

Oxo-vanadium(IV) Schiff base complex supported on modified MCM-41: a reusable and efficient catalyst for the oxidation of sulfides and oxidative S–S coupling of thiols

Mohsen Nikoorazm*, Arash Ghorbani-Choghamarani and Nourolah Noori

Oxo-vanadium(IV) Schiff base complex supported on MCM-41 as an organic–inorganic hybrid heterogeneous catalyst was synthesized with post-grafting of MCM-41 with 3-aminopropyltrimethoxysilane and subsequent reaction with 3,4-dihydroxybenzaldehyde and then complexation with oxo-vanadium acetylacetonate salt. The catalyst was analysed using a series of characterization techniques such as Fourier transform infrared spectroscopy, small-angle X-ray diffraction, nitrogen absorption isotherm, transmission electron microscopy and thermogravimetric analysis. The data collected provided evidence that the vanadium complex was anchored onto MCM-41. High catalytic activity of this catalyst was observed in the oxidation of various sulfides and thiols (into sulfoxides and disulfides, respectively) with urea hydrogen peroxide as oxidant in high to excellent yields and selectivity under mild conditions. The heterogeneous catalyst could be recovered easily and reused several times without significant loss in catalytic activity and selectivity. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: MCM-41; VO(IV)–MCM-41; heterogeneous; sulfoxide; disulfides; urea hydrogen peroxide (UHP)

Introduction

Homogeneous conventional oxidation catalysts (i.e. transition metal complexes and soluble transition metal salts) have been widely employed for the oxidation of organic substrates such as sulfides, thiols, cyclohexene, styrene, etc., because of their high catalytic performance.^[1–3] However, due to the high costs of recovering and recycling these catalysts at the end of the reaction, their applications are seriously constrained. The irreversible deactivation of active metal complex moieties due to the formation of several dimeric and polymeric species, particularly when oxidant is added, is also a limitation.^[4] To make the catalytic process green and sustainable, several methods and strategies have been employed to immobilize homogeneous catalysts using various insoluble supports such as organic polymers, polystyrene or resins,^[5] mesoporous silica (e.g. MCM-41),^[6] clays,^[7] zeolite Y,^[8] etc.

Recently, the focus has shifted towards mesoporous MCM-41 as a major support material because of the particular features that it possesses such as large surface area, variable pore diameter and high-density surface silanol sites.^[9] Mesoporous MCM-41 provides an anchoring for valuable homogeneous catalysts/active organic moieties or the incorporation of redox metal ions into framework positions in a quite simple way, and thus increases their intrinsic catalytic activity as a result of the amorphous nature of the pore walls.^[10–13] For example, MCM-41-supported oxo-vanadium shows high selectivity for organic reactions such as epoxidation of olefins and bromination of hydroxyl aromatic compounds and alcohols.^[14–16] Furthermore, the selective oxidation reaction of sulfides to sulfoxides is very significant because of critical applications in organic synthetic chemistry, and also sulfoxides are beneficial

synthetic intermediates for the construction of various chemically and biologically crucial molecules,^[17] particularly drugs and natural products.^[18] Likewise, oxidative coupling of thiols to disulfides is important in biological processes and synthetic organic chemistry.^[19] In biological systems, thiols are oxidized by flavins, cytochromes and dehydroascorbic acid; due to this process the cellular redox potential is controlled and oxidative damage is prevented.^[20,21] Also, disulfides are important reagents in organic synthesis and can be used to prepare sulfinyl and sulfenyl compounds.^[22]

In continuation of our studies of the application of new heterogeneous systems in organic reactions, herein we report the synthesis and characterization of oxo-vanadium(IV) grafted/immobilized onto MCM-41 (VO(IV)–MCM-41). The heterogenized complex was used in catalytic studies of sulfoxidation and oxidative coupling of thiols in the presence of urea hydrogen peroxide (UHP) as oxidant.

Experimental

Materials and Physical Techniques

The cationic surfactant cetyltrimethylammonium bromide (CTAB; 98%), 3,4-dihydroxybenzaldehyde, tetraethylorthosilicate (TEOS),

* Correspondence to: Mohsen Nikoorazm, Department of Chemistry, Faculty of Science, 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

3-aminopropyltrimethoxysilane (APTES), sodium hydroxide, VO(acac)₃, organic sulfides, UHP and solvents were purchased from Merck, Fluka and Aldrich. The physicochemical characteristics were determined using powder X-ray diffraction (XRD) with a Philips X'pert diffractometer with monochromatized Cu K α radiation under the conditions of 40 kV, $\lambda = 1.5418 \text{ \AA}$ and 30 mA. FT-IR spectra of samples were recorded using KBr matrix in the range 400–4000 cm⁻¹ with a Bruker VRTX 70 FT-IR spectrometer. Nitrogen adsorption-desorption isotherm and Barrett-Joyner-Halenda (BJH) pore size distribution were recorded with a BELSORP-MINI. TGA of the samples was carried out using a Shimadzu DTG-60 automatic thermal analyser in the temperature range 30–900 °C at a heating rate of 10 °C min⁻¹ in air.

