

Immobilization of a vanadium complex onto functionalized nanoporous MCM-41 and its application as a catalyst for the solvent-free chemoselective oxidation of sulfide to sulfoxide

M. Nikoorazm*, A. Ghorbani-Choghamarani and M. Khanmoradi

A complex moiety containing VO(IV) was anchored covalently into organic-modified Si-MCM-41 to prepare a new catalyst. The prepared materials were characterized using various techniques. Several types of aromatic and aliphatic sulfides were successfully oxidized to the corresponding sulfoxides in good to excellent yields using H₂O₂ in the presence of a catalytic amount of the catalyst under solvent-free conditions. The results showed that the OH groups of the various compounds such as 2,2-(phenylthio)ethanol and 2-(methylthio)ethanol remained intact under similar conditions. Meanwhile the catalyst was stable in the reaction system, and could be reused at least four times without significant loss of its activity and chemoselectivity. Copyright © 2016 John Wiley & Sons, Ltd.

Keywords: MCM-41; mesostructured; vanadyl ion; hydrogen peroxide; sulfide

Introduction

Oxo-vanadium complexes have been extensively studied because of their potential applicability as catalysts or mediators for oxidations by molecular oxygen, peroxidative oxygenations (both including epoxidations), halogenations and carboxylations of aliphatic and aromatic hydrocarbons, and/or olefins, toward the syntheses of a variety of organic compounds, such as alcohols, ketones, epoxides, aldehydes, organohalides and carboxylic acids,^[1] and oxidation of organic sulfides to sulfoxides.^[2–5] Some of these systems operate in liquid media, whereas others involve VO catalysts immobilized on solid supports. The easily reversible interconversion of the vanadium oxidation states +IV and +V and the easy formation of epoxide to act as Lewis acidic and basic sites or undergo radical-mediated transformations during catalytic reactions make vanadium one of the best-suited elements for catalytic oxidations and oxygen-transfer reactions.

The immobilization of catalyst or catalyst precursor complexes on supports is a common and suitable procedure for combining the advantages of homogeneous and heterogeneous catalysis. Several types of inorganic supports, such as silica gel,^[6] USY zeolites,^[7,8] alumina^[6] and mesoporous silicas,^[9] have been used for oxo-vanadium catalysis. MCM-41 gives much opportunity for the preparation of heterogeneous catalysts due to outstanding properties like uniform pore structure, large surface area and wide range of pore dimensions that ensure easy accessibility of reactants to active sites, and also provides a unique inorganic support that can anchor the active sites on inorganic oxides.^[10,11]

Sulfoxides are useful building blocks especially as chiral auxiliaries in organic synthesis.^[12–15] Sulfoxides are important intermediates in the synthesis of various natural products,^[16–19] and they also can play a key role in the activation of enzymes.^[20]

Although many of these methods are quite useful, there still remains much room for improvements especially in the case of the selectivity and eco-friendliness of the reactions. The goal of the work reported in this paper was to develop an efficient heterogeneous catalytic system for the oxidation of sulfides to sulfoxides with H₂O₂ using vanadyl acetylacetonate complex grafted on 2-amino-3-hydroxypyridine-modified mesoporous silica MCM-41 (VO-2A3HP-MCM-41) as a stable catalyst under solvent-free conditions at room temperature.

Experimental

Materials

The cationic surfactant cetyltrimethylammonium bromide (CTAB; 98%), tetraethyl orthosilicate (TEOS; 98%), hydrogen peroxide (30% aqueous), 3-chloropropyl-1-triethoxysilane, vanadyl acetylacetonate (VO(acac)₂), organic sulfides, solvents and other materials were purchased from Merck, Aldrich or Fluka and were used without further purification.

