zandi, A. Aghakhani. *Anal. Chim. Acta*, **692**, 80 (2011).
[18] S. Čampelj, D. Makovec, M. Drofenik. *J. Mag. Mag. Mater.*, **321**, 1346 (2009).
[19] K.D. Kim, S.S. Kim, Y.-H. Choa, H.T. Kim. *J. Ind. Eng. Chem.*, **13**, 1137 (2007).
[20] W. Wang, B. Gu, L. Liang, W. Hamilton. *J. Phys. Chem. B*, **107**, 3400 (2003).
[21] N. de Silva, S.-J. Hwang, K.A. Durkin, A. Katz. *Chem. Mater.*, **21**, 1852 (2009).
[22] P.L. Maux, G. Simonneaux. *Chem. Commun.*, **47**, 6957 (2011).
[23] S. Kumar, S. Verma, S.L. Jain, B. Sain. *Tetrahedron Lett.*, **52**, 3393 (2011).
[24] M. Munoz, G. Romanelli, I.L. Botto, C.I. Cabello, C. Lamonier, M. Capron, P. Baranek, P. Blanchard, E. Payen. *Appl. Catal. B: Environ.*, **100**, 254 (2010).
[25] F. Bigi, A. Corradini, C. Quarantelli, G. Sartori. *J. Catal.*, **250**, 222 (2007).