Accepted Manuscript

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PII:	S1381-1169(14)00570-6			
DOI:	http://dx.doi.org/doi:10.1016/j.molcata.2014.12.010			
Reference:	MOLCAA 9372			
To appear in:	Journal of Molecular Catalysis A: Chemical			
Received date:	16-5-2014			
Revised date:	13-9-2014			
Accepted date:	7-12-2014			

Please cite this article as: Amin Rostami, Bahareh Atashkar, Chiral oxo-vanadium (+)-pseudoephedrine complex immobilized on magnetic nanoparticles: A highly efficient and recyclable novel nanocatalyst for the chemoselective oxidation of sulfides to sulfoxides using H2O2, Journal of Molecular Catalysis A: Chemical http://dx.doi.org/10.1016/j.molcata.2014.12.010

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Chiral oxo-vanadium (+)-pseudoephedrine complex immobilized on magnetic nanoparticles: a highly efficient and recyclable novel nanocatalyst for the chemoselective oxidation of sulfides to sulfoxides using H₂O₂

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Graphical Abstract

Chiral oxo-vanadium (+)-pseudoephedrine complex immobilized on magnetic nanoparticles Fe_3O_4 : a highly efficient and recyclable novel nanocatalyst for the chemoselective oxidation of sulfides to sulfoxides using H_2O_2

Highlights

- The first chiral VO(Pseudoephedrine)@MNPs was easily synthesized and characterized.
- ✤ It catalyzed highly efficient chemoselective oxidation of sulfides.
- ✤ The catalyst allows for greener method while keeping high yields and low times.
- The catalyst was easily reused up to 20 runs without significant loss of activity.

ABSTRACT

The first chiral oxo-vanadium (+)-pseudoephedrine complex supported on magnetic nanoparticles Fe_3O_4 [VO(Pseudoephedrine)@MNPs] as novel magnetically interphase

nanocatalyst was designed and characterized using the most common techniques. VO(Pseudoephedrine)@MNPs catalyzed the chemoselective oxidation of sulfides to sulfoxides using hydrogen peroxide as a green oxidant in high yields with 20-27% enantiomeric excesses under solvent-free conditions at room temperature. The catalyst was recycled up to 20 times with little loss of activity and enantioselectivity.

Keywords

sulfides, sulfoxides, hydrogen peroxide, oxo-vanadium (+)-pseudoephedrine complex, magnetically catalyst

1.Introduction

Compare to heterogeneous catalysis, in homogeneous catalysis, the chemo-, regio-, and enantioselectivity of the catalyst is better, but the difficulty of catalyst separation from the final product creates economic and environmental barriers. Magnetic nanoparticles (MNPs) have recently considered as ideal supports for the heterogenization of homogeneous catalysts due to their easy preparation and functionalization, large surface area ratio, facile recovery and recyclability via magnetic force, as well as low toxicity and price [1-4].

Recently, there has been increasing interest in the synthesis of vanadium (V) Schiff base complexes derived from chiral and achiral amino alcohols and their catalytic activity. These complexes have been used successfully as catalyst in enantioselective oxidation of organic sulfides [5-6], asymmetric alkynylation of aldehydes [6], epoxidation of cyclooctene [7] and stereoselective synthesis of functionalized cyclic ethers [8-9]. However, the main disadvantage of a catalyst based on chiral vanadium complexe is their separation from the products, which needs solid-liquid or liquid-liquid techniques in many reactions. This drawback can be overcome by immobilization of these catalysts on MNPs.

Chiral and achiral sulfoxides are valuable intermediates for the synthesis of fine chemicals, pharmaceuticals and biologically active molecules [10-14]. The main synthetic route for the preparation of these valuable materials is via oxidation of the corresponding sulfides.

Concerning the green oxidant, hydrogen peroxide is one of the most powerful candidates, since it is inexpensive, readily available, high atom efficiency, and water is expected as the only by-product to be generated from the reaction. Oxidation of sulfides with H_2O_2 is slow; hence extensive catalysts have been undertaken for the activation of H_2O_2 for this reaction. Although reported catalysts display considerable progress, the separation and reuse of the catalysts are difficult [15-17].

In continuation of our studies on preparation and applications of magnetic nanocatalysts [18-20], herein, we report the synthesis, characterization and catalytic properties of new chiral VO(Pseudoephedrine)@MNPs in the chemoselective oxidation of sulfides to sulfoxides using H_2O_2 as a green oxidant.