Instrumentation

Powder X-ray diffraction (XRD) of the VO-2A3HP-MCM-41 catalyst was conducted using a Philips diffractometer with Cu K α radiation at 40 kV and 30 mA. The particle size and morphology were investigated using a JEOL JEM-2010 scanning electron microscopy (SEM)

* Correspondence to: M. Nikoorazm, Department of Chemistry, Ilam University, PO Box 69315516, Ilam, Iran. E-mail: e_nikoorazm@yahoo.com

Department of Chemistry, Faculty of Science, Ilam University, PO Box 69315516, Ilam, Iran

instrument at an accelerating voltage of 200 kV. The measurement of product components was carried out using energy-dispersive spectroscopy (EDS) with a Tacnai TF20 high-resolution transmission electron microscope. Thermogravimetric analysis (TGA) curves were recorded using a PL-STA 1500 device (Thermal Sciences). Fourier transform infrared (FT-IR) spectra of samples were recorded in KBr discs using a Nicolet Impact 410 spectrometer. Transmission electron microscopy (TEM) images were obtained using a Philips CM10 microscope operating at 200 kV. Specific surface area of samples was obtained using the Brunauer–Emmett–Teller (BET) method using a NOVA 1000 instrument.

Synthesis of MCM-41 modified with (3-chloropropyl) triethoxysilane

Pure silica MCM-41 was prepared by adding 1 g of CTAB to an aqueous solution containing 3.5 ml of NaOH solution (2 M) and deionized water (480 ml). The resulting mixture was stirred continuously at 80°C. Then, 5 ml of TEOS was slowly added into the solution. The resulting mixture was refluxed for 2 h at 80°C. The collected product was washed with deionized water and calcined at 823 K for 5 h at a rate of 2°C min⁻¹ to remove the residual surfactant. This mesoporous material was designated as Si-MCM-41. Post-synthesis organic modification of MCM-41 was performed by refluxing 4.8 g of MCM-41 and 4.8 g of 3-chloropropyl-1-triethoxysilane in *n*-hexane for 24 h to obtain a white solid of the functionalized MCM-41 (nPrCl-MCM-41). The resulting material was filtered, washed with *n*-hexane and dried under vacuum.

Preparation of heterogeneous VO-2A3HP-MCM-41 catalyst

For the preparation of 2A3HP-MCM-41, 0.5 g of nPrCl-MCM-41 was refluxed with triethylamine (2 mmol, 0.202 g) and 2-amino-3-hydroxypyridine (2A3HP; 1 mmol, 0.110 g) in toluene for 24 h. The resulting solid was washed with ethanol, collected by filtration and dried under vacuum. Ultimately, VO-2A3HP-MCM-41 was prepared by refluxing VO(acac)₂ (0.63 mmol, 0.168 g) with 0.250 g of 2A3HP-MCM-41 in ethanol (20 ml) for 20 h. The obtained VO-2A3HP-MCM-41 product was washed with ethanol, collected by filtration and dried under vacuum (Scheme 1). Characterization of the VO-2A3HP-MCM-41 catalyst was performed using TGA, FT-IR, XRD, SEM, BET and TEM techniques.

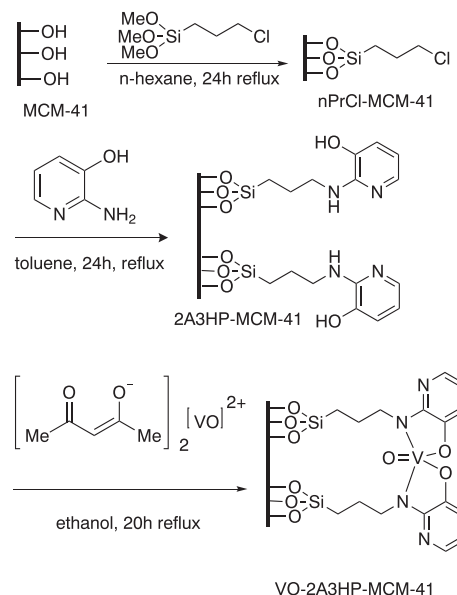
Catalytic oxidation of organic compounds

In order to examine the catalytic activity of the catalyst, VO-2A3HP-MCM-41 (10 mg) was added to a mixture of sulfides (1 mmol) and H₂O₂ (0.4 ml) under solvent-free conditions with stirring at room temperature. After completion of the reaction, the catalyst was separated using simple filtration and washed with dichloromethane (3 × 10 ml).