Preparation of Mesoporous Silica MCM-41

Parent silica MCM-41 was prepared using a standard procedure.^[23] The source of silicon was TEOS and the structure-directing agent was CTAB. A typical synthesis gel was prepared by adding gradually 5.78 g of TEOS to an aqueous solution containing 1.01 g of CTAB, 0.34 g of NaOH and 30 ml of deionized water. After stirring for about 1 h at room temperature, the resulting homogeneous mixture was crystallized under static hydrothermal conditions at 383 K in a Teflon-lined autoclave for 96 h. After cooling to room temperature the resultant solid was recovered by filtration, washed with deionized water and dried in air at 353 K. The collected product was calcined at 813 K for 5 h with a ramp of 2 °C min⁻¹ to remove the CTAB surfactant. Finally, we obtained mesoporous MCM-41.

Organic Modification of MCM-41 with APTES

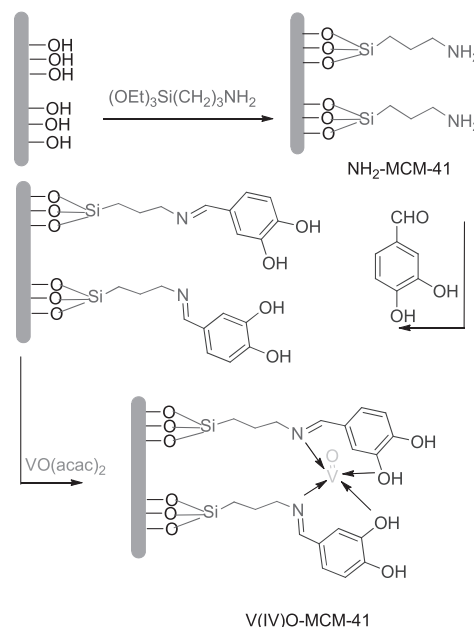
Silica MCM-41 (4.8 g) with 4.8 g of APTES in *n*-hexane (96 ml) was stirred under reflux conditions and nitrogen atmosphere for 24 h. After completion of the reaction, the white solid of APTES-functionalized MCM-41 (APTES@MCM-41) was filtered, washed with *n*-hexane and dried under vacuum (Scheme 1).

Preparation of VO(IV)–MCM-41

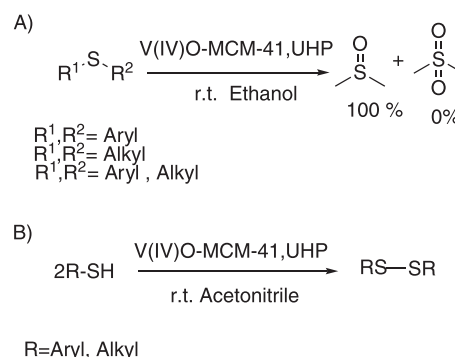
MCM-41-supported vanadium catalysts were prepared from the reaction of APTES@MCM-41 (1 mmol, 1 g) with 3,4-dihydroxybenzaldehyde (1 mmol, 0.134 g) in ethanol under reflux conditions and nitrogen atmosphere for 3 h. The yellowish solid was collected by filtration, washed with ethanol and dried under vacuum. VO(IV)–MCM-41 was prepared by dissolving (0.25 mmol, 0.066 g) of VO(acac)₃ and the yellowish solid obtained as described above in chloroform (20 ml). This mixture was stirred for 24 h at 60 °C. The resulting light greenish solid was recovered by vacuum filtration, washed with chloroform using Soxhlet extraction for 12 h to remove any unanchored vanadyl species and dried under vacuum (Scheme 1).

Oxidation of Sulfides into Sulfoxides using Catalytic Amounts of VO(IV)–MCM-41 and UHP

The catalytic activity of VO(IV)–MCM-41 in the oxidation reactions of various sulfides was investigated using the following procedure. A mixture of sulfide (1 mmol), UHP (5 mmol) and VO(IV)–MCM-41 (20 mg) was added to ethanol (4 ml; Scheme 2), and the mixture was stirred magnetically at room temperature for the appropriate time. The reaction progress was monitored using TLC. After completion of the reaction, the product was extracted with CH₂Cl₂



Scheme 1. Preparation of VO(IV)–MCM-41.