2. Experimental

2.1. General remarks

The materials were purchased from Merck and Fluka and were used without any additional purification. All reactions were monitored by thin layer chromatography (TLC) on gel F254 plates. Melting points were obtained in open capillary tubes and also were measured on an Electrothermal 9100 apparatus. The X-ray diffraction (XRD) data were collected on an X'Pert MPD Philips diffractometer with Cu Ka radiation source (λ =1.54050Å) at 40 kV voltage and 40 mA current. The scanning electron microscopy (SEM) image was obtained by VEGATESCAN. The thermogravimetric analysis (TGA) was carried out on a Bähr STA 503 instrument (Germany) under air atmosphere, heating rate 10°C/min. The magnetic measurements were carried out in an Alternating Gradient Force Magnetometer (AGFM,

Meghnatis Daghigh Kavir Co., Made in Iran) at room temperature. UV-Vis spectra were recorded on a JASCOV-550 UV-Vis spectrophotometer.

2.2. Preparation of large-scale the magnetic Fe₃O₄ nanoparticles (MNPs)

FeCl₃· $6H_2O$ (4.865 g, 0.018 mol) and FeCl₂· $4H_2O$ (1.789 g, 0.0089 mol) were added to 100 mL deionized water and sonicated until the salts dissolved completely. Then, 10 mL of 25% aqueous ammonia was added quickly into the reaction mixture in one portion under N₂ atmosphere at room temperature followed by stirring about 30 min with mechanical stirrer. The black precipitate was washed with doubly distilled water (five times). The product stored in a refrigerator to use.

2.3. Preparation of Fe₃O₄@SiO₂ core-shell (SMNPs)

The synthesized MNPs Fe_3O_4 (1gr) suspended in 2-propanol (200 mL) and sonicated for 20 min. PEG (5.36 g), water (20 mL), ammonia solution (28 wt.%,10 mL) and tetraethyl orthosilicate (1.2 mL) were respectively added into the suspension, and continuously reacted for 24h under stirring at room temperature. The iron oxide nanoparticles with a thin layer of silica (Fe₃O₄@SiO₂) were separated by an external magnet, washed three times with ethanol and water and dried under vacuum.

2.4. Preparation of the N-(3-trimethoxysilane)propyl pseudoephedrine (TMSP-Pseudoephedrine) ligand

(+)-Pseudoephedrine hydrochloride (0.403 g, 0.002 mol) was dissolved in 25 mL of H_2O /ethanol (1:1). Then 0.380 mL (0.002 mol) of (3-chloropropyl) trimethoxysilane (CPTMS), and sodium bicarbonate (0.168 g, 0.004 mol) were added and the mixture was refluxed for 24h. After this time, the yellow-orange solution was obtained. The concentrated product stored in a refrigerator to use.

2.5. Preparation of the VO(TMSP-Pseudoephedrine) complex

To the solution of the TMSP-Pseudoephedrine ligand (0.002 mol) in 25 mL of H_2O /ethanol (1:1), vanadyl acetylacetonate (0.265 g, 0.001 mol) was added and the mixture was refluxed for 24h. The dark-green solution was obtained. The concentrated product stored in a refrigerator to use.

2.6. Preparation of the VO(Pseudoephedrine)@MNPs

 $Fe_3O_4@SiO_2$ (1 g) was added to the solution of VO(TMSP-Pseudoephedrine) complex (0.001 mol) in 25 mL of H₂O/ethanol (1:1) and then the mixture was reflux for 24h. The final sample was separated by magnetic decantation and washed two times with dry CH₂Cl₂, EtOH and CH₂Cl₂ respectively to remove the unattached complex. The product stored in a refrigerator to use.

2.7. General procedure for the oxidation of sulfides to sulfoxides

The sulfide (1 mmol) was added to a mixture of 30% H_2O_2 (1 g, 2.4 equiv) and VO(Pseudoephedrine)@MNPs (40 mg, 1.4 mol%), and then the mixture was stirred at room temperature for the time specified. The progress was monitored by TLC (EtOAc/*n*-hexane, 1/2). After completion of the reaction, the catalyst was separated from the product by an external magnet (within 5 seconds), washed with Et₂O (2×5 mL) and decanted. The combined organics were washed with brine (5 mL) and dried over anhydrous Na₂SO₄.The evaporation of Et₂O under reduced pressure gave the pure products in 80-97% yields and 9-15% ee.