Results and discussion

Characterization of VO-2A3HP-MCM-41

Scheme 1 shows the preparation route of VO-2A3HP-MCM-41. Characterization of the VO-2A3HP-MCM-41 catalyst was performed using TGA, FT-IR, XRD, SEM, BET and TEM techniques. The results indicate that, using this method (sol-gel), VO(acac)₂ is successfully immobilized onto the MCM-41.



Scheme 1. Procedure for preparation of VO-2A3HP-MCM-41 catalyst.

Figure 1 shows the XRD patterns of MCM-41 and VO-2A3HP-MCM-41. They have one strong and two weak peaks. All three XRD reflections represent the hexagonal lattice of MCM-41. The spectra display hexagonal symmetry with (100), (110) and (200) diffraction peaks that relate to 2θ values of 2.77°, 4.57° and 5.21°, respectively. The decrease in the peak intensities in the XRD pattern of VO-2A3HP-MCM-41 is an indication of the MCM-41 pore surface silanol groups reacting with vanadyl ions.^[20]

The FT-IR spectrum of the MCM-41 sample (Fig. 2(a)) indicates the characteristic bands of the MCM-41 framework related to Si O stretching of surface Si OH groups and three peaks at 1059, 962 and 454 cm⁻¹ correspond to asymmetric stretching, symmetric stretching and bending vibrations of Si O Si, respectively. The presence of anchored 3-chloropropyl(triethoxy)silane (nPrCl) is confirmed by the CH stretching vibration appearing at about 2900 cm⁻¹ (Fig. 2(b)). The free ligand signals at 1265 cm⁻¹ (CO) and 1650 cm⁻¹ (CN) emphasize that 2A3HP is successfully anchored on modified MCM-41 (Fig. 2(c)). The band near 3468 cm⁻¹ of the free ligand is assigned to $\nu(\text{NH}_2)$ bending; this band is shifted to lower wavenumber in the spectrum of the complex due to the coordination of the amino group nitrogen atom to the metal ion (Fig. 2(d)).^[21]

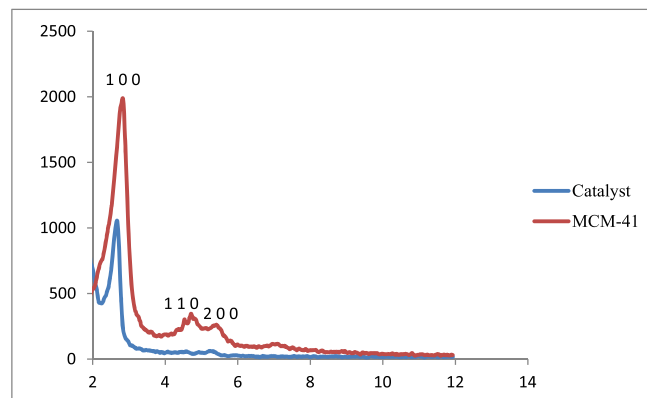


Figure 1. XRD patterns of MCM-41 and VO-2A3HP-MCM-41.