Scheme 2. Oxidation of sulfides and oxidative coupling of thiols catalysed by VO(IV)–MCM-41.

(3 × 10 ml) and was dried over anhydrous Na₂SO₃. Simple filtration followed by evaporation of the solvent from the filtrate gave the pure product. Oxidation products were obtained in very high isolated yields.

General Procedure for Oxidative Coupling of Thiols to Disulfides

A 25 ml round-bottom flask was charged with thiol (1 mmol), UHP (5 mmol), VO(IV)–MCM-41 (20 mg) and acetonitrile (4 ml) as solvent (Scheme 2). The reaction mixture was stirred at room temperature, and the progress of the reaction was monitored using TLC. After completion of the reaction, the corresponding disulfides were easily obtained by extraction with CH₂Cl₂.

Results and Discussion

Small-Angle XRD Patterns

The powder XRD patterns for the parent MCM-41 and samples derived by post-synthetic grafting are shown in Fig. 1. After post-synthetic grafting, the position of *d*₁₀₀ ($2\theta = 2.21^\circ$) reflection

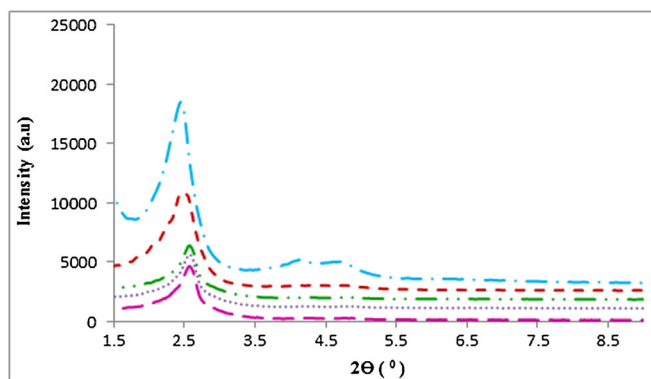


Figure 1. X-ray diffractograms of (top to bottom) MCM-41, MCM-41-NH₂, ligand, VO(IV)-MCM-41 and recovered VO(IV)-MCM-41.

remains virtually constant in all samples, suggesting that the hexagonal pore arrangement of MCM-41 is intact. Comparison of powder XRD patterns of MCM-41 and VO(IV)-MCM-41 shows that after anchoring VO(IV) through complex formation into MCM-41, the d_{110} and d_{200} reflections are no longer observed. A similar type of behaviour was observed by Joseph *et al.*^[24] Furthermore an overall decrease in the intensity of d_{100} is seen, this decrease in intensity being significant for the VO(IV)-MCM-41 sample. This is probably due to the difference in the scattering contrast of the pores and the walls, and to the irregular immobilization grafting of vanadium complex on the nano-channels of MCM-41.

FT-IR Spectroscopy

The FT-IR spectra of the samples in the range 400–4000 cm⁻¹ are depicted in Fig. 2. The absorption band around 1100–1200 cm⁻¹ is due to Si–O asymmetric stretching vibrations of Si–O–Si bridges which indicates the presence of silica in MCM-41. The spectrum of functionalized MCM-41 shows C–H stretching vibration at 2932 cm⁻¹ and also two bands (N–H group) appearing at 1642

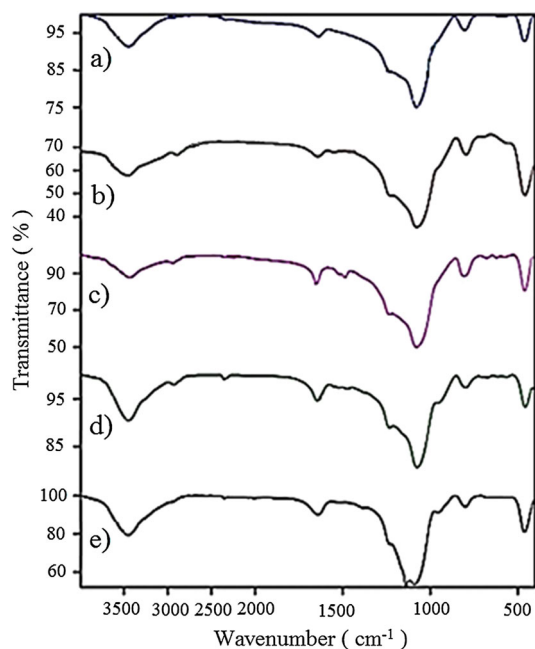


Figure 2. FT-IR spectra of (a) MCM-41, (b) MCM-41-NH₂, (c) ligand, (d) VO(IV)-MCM-41 and (e) fifth-stage recovery of VO(IV)-MCM-41.

and 1468 cm⁻¹. The band at 1657 cm⁻¹ is assigned to C=N stretching vibration of the imine group. The FT-IR spectrum of VO(IV)-MCM-41 displays a peak for C=N stretching at 1644 cm⁻¹. This shift to lower wavenumber is probably attributed to coordination of the complex with lone electron pair of nitrogen group of (C=N) as a sigma donor ligand. This result is evidence for the successful coordination of vanadium ion to functionalized MCM-41.