3. Results and discussions

3.1. Preparation and Characterization of VO(Pseudoephedrine)@MNPs

To prepare the catalyst, firstly (+)-Pseudoephedrine hydrochloride was reacted with CPTMS to give TMSP-Pseudoephedrine, subsequently this compound was allowed to react with VO(acac)₂ to produce VO(TMSP-Pseudoephedrine) complex. Ultimately, the resulting

oxo-vanadium complex were subjected with SMNPs [21], to prepare the corresponding VO(Pseudoephedrine)@MNPs (Scheme 1) [22].

The catalyst has been characterized by UV-Vis spectrophotometer, SEM, XRD, TGA, fourier transform infrared spectroscopy (FT-IR), Energy-dispersive X-ray spectroscopy (EDX) and AGFM. UV-Vis spectroscopy was applied to the characterization of VO(TMSP-Pseudoephedrine) complex. UV-Vis spectrum of the VO(acac)₂ shows two bands at 585 nm [d–d transitions] and 706 nm [ligand-to-metal charge transfer (LMCT)] (Figure 1a) [23].

UV-Vis spectrum of the VO(TMSP-Pseudoephedrine) complex (Figure 1b) shows three bands at 265-312 nm (π - π * transition of phenyl ring on ligand), 320-420 nm (may be assigned as a ligand-to-metal charge transfer (LMCT) transition originating from the oxygen and nitrogen on pseudoephedrine ligand to the empty d orbital at the vanadium (V) center) and 420-650 nm (d–d transition) [24].

The SEM image of the VO(Pseudoephedrine)@MNPs confirmed that the catalyst was made up of uniform nanometer-sized particles less than 33 nm (Figure 2).

The XRD pattern of the VO(Pseudoephedrine)@MNPs is shown in Figure 3. Weak broad bands (2θ =11.5-23°) appeared in XRD pattern which could be attributed to the amorphous silane shell formed around the magnetic cores [22]. The interlayer spacing (d_{hkl}), calculated using the Bragg equation, agrees well with the data for standard magnetic Fe₃O₄ [25] (Table 1).

One indication of bond formation between the nanoparticles and the catalyst can be inferred from TGA. The TGA curve of the VO(Pseudoephedrine)@MNPs shows the mass loss of the organic functional group as it decompose upon heating (Figure 4). The weight loss

at temperatures below 200 °C is due to the removal of physically adsorbed solvent and surface hydroxyl groups [26]. Organic spacers have been reported to desorb at temperatures above 260 °C. The curve shows a weight loss of about 19% from 260 to 600 °C, resulting from the decomposition of VO (*N*-(3-silane) propyl pseudoephedrine) complex grafting to the SMNPs surface. The loading of the complex in VO(Pseudoephedrine)@MNPs can be calculated from TGA, which confirmed a loading of approximately 0.35 mmol/g.

The EDX spectrum shows the kinds of elements present (V, Fe, Si and N) in the VO(Pseudoephedrine)@MNPs (Figure 5).

Figure 6 shows FTIR spectra for (+)-pseudoephedrine hydrochloride, TMSP-Pseudoephedrine ligand, VO(acac)₂, VO(TMSP-Pseudoephedrine) complex and VO(Pseudoephedrine)@MNP. The FTIR spectrum for the (+)-pseudoephedrine hydrochloride (Fig. 6a) shows stretching vibrations at 3341 and 3380 cm⁻¹ which incorporates the N-H and O-H bonds. Vibrations in the range of $1428-1652 \text{ cm}^{-1}$ are attributed to the aromatic ring. The FTIR spectrum for the TMSP-Pseudoephedrine (Fig. 6b) shows the bands at 1110 and 2924 cm⁻¹ assigned to the Si-O and C-H stretching vibrations respectively. In the FTIR spectrum of the VO(acac)₂, the bands at 799 and 997cm⁻¹ assigned to the V-O and V=O respectively and the bands at 1527 and 1556cm⁻¹ assigned to the C=O stretching vibrations(Fig. 6c) [27]. The complexation reaction between TMSP-Pseudoephedrine and $VO(acac)_2$ is confirmed by comparing the spectra of $VO(acac)_2$ and VO(TMSP)pseudoephedrine) complex that show the V-O and V=O vibrations in the same vicinity (Fig. 6d). The introduction of VO(TMSP-Pseudoephedrine) complex to the surface of SMNPs is confirmed by the band at 1090cm⁻¹assigned to the Si-O-Si stretching vibration (Fig. 6e) [27]. The bands at low wave numbers ($\leq 700 \text{ cm}^{-1}$) come from vibrations of Fe-O bonds of iron oxide, in which for the bulk Fe_3O_4 samples appear at 570 and 375 cm⁻¹ but for Fe_3O_4 nanoparticles at 622 and 582 cm^{-1} as a blue shift, due to the size reduction [28, 29].