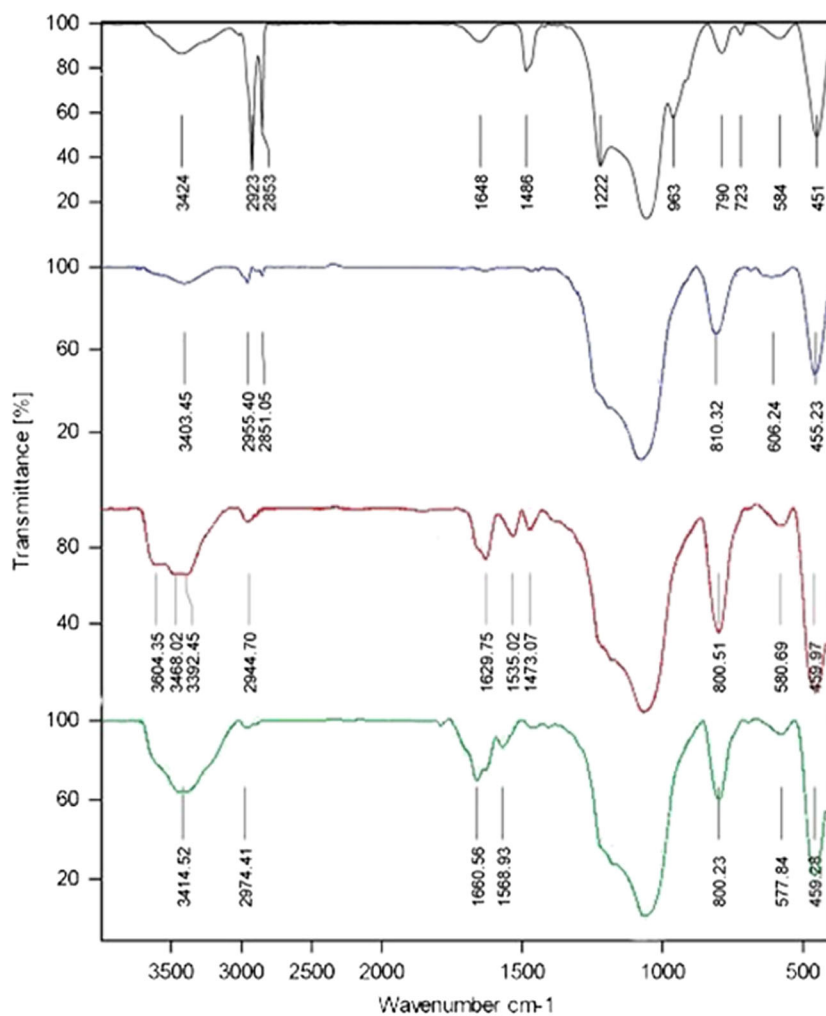


Figure 2. FT-IR spectra of (a) MCM-41, (b) nPrCl-MCM-41, (c) 2A3HP-MCM-41 and (d) VO-2A3HP-MCM-41.

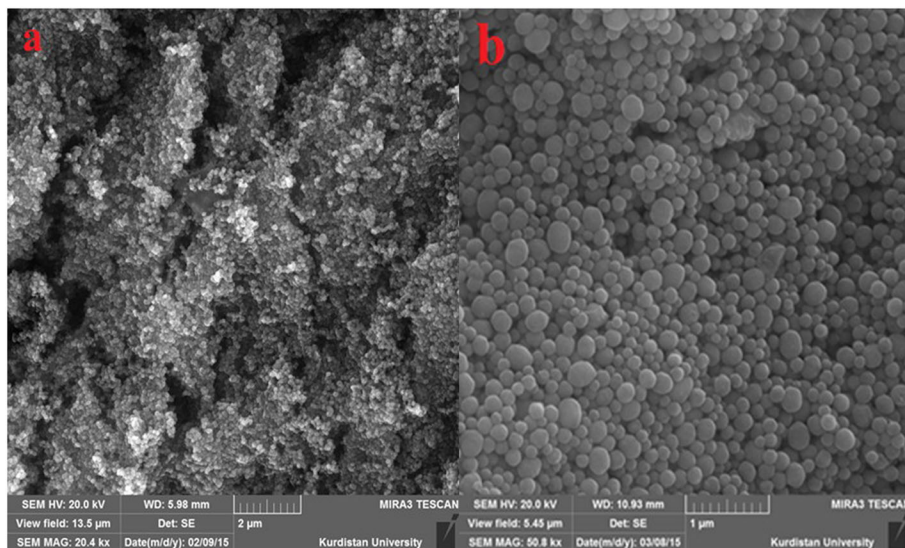


Figure 3. SEM images of (a) MCM-41 and (b) VO-2A3HP-MCM-41.

Figure 3 shows SEM micrographs of MCM-41 and VO-2A3HP-MCM-41. This analysis shows diameters of approximately 77.01–226.99 nm for the VO-2A3HP-MCM-41 nanoparticles with a spherical shape. The EDS spectrum (Fig. 4) evidently shows the presence of vanadium in the catalyst. The sample consists of carbon with oxygen most likely due to the presence of a few unreacted oxygen functional groups. It also shows the presence of nitrogen and silicon indicating the presence of these elements in VO-2A3HP-MCM-41.

Furthermore the TEM image (Fig. 5) clearly shows that nanoparticles are present, and VO-2A3HP-MCM-41 particles have spherical shapes with hexagonal channels. It can be seen that the catalyst is homogeneously dispersed on the surface of the silica matrix, and no obvious aggregation is observed.