BET Measurements

Figure 3 shows the nitrogen adsorption–desorption isotherms of MCM-41, MCM-41-NH₂ and VO(IV)-MCM-41. Isotherm data exhibit typical irreversible type IV sorption isotherms as defined by IUPAC with a small hysteresis loop in the P/P_0 range 0.5 to 0.8 for MCM-41, MCM-41-NH₂ and VO(IV)-MCM-41. The nitrogen sorption analysis indicates that the surface areas of MCM-41 and VO(IV)-MCM-41 are 986.16 and 258.10 m² g⁻¹, respectively. The average pore diameter is calculated to be 3.65 using the BJH method. The pore diameter and pore volume of the mesopores indicate a marked decrease as a result of grafting vanadium Schiff base complex on the surface of the functionalized MCM-41 material. The results indicate that due to the presence of the large organic moieties within the pore channels of mesoporous silica the vanadium complex loading appears as a thin layer on the inner surface of MCM-41. The results are summarized in Table 1.

Transmission Electron Microscopy (TEM)

A TEM image of MCM-41 sample (Fig. 4) shows an arrangement of well-ordered hexagonal arrays of mesopores (two-dimensional channels) and long-range mesoporous architecture (50 nm). This is in good agreement with the XRD and BET results discussed as above.

Thermogravimetric Analysis (TGA)

The TGA results of MCM-41, MCM-41-NH₂ and VO(IV)-MCM-41 are shown in Fig. 5. TGA patterns of MCM-41 indicate a sharp weight

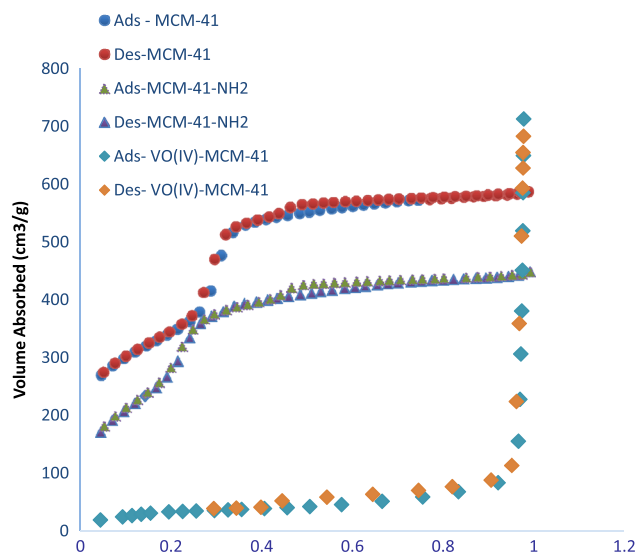
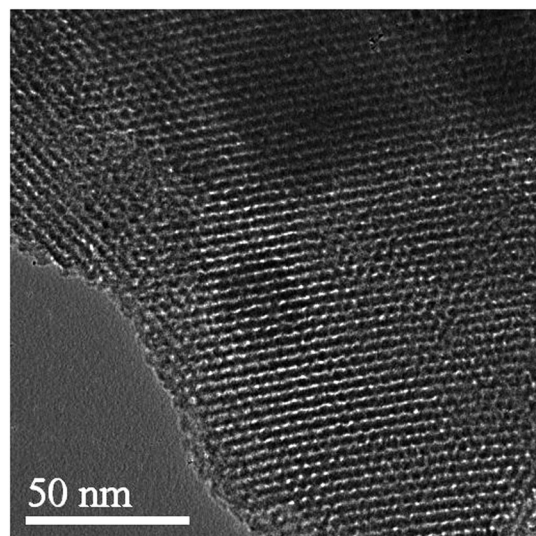


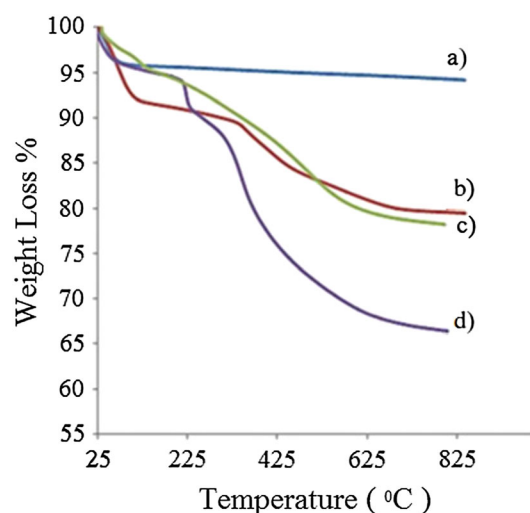
Figure 3. Nitrogen adsorption–desorption isotherms of (top to bottom) MCM-41, MCM-41-NH₂ and VO(IV)-MCM-41.