Superparamagnetic particles are beneficial for magnetic separation, the magnetic property of the MNPs and VO(Pseudoephedrine)@MNPs were characterized by AGFM. The room temperature magnetization curves of the MNPs and the VO(Pseudoephedrine)@MNPs are shown in Figures 7a and 7b. As expected, the bare MNPs, showed the higher magnetic value (saturation magnetization, Ms=74.3 emug⁻¹) [30], and the Ms value of VO(Pseudoephedrine)@MNPs is decreased due to the silica coating and the layer of the grafted catalyst (Ms=30.4 emug⁻¹). The MNPs and VO(Pseudoephedrine)@MNPs have an coercivity (Hc) of 1.45 and 1.12 Oe, respectively and the remnant magnetization (Mr) of ~1.52 and 1.23 emug⁻¹, respectively. As a result, the VO(Pseudoephedrine)@MNPs have a typical superparamagnetic behaviour [31-33] and can be efficiently attracted with a small magnet.

These analysis indicated the successful anchoring of the VO(TMSP pseudoephedrine) complex on the surface of magnetic nanoparticles. Unfortunately, due to the magnetic properties of VO(Pseudoephedrine)@MNPs it is actually impossible to further characterize this material by using solid-state NMR spectroscopy.

3.2. The catalytic application of VO(Pseudoephedrine)@MNPs in the oxidation of sulfides to sulfoxides

The catalytic activity of VO(Pseudoephedrine)@MNPs as reusable organic-inorganic hybrid catalyst was tested in the chemo-, and enantiselective oxidation of sulfides to sulfoxides using 30% H_2O_2 under solvent-free conditions at room temperature (Scheme 2).

In order to optimize the reaction conditions, we evaluated the influence of different amounts of catalyst and hydrogen peroxide on the oxidation of methyl phenyl sulfide as a model compound under solvent-free conditions at room temperature (Table 2).

As shown in Table 2, in the absence of a catalyst the reaction was incomplete even after

24 hours. The optimum amount of H_2O_2 (2.4 equivalent) in the presence of VO(seudoephedine)@MNPs(40 mg) is ideal for complete conversion of methyl phenyl sulfide to methyl phenyl sulfoxide.

In order to generalize the scope of the reaction, a series of structurally diverse sulfides was subjected to oxidation under the optimized reaction conditions, the results are presented in Table 3. The reactions went on well to afford products in short times and good to high yields.

The overall products yields were in the range of 80-97% and enantiomeric excess (ee's) of 9-15% of the sulfoxide was obtained (Table 3, entries 1-7). When the reaction was carried out at-20 °C, enantioselectivities improve to 20-27% ee after 300 min (Table 3, entries 10-12). The influence of the solvents (H₂O, EtOH, CH₂Cl₂ and CH₃CN) and different amounts of hydrogen peroxide and catalyst in the oxidation of benzyl phenyl sulfide on the enantiomeric excess were evaluated; in all cases the observed enantiomeric excess was low.

To show the chemoselectivity of this method, the sulfides containing oxidation-prone and acid-sensitive functional groups such as OH, CHO and COOCH₃ were subjected to the sulfoxidation reaction; these functional groups remained intact during the conversion of sulfides to sulfoxides (Table 3, entries 5-7).

For practical purposes, the ability to easily recover and recycle of the catalyst is highly desirable. We found that this catalyst rapidly recovered and demonstrated remarkably excellent recyclability; after the first use of the catalyst in the oxidation of methyl phenyl sulfide to give methyl phenyl sulfoxide, the catalyst was separated by an external magnet and was washed thoroughly with ether. It was reused for subsequent experiments under similar reaction conditions. As shown in Figure 6, the catalyst can be recycled up to 20 runs without any significant loss of activity and enantioselectivity.

Conclusion

We have designed the first chiral VO(Pseudoephedrine)@MNPs that catalyze the oxidation of sulfides to sulfoxides using H_2O_2 with remarkably high activity and chemoselectivity. Also, the enantioselectivity in this reaction was observed. When the reaction was carried out at room temperature, enantiomeric excess (ee's) of 9-15% and in -20°C ee's of 20-27% of sulfoxides were obtained. The heterogenized catalyst can be readily recovered by using an appropriate external magnet, which minimizes the loss of catalyst during separation and can be reused for up to 20 times without significant loss of activity and enantioselectivity. The other merits of the protocol are the use of a commercially available, eco-friendly, cheap and chemically stabile oxidant, the mild reaction conditions, operational simplicity, practicability, short reaction times and good to high yields of products.

