CHINESE JOURNAL OF CATALYSIS
Volume 31, Issue 10, 2010
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com

Cite this article as: Chin J Catal, 2010, 31: 1217–1220.

RESEARCH PAPER

Catalytic Oxidation of Aryl Alkyl Sulfides Using Immobilized Vanadyl Ions within Nanoreactors of Al-MCM-41

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Abstract: $VOSO_4$ immobilized within nanoreactors of Al-MCM-41 (VO^{2+}/Al-MCM-41) was synthesized and characterized by X-ray diffraction, Fourier transform infrared spectroscopy, nitrogen adsorption-desorption, and chemical analysis techniques. The prepared VO^{2+}/Al-MCM-41 successfully catalyzes the oxidation of aryl alkyl sulfides and up to 99% conversion and 90% selectivity for the corresponding sulfoxides were obtained with H_2O_2 as oxidant in acetonitrile at room temperature in 30 min.

Key words: Al-MCM-4; vanadyl ion; hydrogen peroxide; sulfoxidation

Organic sulfoxides are useful synthetic intermediates for the preparation of various chemically and biologically active molecules [1,2]. The study of the oxidation of sulfides to sulfoxides with different methodology is an interesting subject. In general, sulfoxides are obtained by the partial oxidation of sulfides with oxidants such as tert-butyl hydroperoxide or H_2O_2 [3]. These oxidants are relatively weak and need to be activated by the addition of transition metal ions to produce reactive peroxo species [2–4]. Therefore, many catalytic sulfoxidation reactions have been carried out in the liquid phase in the presence of soluble Ti, Mn, Cr, Re, W, or V complexes [2,5–8]. In recent years, the chemistry of vanadium complexes has attracted considerable attention because of their potential application as catalysts for the oxidation of various organic sulfides [2,9–10]. Easier and more environmentally benign processes can be obtained by heterogenizing the homogeneous catalysts. Several supported metals such as vanadium compounds on TiO_2 [11], mesoporous silica [12], USY zeolites [13,14], VO_x/Al_2O_3 or VO_x/SiO_2 [15], and $VO(acac)_2$ exchanged sulfonic acid resin have been used in sulfoxidation reactions [16].

In this study, we attempted to use VO^{2+}/Al-MCM-41 as a stable catalyst for the sulfoxidation of aryl and alkyl sulfides.

1 Experimental

1.1 Immobilization of $VOSO_4$ within Al-MCM-41

$VOSO_4$ (0.2 g) in ethanol (10 ml) was added to Al-MCM-41 (1.0 g, synthesized as reported previously [17]) in ethanol (10 ml). The resultant mixture was refluxed for 8 h. The mixture was then filtered and washed with hot ethanol. The percentage of vanadium was determined to be 1.660% by ICP.

1.2 General procedure of oxidation of aryl alkyl sulfide

Typically, a mixture of 0.05 g of VO^{2+}/Al-MCM-41 catalyst and 20 mmol of substrate in 10 ml of acetonitrile was slowly stirred in a round bottom flask. H_2O_2 (30% aqueous solution, 24 mmol) was then added to the reaction mixture after a few minutes and further stirred at room temperature. The solid was then filtered and washed with fresh solvent. The filtrate was analyzed by GC and GC-MS.

1.3 Characterization of the catalyst

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. Electronic spectra for the solid catalysts were recorded in Nujol on a Perkin Elmer Lambada 35 UV-Vis spectrophotometer. The products were analyzed by GC and GC-MS using an Agilent 6890 Series instrument with an FID detector, a HP-5, 5%

Received date: 26 March 2010.

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Foundation item: Supported by the Research Council of the University of Alzahra, Iran.

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DOI: 10.1016/S1872-2067(10)60114-3

phenylmethylsiloxane capillary, and an Agilent 5973 Network system, a mass selective detector and a HP-5 MS 6989 Network GC system. X-ray powder diffraction (XRD) data were recorded on a Seifert XRD 3003 PTS diffractometer with Cu $K_{\alpha 1}$ radiation (λ = 0.154 nm). Nitrogen adsorption studies were performed at liquid nitrogen temperature using a Quanta chrome Nova 2200, version 7.11 analyzer. Chemical analysis of the samples was carried out using the ICP technique.