Table 1. Texture parameters obtained from nitrogen sorption studies

Sample	SBET (m ² g ⁻¹)	Pore diameter by BJH method (nm)	Pore volume (cm ³ g ⁻¹)	Wall diameter (nm)
MCM-41	986.16	3.65	0.711	0.902
NH ₂ -MCM-41	694.98	3.3	0.340	0.906
VO(IV)-MCM-41	258.10	1.34	0.191	1.42

**Figure 4.** TEM image of MCM-41.

loss below 100 °C corresponding to the loss of physisorbed water, and the TGA pattern of MCM-41-NH₂ indicates a three-step weight loss at temperatures ranging from 30 to 800 °C. The weight loss (3 wt%) below 120 °C is the result of physically adsorbed water, the 8% weight loss at 200–300 °C typically is related to the elimination of crystallization and the desorption of physisorbed water, whereas the third weight loss is related to the decomposition of organic groups. The TGA pattern of ligand-grafted MCM-41 indicates 13%

**Figure 5.** TGA curves of (a) MCM-41, (b) MCM-41-NH₂, (c) MCM-41-ligand and (d) VO(IV)-MCM-41.

weight loss above 350 °C that is mainly related to the decomposition of organic groups. Based on TGA, about 1.2 and 0.5 mmol of amine groups and the ligand are grafted on the MCM-41 surface, respectively. The TGA pattern of VO(IV)-MCM-41 indicates three weight loss steps: the first (4 wt%) below 120 °C is the result of physically adsorbed water, the second (5%) at 250–370 °C is attributed mostly to the combustion of amine and the third (4 wt%) at 450–650 °C is likely related to the decomposition of Schiff base groups.

Oxidation of Sulfides and Oxidative Coupling of Thiols with UHP Catalysed by VO(IV)-MCM-41

The catalytic activity of VO(IV)-MCM-41 was evaluated for the oxidation of sulfides and oxidative coupling of thiols with UHP under mild conditions (Scheme 2). To achieve optimum reaction conditions, various parameters, namely the nature of solvent, amount of catalyst and UHP, were studied.

Dibenzylsulfide and 4-methylthiophenol were selected as model substrates to optimize reaction conditions. In order to find an appropriate solvent for the oxidation of sulfides and oxidative coupling of thiols, we designed typical reactions for these transformations in various organic solvents. Ethanol was chosen as reaction medium for the oxidation of sulfides while for oxidative coupling of thiols, acetonitrile was selected based on reactivity and selectivity (Table 2).

After optimizing the solvent, catalyst amounts were varied from 0.003 to 0.025 g for reactions carried out at room temperature. The results are shown in Fig. 6. There is a general trend of increasing conversion of thiol and sulfide to the oxidized products (blank substrates) with increasing amount of catalyst. These results demonstrate clearly that VO(IV)-MCM-41 catalyst is very active in this reactions system, and that even a small amount (20 mg) can lead to significant conversion.

Finally the variation of substrate/UHP molar ratio was investigated. The optimum ratio of blank substrate to UHP of 1:6 mmol in the presence of catalyst is found to be ideal for oxidative coupling of thiols and oxidation of sulfides. It is observed that for a fixed amount of substrate (1 mmol), 20 mg of catalyst and 6 mmol of UHP in 4 ml of solvent are found to be the best conditions under which to achieve 100% conversion of substrates (sulfides and thiols). The results are summarized in Tables 3 and 4. An examination of the data in Table 3 indicates that various types of aryl- and alkylsulfides are converted successfully to sulfoxides in good yields at room temperature. All the reactions take place with total selectivity

Table 2. Effect of various solvents on the oxidation of sulfides and oxidative coupling of thiols

Entry	Solvent	Yield (%) ^a	Yield (%) ^b	Time (h) ^a	Time (h) ^b
1	Ethanol	98	83	1.75	0.66
2	Chloroform	85	80	5	4.25
3	Acetonitrile	91	94	3.25	0.33
4	Water	87	83	10	8
5	Dichloromethane	88	89	7.5	12
6	<i>n</i> -Hexane	90	87	11	7

^aReaction conditions: dibenzylsulfide (1 mmol), UHP (5 mmol), catalyst (20 mg), 4 ml solvent.