TGA curves of the MCM-41 support and VO-2A3HP-MCM-41 are shown in Fig. 6. The pure MCM-41 shows a weight loss (4.0 wt%) in one step at 25–100°C. This behaviour indicates a poor capacity for water adsorption. The TGA curve of VO-2A3HP-MCM-41 shows a weight loss (around 10 wt%) appearing at a temperature <150°C corresponding to the loss of water and other solvents. The other weight loss at about 250–500°C (15 wt%) is related to decomposition of organic moieties.

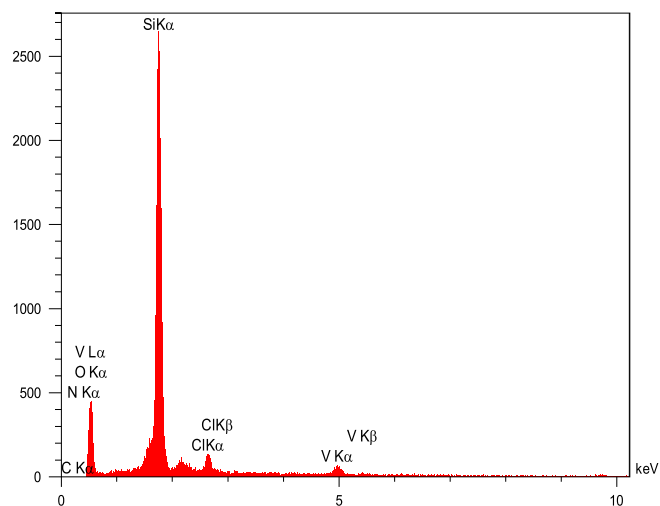


Figure 4. EDS spectrum of VO-2A3HP-MCM-41.

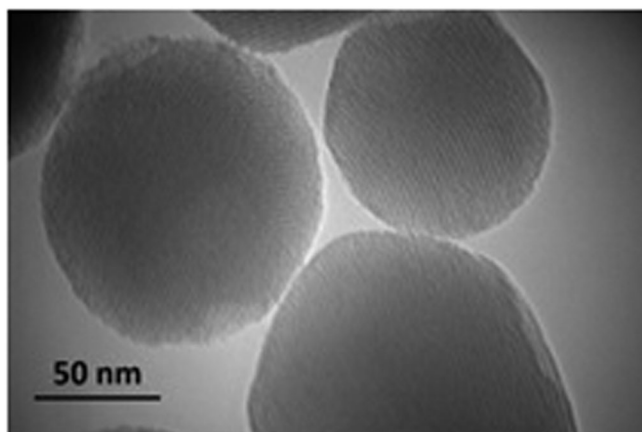


Figure 5. TEM image of VO-2A3HP-MCM-41.

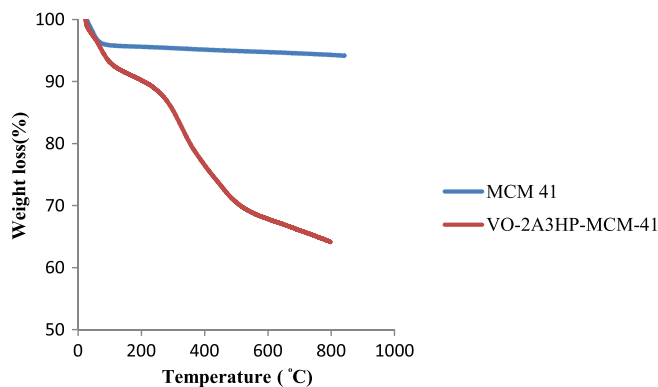


Figure 6. TGA thermograms of (a) MCM-41 and (b) VO-2A3HP-MCM-41.