Acknowledgment

We are grateful to the University of Kurdistan Research Councils for partial support of this work.

References

[1] S. Shylesh, V. Schunemann, W.R. Thiel, Angew. Chem. Int. Ed. 49 (2010) 3428-3459.

[2] V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J.-M. Basset, Chem. Rev. 111 (2011) 3036-3075.

[3] R.B. Nasir-Baig, R.S. Varma, Green Chem. 15 (2013) 398-417.

[4] B. Karimi, H.M. Mirzaei, E. Farhangi, Chem. Cat. Chem. 6 (2014) 758-762.

[5] Q. Zeng, H. Wang, W. Weng, W. Lin, Y. Gao, X. Huang, Y. Zhao, New J. Chem. 29 (2005) 1125-1127.

[6] S.H. Hsieh, Y.P. Kuo, H.M. Gau, Dalton Trans. (2007) 97-106.

[7] C. Cordelle, D. Agustin, J.C. Daran, R. Poli, Inorg. Chim. Acta. 364 (2010) 144-149.

[8] J. Hartung, Pure Appl. Chem. 77 (2005)1559-1574.

[9] J. Hartung, S. Drees, M. Grab, P. Schmidt, I. Svoboda, H. Fuess, A. Murso, D. Stalke, Eur. J. Org. Chem. (2003) 2388-2408.

[10] K. Leon-Prasanth, H. Maheswaran, J. Mol. Catal. A: Chem. 268 (2007) 45-49.

[11] O. Shigeru, O. Yutaka, K. Seizi, T. Waichiro, Bull. Chem. Soc. Jpn. 39 (1966) 364-366.

[12] K. Sato, M. Hyodo, M. Aoki, X.Q. Zheng, R. Noyori, Tetrahedron 57 (2001) 2469-2476.

[13] B.M. Choudary, B. Bharathi, C.V. Reddy, M.L. Kantam, J. Chem. Soc. Perkin Trans. 1 (2002) 2069-2074.

[14] D. Habibi, M.A. Zolfigol, M. Safaee, A. Shamsian, A. Ghorbani-Choghamarani, Catal. Commun.10 (2009) 1257-1260.

[15] D. Bethell, P.C. B. Page, H. Vahedi, J. Org. Chem. 65 (2000) 6756-6760.

[16] I. Fernanez, N. Khiar, Chem. Rev. 103 (2003) 3651-3706.

[17] H. Srour, J. Jalkh, P.L. Maux, S. Chevance, M. Kobeissi, G. Simonneaux, J. Mol. Catal. A: Chem.370 (2013) 75-79.

[18] A. Rostami, B. Atashkar, D. Moradi, Appl. Catal. A: Gen. 467 (2013) 7-16.

[19] A. Rostami, Y. Navasi, D. Moradi, A. Ghorbani-Choghamarani, Catal. Commun.43 (2014) 16-20.

[20] A. Rostami, B. Tahmasbi, F. Abedi, Z. Shokri, J. Mol. Catal. A: Chem. 378 (2013) 200-205.

[21] Y. Zhang, G-M. Zeng, L. Tang, D-L. Huang, X-Y. Jiang, Y-N. Chen, Biosens. Bioelectron. 22 (2007) 2121-2126.

[22] M. Esmaeilpour, A.R. Sardarian, J. Javidi, Appl. Catal. A: Gen. 445 (2012) 359-367.

[23] E.G. Ferrer, M.V. Salinas, M.J. Correa, F. Vrdoljak, P.A.M. Williams, Zeitschrift Naturforschung (2005) 305-311.

[24] H. Yang, L. Zhang, P. Wang, Q. Yang, C. Li, Green Chem. 11 (2009) 257-264. .

[25] F. Brackmann, H. Schill, A. Meijere, Chem. Eur. J. 11 (2005) 6593-6600.

[26] M. Kassaee, H. Masrouri, F. Movahed, Appl. Catal. A: Gen. 395 (2011) 28-33. .

[27] Y. Liang, J. Ouyang, H. Wang, W. Wang, P. Chui, K. Sun, Appl. Surf. Sci. 258 (2012) 3689-3694.

[28] Z. Rao, T.H. Wu, S.Y. Peng, Acta. Phys. Chim. Sin.11 (1995) 395-399.

[29] R.D. Waldron, Phys. Rev.99 (1955) 1727-1735.