^bReaction conditions: 4-methylthiophenol (1 mmol), UHP (5 mmol), catalyst (20 mg), 4 ml solvent.

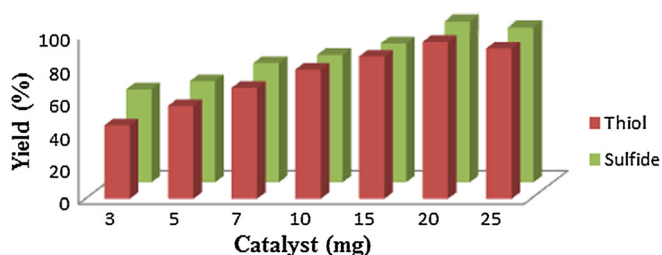


Figure 6. Effect of amount of catalyst on the oxidation of dibenzylsulfide and oxidative coupling of 4-methylthiophenol.

for sulfoxide formation; no over-oxidation products such as sulfones are found in the reaction mixtures. A similar mesoporous catalyst has previously been reported by Gao and co-workers^[13] with hydrogen peroxide at higher temperature with lower yields; therefore our procedure shows more activity and efficiency compared with similar previously reported procedures.

The data in Table 4 also demonstrate that all oxidative coupling reactions are conducted under totally heterogeneous conditions at room temperature and they are successfully converted into disulfide with good to excellent yields (except entry 12).

A possible mechanism for the oxidation of sulfides and thiols to the corresponding sulfoxides and disulfides using UHP as oxidant in the presence of VO(IV)–MCM-41 is outlined in Scheme 3.

Finally, the reusability of the VO(IV)–MCM-41 catalyst was investigated. Fig. 7 shows the yield of four consecutive cycles for the oxidation of dibenzylsulfide and 4-methylthiophenol. After the reaction reached completion, the catalyst was recovered, washed with ethanol and water then reused in the next cycle. The results show only an 11% decrease in the conversion after four cycles. Therefore these results demonstrate that the reusability of the catalyst satisfactory.

Table 3. Oxidation of various sulfides by UHP catalysed by V(IV)–MCM-41 in ethanol^a $R^1-S-R^2 \rightarrow R^1-(S=O)-R^2$

Entry	R^1	R^2	Yield (%) ^b	Time (h)	M.p. (°C)
1	Ph	CH_2CH_2OH	93	20	147–149 ^[25]
2	$PhCH_2$	$PhCH_2$	98	1.75	131–134 ^[25]
3	Ph	Ph	89	12 days	68–70 ^[26]
4	Ph	$PhCH_2$	95	18	120–122 ^[25]
5	$C_{12}H_{25}$	$C_{12}H_{25}$	94	8.25	88–90 ^[27]
6	CH_3CH_2	CH_3CH_2	95	1	103–104 ^[26]
7	Furan	Furan	94	3.25	83–85 ^[28]
8	Furyl- CH_2	CH_3	93	1	Oil ^[29]
9	$PhCH_2$	CH_3	96	1.5	Liquid ^[30]
10	Ph	CH_3	95	8	29–31 ^[25]
11	Tetrahydrothiophene	—	92	0.75	106–109 ^[31]
12	CH_3	$CH_2CH_2COOCH_3$	89	1.75	Liquid ^[30]
13	Ph	$PhCHCOOH$	90	10	73–81
14	CH_3	CH_2CH_2CHO	93	1.33	Oil ^[31]

^aReactions were run under air at room temperature and in the presence of substrate (1 mmol), UHP (5 mmol) and 20 mg of catalyst.

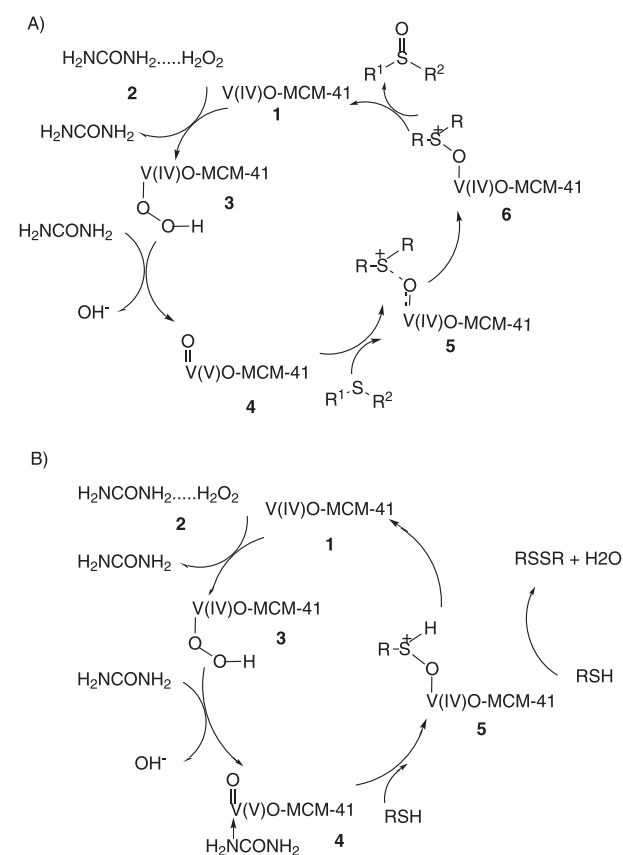
^bIsolated yield.