In order to determine the textural properties of the catalyst, nitrogen adsorption and desorption isotherms of MCM-41 and VO-2A3HP-MCM-41 were measured and the results are shown in Fig. 7. BET analysis of MCM-41 shows a surface area of 1372 m² g⁻¹ and a pore volume of 1.521 cm³ g⁻¹. In comparison with MCM-41, the relative pressure is transformed into a lower value for VO-2A3HP-

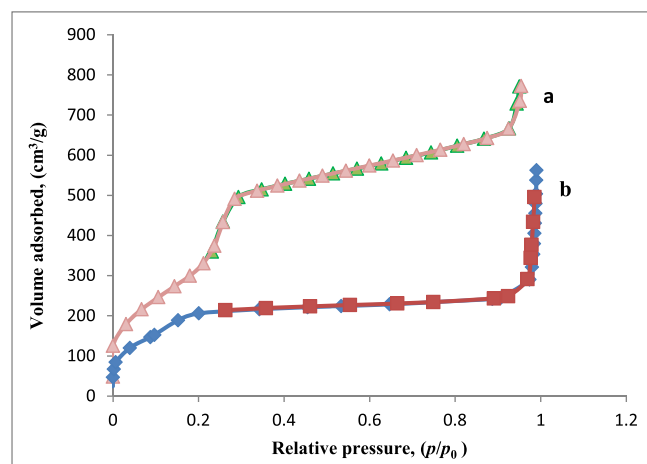


Figure 7. Nitrogen adsorption–desorption isotherms of (a) MCM-41 and (b) VO-2A3HP-MCM-41.

MCM-41, which leads to a reduction of BET specific area, pore volume and pore diameter. These results are summarized in Table 1. The wall thickness of MCM-41 and VO-2A3HP-MCM-41 was calculated using the following equation:

$$\text{Wall thickness} = \frac{2d_{100}}{\sqrt{3}} - D_{\text{BJH}}$$

Application of VO-2A3HP-MCM-41 complex in oxidation reactions

In continuation of our previous work on oxidation of sulfides into sulfoxides,^[22–24] here we report an easy way to accomplish catalytic sulfoxidation with hydrogen peroxide in the presence of VO-2A3HP-MCM-41 to afford sulfoxides in high yields and good chemoselectivity. Initially, the reaction without using any catalyst was conducted, giving the product in very low yield. In order to find the optimum reaction conditions, we tried to oxidize methylphenylsulfide as a model substrate with H₂O₂ in the presence of the catalyst under solvent-free conditions at room temperature. As evident from Table 2, the model compound selectively converts to the corresponding sulfoxide in excellent yield. Performing the oxidation of methylphenylsulfide with various molar ratio of H₂O₂ to sulfide shows that the amount of oxidant considerably affects the yield of sulfoxide. As the results

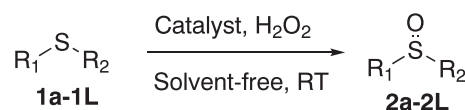
show, increasing the amount of oxidant leads to higher conversions. Methylphenylsulfide is completely converted to sulfoxide with 5 equiv. of H₂O₂. An attempt to carry out the reaction without the catalyst proved the reaction could occur rather slowly (5 h). However, when a similar oxidation reaction is conducted in the presence of the catalyst (10 mg), the reaction is completed (with a yield of 98%) in 2 h.

After optimization of the reaction parameters, the scope of applicability of the catalyst was investigated for oxidation of a variety of substituted aromatic and aliphatic sulfides (Scheme 2). The results are summarized in Table 3. Both alkyl and aryl sulfides selectively convert to the corresponding sulfoxides in excellent yield. The advantage of this method over conventional homogeneous reactions is that it provides greater selectivity, proceeds with enhanced reaction rates, gives cleaner products and involves simple manipulation. Upon completion of the reaction, the catalyst was filtered off, rinsed with CH₂Cl₂, dried and reused for at least four times with similar activity. It is evident that the catalyst possesses high stability in the oxidation of sulfides with H₂O₂ which demonstrates that VO-2A3HP-MCM-41 can be totally recovered after the oxidation without any decomposition. One of the most important factors that affect catalytic performance in sulfoxidations is Lewis acidity behaviour of the oxo-vanadium(IV) complex. This complex can readily withdraw electrons from the peroxide oxygens making them more susceptible to be attacked by nucleophilic sulfide compound. Functional groups such as hydroxyl groups remain unaffected (Table 3, entries 8 and 9).