[30] K. Naka, A. Narital, H. Tanakal, Y. Chujo, M. Morita, T. Inubushi, I. Nishimura, J. Hiruta, H. Shibayama, M. Koga, S. Ishibashi, J. Seki, S. Kizaka-Kondoh, M. Hiraoka, Polym. Adv. Technol.19 (2008) 1421-1429.

[31] R.C. Ohandley, Modern Magnetic Materials: Principles and Applicat Ions; Wiley: New York, (2000).

[32] R.H. lida, K. Takayanagi, T. Nakanishi, T.J. Osaka, Colloid Interface Sci. 314 (2007)274-280.

[33] G.W. Cheng-Lin, H. Huan, G. Hong-Jun, L. Gan, M. Ru-Jiang, A. Ying-Li, S. Lin-Qi, Sci. China Chem. 53 (2010) 514-518.

Scheme 1. The preparation of the VO(Pseudoephedrine)@MNPs

Scheme 2. VO(Pseudoephedrine)@MNPs catalyzed the oxidation of sulfides to sulfoxides using H_2O_2

Figure 1. UV-Vis spectra of a) VO(acac)₂ and b) VO(TMSP-Pseudoephedrine) complex

Figure 2. SEM image of the VO(Pseudoephedrine)@MNPs

Figure 3. XRD pattern of the VO(Pseudoephedrine)@MNPs

Figure 4. TGA profile of the VO(Pseudoephedrine)@MNPs

Figure 5. EDX spectrum of the VO(Pseudoephedrine)@MNPs

Figure 6. FTIR Spectra of (a) (+)-Pseudoephedrine hydrochloride,(b) TMSP-Pseudoephedrine, (c) VO(acac)₂ (d) VO(TMSP-Pseudoephedrine) complex and (e) VO(Pseudoephedrine)@MNPs **Figure 7.** Hysteresis loop of(a) the MNPs and (b)

VO(Pseudoephedrine)@MNPs at room temperature (left inset:

the magnified field from -30 to 30 Oe)

Figure 6. The recycling experiment of VO(Pseudoephedrine)@MNPs for the oxidation of methyl phenyl sulfide (1 mmol) using H_2O_2 at room temperature for 5 min

Table 1. Interlayer spacing (d _h Sample	hkl) for VO(Pseudoephedrine)@MNPs d _{hkl} (Å)					
	1	2	3	4	5	6
Standard magnetic Fe ₃ O ₄	2.96	2.53	2.09	1.71	1.61	1.48
VO(Pseudoephedrine)@MNPs	2.97	2.53	2.09	1.71	1.61	1.48

Entry	Catalyst (mg)	H ₂ O ₂ (equiv.)	Time (min)	Conversion (%) ^a
1	Catalyst-free	2.4	24h	40
2	Fe ₃ O ₄ NP (40)	2.4	24h	50
3	VO(Pseudoephedrine)@MNPs (30)	2.4	60	100
4	VO(Pseudoephedrine)@MNPs (35)	2.4	25	100
5	VO(Pseudoephedrine)@MNPs (40)	2.4	5	100
6	VO(Pseudoephedrine)@MNPs (45)	2.4	5	100
7	VO(Pseudoephedrine)@MNPs (50)	2.4	2	100
8	VO(Pseudoephedrine)@MNPs (40)	0.6	25	100
9	VO(Pseudoephedrine)@MNPs (40)	1.2	20	100

Table 2. The selective oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide under different conditions

Table 3. VO(Pseudoephedrine)@MNPs (40 mg) catalyzed selective oxidation of sulfides (1 mmol) to sulfoxides using 30% H₂O₂ (2.4 equiv.) under solvent-free conditions

Entry	Sulfide	Time (min)	Sulfoxide ^a	Yield (%) ^b	T (°C)	ee (%) ^c
1	CH3	5		97	rt	9
2	S√ S√	8	o s s	96	rt	10
3	S_ph	10	O S Ph	97	rt	12
4	s_	8		85	rt	15
5	~\$~он	5	ОН	83	rt	11
6	S→→→ O	7	O S S S S S S S S S S S S S S S S S S S	80	rt	13
7	~ ^{\$} 0	10		81	rt	10
8	S	15	O S	80	rt	



^aThe products are known and were characterized by IR, ¹H NMR, and by melting point comparisons with those of authentic samples.¹¹⁻¹⁵

^bIsolated yield.

^cEnantiomeric Excess (ee) was determined by polarimeter.







Fig.2







Fig.1





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