Table 4. Oxidation of various thiols using UHP, catalysed by VO(IV)–MCM-41 in acetonitrile^a $R-SH \rightarrow R-S-S-R$

Entry	R	Yield (%) ^b	Time (min)	M.p. (°C)
1	$p\text{-MeC}_6\text{H}_4\text{--}$	96	20	41–43 ^[32]
2	$\text{--CH}_2\text{COOH}$	92	11	Oil ^[32]
3	2-Naphthyl	90	50	142–144 ^[32]
4	2,6-Di- $\text{ClC}_6\text{H}_3\text{--}$	94	21	76–90 ^[33]
5	$p\text{-BrC}_6\text{H}_4\text{--}$	91	20	90–92 ^[33]
6	2-Pyridyl-	95	11	55–56 ^[34]
7	$\text{C}_6\text{H}_5\text{--}$	30	87	55–57 ^[30]
8	2-Benzoxazole	89	85	85–89 ^[32]
9	2-Benzothiazole	94	18	175–178 ^[32]
10	$\text{HOCH}_2\text{CH}_2\text{--}$	93	24	Oil ^[30]
11	2- $\text{COOHCH}_2\text{--}$	90	25	276–282 ^[32]

^aReactions were run under air at room temperature and in the presence of substrate (1 mmol), UHP (5 mmol) and 20 mg of catalyst.

^bIsolated yield.



Scheme 3. A possible mechanism path for (A) oxidation of sulfides to sulfoxides and (B) oxidative coupling of thiols to disulfides.

Conclusions

We have succeeded in preparing a heterogeneous catalyst by post-grafting VO(acac)₂ to form a Schiff base complex into functionalized MCM-41. VO(IV)–MCM-41 showed excellent catalytic activity in the oxidation reactions of various sulfides and thiols with good conversion and 100% selectivity using UHP as the oxidant. In addition, the catalyst can be recycled several times

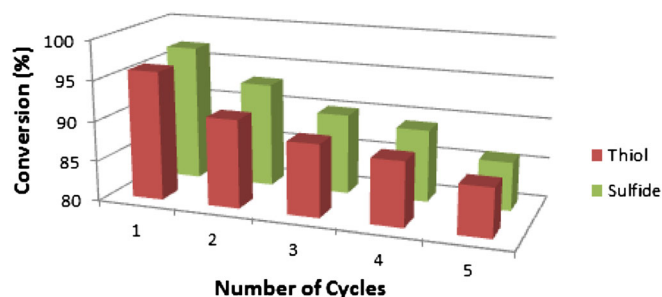


Figure 7. Reuse of the VO(IV)-MCM-41 catalyst.

without any loss in selectivity. The advantages of this synthesized catalyst are that it is cheap, environmentally friendly, efficient and selective.

Acknowledgments

The authors thank the research facilities of Ilam University, Ilam, Iran, for financial support of this research project.