Table 1. Textural parameters deduced from nitrogen sorption isotherms

Sample	S _{BET} (m ² g ⁻¹)	Pore diameter (nm) ^a	Pore volume (cm ³ g ⁻¹)	Wall diameter (nm)
MCM-41	1372.275	2.45	1.521	0.808
VO-2A3HP-MCM-41	846.01	1.21	0.846	1.64

^aObtained using the Barrett–Joyner–Halenda (BJH) method.



Scheme 2. Oxidation of sulfides to sulfoxides in the presence of VO-2A3HP-MCM-41.

Table 2. Comparison between various solvents and amount of VO-2A3HP-MCM-41 for the oxidation of methylphenylsulfide in 2 h at room temperature^a

Condition	Solvent	Yield (%) ^b
Solvent	Dichloromethane	45
	Ethanol	90
	Acetonitrile	98
	Ethyl acetate	80
	Solvent free	98
Amount of VO-2A3HP-MCM-41 (mg)	10	98
	8	82
	6	78
Amount of oxidant (equiv.)	Abs ^c	No reaction
	3	73
	4	89
	5	98

^aReaction conditions: methylphenylsulfide (1 mmol), H₂O₂ (0.4 ml, 1 mmol) at 40°C.

^bIsolated yields.

^cReaction proceeds in the absence of catalyst.

Table 3. Oxidation of various sulfides using H₂O₂, catalysed by VO-2A3HP-MCM-41

Entry	Substrate	Product	Time (min)	Yield (%) ^a	Melting point (°C)
1	Methyl(phenyl)sulfide	2a	120	96	31–33 ^[18]
2	Tetrahydrothiophene	2b	10	93	Oil ^[18]
3	Methyl(<i>p</i> -tolyl)sulfide	2c	45	95	120–123 ^[18]
4	Diphenylsulfide	2d	1800	86	66–69 ^[25]
5	Dipropylsulfide	2e	100	98	Oil ^[18]
6	Dodecyl(methyl)sulfide	2f	30	92	61–65 ^[18]
7	<i>n</i> -Dodecylsulfide	2g	60	91	Oil ^[18]
8	2-(phenylthio)ethanol	2h	15	90	Oil ^[18]
9	2-(methylthio)ethanol	2i	60	98	Oil ^[18]
10	4-Chlorophenyl(methyl)sulfide	2j	50	95	Oil ^[19]
11	Methyl-3-(methylthio)propionate	2k	240	93	Oil ^[18]
12	Allyl(methyl)sulfide	2L	60	94	Oil ^[26]

^aIsolated yields.

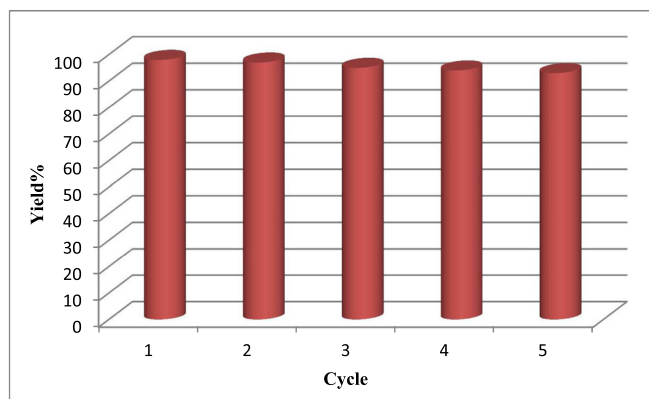


Figure 8. Reusability of VO-2A3HP-MCM-41 for the reaction of methylphenylsulfide.

Reuse of heterogeneous VO-2A3HP-MCM-41 catalyst

In order to investigate the recyclability of the catalyst, oxidation of methylphenylsulfide to the corresponding disulfoxide was examined. The catalyst was filtered off, rinsed with CH_2Cl_2 and dried after each run. As is evident from Fig. 8, the catalyst can be reused four times with only a slight loss of activity.

Conclusions

Our methodology provides an environmentally benign method for the preparation of VO-2A3HP-MCM-41 catalyst, which can be applied to the selective oxidation of sulfides to sulfoxides without over-oxidation to sulfones. The reaction proceeds at room temperature with regeneration of the catalyst.