References

- [1] A. Patel, K. Patel, *Inorg. Chim. Acta* **2014**, 419, 130–134.
- [2] M. Bagherzadeh, L. Tahsini, R. Latifi, V. Amani, A. Ellern, L. K. Woo, *Inorg. Chem. Commun.* **2009**, 12, 476–480.
- [3] Z. Biyiklioglu, E. T. Saka, S. Gokce, H. Kantekin, *J. Mol. Catal. A* **2013**, 378, 156–163.
- [4] M. R. Maurya, A. K. Chandrakar, S. Chand, *J. Mol. Catal. A* **2007**, 263, 227–237.
- [5] M. R. Maurya, A. Kumar, *J. Mol. Catal. A* **2006**, 250, 190–198.
- [6] M. Hatefi, M. Moghadam, I. Sheikhshoei, V. Mirkhani, S. Tangestaninejad, I. Mohammadpoor-Baltork, H. Kargar, *Appl. Catal. A* **2009**, 370, 66–71.
- [7] L. Q. Pereira, S. B. Cordeiro, M. S. Cosme, M. F. V. Marques, *Appl. Catal. A* **2014**, 475, 179–185.
- [8] F. Farzaneh, S. Sohrabi, M. Ghiasi, M. Ghandi, V. Daadmehr, *J. Porous Mater.* **2013**, 20, 267–275.
- [9] S. Shylesh, A. P. Singh, *J. Catal.* **2005**, 233, 359–371.
- [10] S. H. Shen, J. Chen, R. T. Koodali, Y. F. Hu, Q. F. Xiao, J. G. Zhou, X. X. Wang, L. J. Guo, *Appl. Catal. B* **2014**, 150, 138–146.
- [11] W. D. Zhang, L. X. Xu, W. Shi, C. C. Wang, Y. H. Hui, Z. F. Xie, *Russ. J. Gen. Chem.* **2014**, 84, 782–788.
- [12] U. G. Singh, R. T. Williams, K. R. Hallam, G. C. Allen, *J. Solid State Chem.* **2005**, 178, 3405–3413.
- [13] J. B. Gao, L. Lu, W. J. Zhou, G. H. Gao, M. Y. He, *J. Porous Mater.* **2008**, 15, 127–132.
- [14] S. Bhunia, S. Koner, *J. Porous Mater.* **2011**, 18, 399–407.
- [15] S. Bhunia, D. Saha, S. Koner, *Langmuir* **2011**, 27, 15322–15329.
- [16] S. Verma, M. Nandi, A. Modak, S. L. Jain, A. Bhaumik, *Adv. Synth. Catal.* **2011**, 353, 1897–1902.
- [17] K. P. Volcho, N. F. Salakhutdinov, *Russ. Rev.* **2009**, 78, 457–464.
- [18] R. Hoekstra, G. A. A. Nibourg, T. V. van der Hoeven, G. Plomer, J. Seppen, R. P. O. Elferink, M. T. Ackermans, W. Kulik, T. M. van Gulik, *Dispos.* **2013**, 41, 562–567.
- [19] A. Chaudhuri, *Curr. Sci. India* **1995**, 68, 692–698.
- [20] C.-G. Sun, B.-C. Hu, W.-Y. Zhou, S.-C. Xu, Z.-L. Liu, *J. Chem. Res.* **2011**, 35, 681–685.
- [21] D. Every, W. B. Griffin, P. E. Wilson, *Cereal Chem.* **2003**, 80, 35–39.
- [22] D. Alves, R. G. Lara, M. E. Contreira, C. S. Radatz, L. F. B. Duarte, G. Perin, *Tetrahedron Lett.* **2012**, 53, 3364–3368.
- [23] H. Chen, Y. Wang, *Ceram. Int.* **2002**, 28, 541–547.
- [24] T. Joseph, M. Hartman, S. Ernst, S. B. Halligudi, *J. Mol. Catal. A* **2004**, 207, 131–137.
- [25] M. M. Lakouraj, M. Tajbakhsh, F. Shirini, M. V. Asady Tamami, *Synth. Commun.* **2005**, 35, 775–784.
- [26] A. Shaabani, A. Bazgir, K. Soleimani, P. Salehi, *Synth. Commun.* **2003**, 33, 2935–2944.
- [27] M. Abdo, Y. Zhihang, V. L. Schramm, S. Knapp, *Org. Lett.* **2010**, 12, 2982–2985.
- [28] Y. Inbushi, M. Yoshihara, *Phosphorus Sulfur* **1995**, 103, 101–110.
- [29] F. R. Bisogno, A. Rioz-Martnez, C. Rodriguez, I. Lavandera, G. de Gonzalo, D. E. Torres Pazmino, M. W. Fraaije, V. Gotor, *Chem. Catal.* **2010**, 2, 946–949.
- [30] A. Ghorbani-Choghamarani, G. Azadi, B. Tahmasbi, M. Hadizadeh-Hafshejani, Z. Abdi, *Phosphorus Sulfur* **2014**, 189, 433–439.
- [31] A. Ghorbani-Choghamarani, H. Goudarziafshar, M. Nikoorazm, S. Yousefi, *Lett. Org. Chem.* **2009**, 6, 335–339.
- [32] A. Ghorbani-Choghamarani, S. Sardari, *J. Sulfur Chem.* **2011**, 32, 63–69.
- [33] A. Ghorbani-Choghamarani, M. Nikoorazm, H. Goudarziafshar, A. Shokr, H. Almasi, *J. Chem. Sci.* **2011**, 123, 453–457.
- [34] B. Karami, M. Montazerzohori, M. H. Habibi, *Molecules* **2005**, 10, 1358–1363.