References

- [1] J. A. L. da Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, *Coord. Chem. Rev.* **2011**, 255, 2232.

- [2] B. Zhang, S. Li, S. Yue, M. Cokoja, M. D. Zhou, S. L. Zang, F. E. Kühn, *J. Org. Chem.* **2013**, 744, 108.
- [3] H. Kominami, K. Nakanishi, S. Yamamoto, K. Imamura, K. Hashimoto, *Catal. Commun.* **2014**, 54, 100.
- [4] E. Zamanifar, F. Farzaneh, J. Simpson, M. Maghami, *Inorg. Chim. Acta* **2014**, 414, 63.
- [5] B. Yu, C. X. Guo, C. L. Zhong, Z. F. Diao, L. N. He, *Tetrahedron Lett.* **2014**, 55, 1818.
- [6] N. Moussa, J. M. Fraile, A. Ghorbel, J. A. Mayoral, *J. Mol. Catal. A* **2006**, 255, 62.
- [7] A. Fuerte, M. Iglesias, F. Sanchez, A. Corma, *J. Mol. Catal. A* **2004**, 211, 227.
- [8] M. R. Maurya, A. K. Chandrakar, S. Chand, *J. Mol. Catal. A* **2007**, 278, 12.
- [9] N. N. Trukhan, A. Y. Derevyankin, A. N. Shmakov, E. A. Paukshtis, O. A. Kholdeeva, V. N. Romannikov, *Micropor. Mesopor. Mater.* **2001**, 603, 44.
- [10] A. Ghorbani-Choghamarani, F. Nikpour, F. Ghorbani, F. Havasi, *RSC Adv.* **2015**, 5, 33212.
- [11] H. Yang, G. Zhang, X. Hong, Y. Zhu, *Micropor. Mesopor. Mater.* **2004**, 68, 119.
- [12] W. Richardhein, J. Melvin, *J. Org. Chem.* **1991**, 26, 4874.
- [13] J. C. Kim, H. X. Li, C. Y. Chen, M. E. Davis, *Micropor. Mater.* **1994**, 2, 413.
- [14] A. Corma, V. Fornes, R. M. Martin-Aranda, H. Garcia, J. Primo, *Appl. Catal.* **1990**, 59, 237.
- [15] A. Guida, M. H. Lhouty, D. Tichit, F. Figueras, P. Geneste, *Appl. Catal. A* **1997**, 164, 251.
- [16] E. N. Prilezhaeva, *Russ. Chem. Rev.* **2000**, 69, 36.
- [17] D. H. Rich, J. P. Tam, *J. Org. Chem.* **1977**, 42, 3815.
- [18] A. Ghorbani-Choghamarani, Z. Darvishnejad, B. Tahmasbi, *Inorg. Chim. Acta* **2015**, 435, 223.
- [19] A. Ghorbani-Choghamarani, G. Azadi, B. Tahmasbi, M. Hadizadeh-Hafshejani, Z. Abdi, *Phosphorus Sulfur Silicon Relat. Elem.* **2014**, 189, 433.
- [20] J. Gao, L. Lu, W. Zhou, G. Gao, M. He, *J. Porous Mater.* **2008**, 15, 127.
- [21] S. I. Mostafs, S. A. Abd El-Maksoud, *Montash. Chem.* **1998**, 129, 455.
- [22] M. Nikoorazm, A. Ghorbani-Choghamarani, N. Noori, *Appl. Organometal.* **2015**, 29, 328.
- [23] M. Nikoorazm, A. Ghorbani-Choghamarani, H. Mahdavi, S. M. Esmaeili, *Micropor. Mesopor. Mater.* **2015**, 211, 174.
- [24] M. Nikoorazm, A. Ghorbani-Choghamarani, F. Ghorbani, H. Mahdavi, Z. Karamshahi, *J. Porous Mater.* **2015**, 22, 261.
- [25] G. W. Wagner, Y. C. Yang, *Ind. Eng. Chem. Res.* **2002**, 41, 1925.
- [26] X.-Y. Shi, J.-F. Wei, *J. Mol. Catal. A* **2008**, 280, 142.