2 Results and discussion

2.1 Characterization of the catalyst

Al-MCM-41 was prepared according to the procedure described previously. Figure 1 shows the XRD pattern of calcined Al-MCM-41. As shown, it has one strong and two weak peaks. All three XRD reflections can be indexed on a hexagonal lattice. The XRD of the calcined Al-MCM-41 is completely consistent with that of the spectrum for Al-MCM-41 [17]. The decrease in the VO^{2+}/Al-MCM-41 XRD peak intensities and the decrease in the *d* value from 3.878 to 3.803 nm is an indication of the Al-MCM-41 pore surface silanol groups reacting with vanadyl ions (Fig. 1 and Table 1).

The N_2 adsorption-desorption isotherms of Al-MCM-41, VO^{2+}/Al-MCM-41, and used VO^{2+}/Al-MCM-41 are shown in Fig. 2. The type IV isotherms [18] indicate that at low relative pressures p/p_0, adsorption take place as thin layers on the walls (monolayer coverage). In addition, the height of the inflection in the nitrogen adsorption isotherm plots for VO^{2+}/Al-MCM-41 is smaller than that of Al-MCM-41. This is attributed to the reduction in pore volume from 1.074 0 to 0.973 5 cm^3/g, which indicates a decrease in the surface area (Table 1). This effect can be attributed to the inclusion of vanadyl ions in the Al-MCM-41 pores. A surface area and pore volume of 1 095 m^2/g and 0.514 8 cm^3/g, respectively, were obtained by N_2 adsorption-desorption isotherms (Fig. 2(c)) and reveals that the used catalyst is stable. The small decrease in these parameters might be because of the adsorption of some water and solvent molecules.

The FT-IR spectra of Al-MCM-41 and VO^{2+}/Al-MCM-41 are shown in Table 2. The broad bands around 3 422 cm^{-1} are attributed to surface silanols and adsorbed water molecules. The adsorption bands at 1 080–1 100 and 1 200–1 223 cm^{-1} are because of the asymmetric stretching vibrations of Si-O-Si bridges, and the band at 950–980 cm^{-1} arises from Si-O-Al vibrations, V-O-Si symmetric vibrations [16,19] and V=O stretching modes.

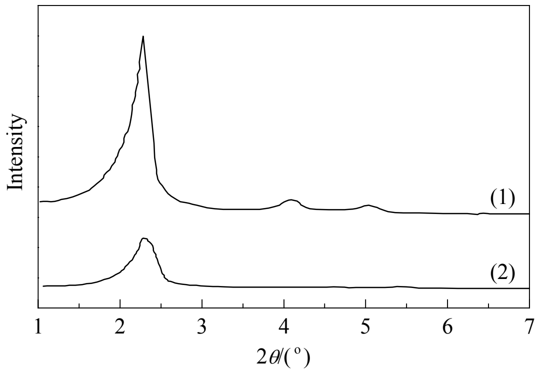


Fig. 1. XRD patterns of calcined Al-MCM-41 (1) and VO^{2+}/MCM-41 (2).

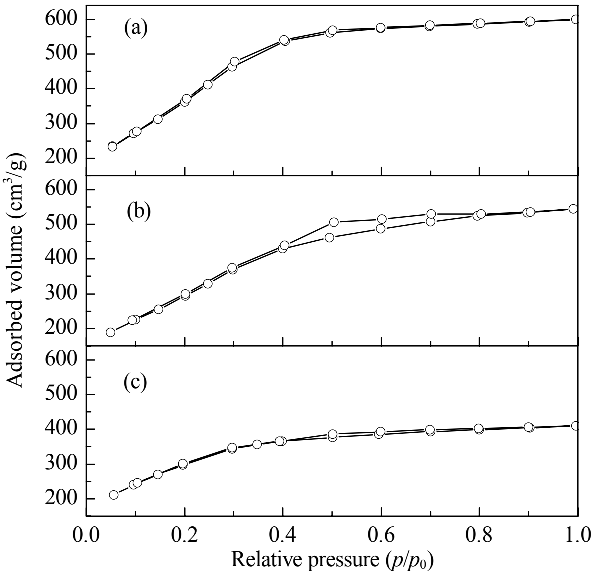


Fig. 2. Nitrogen adsorption-desorption isotherms of Al-MCM-41 (a), VO^{2+}/Al-MCM-41 (b), and VO^{2+}/Al-MCM-41 after the reaction (c).

2.2 Catalytic activity studies

The oxidation of methyl phenyl sulfide as a representative

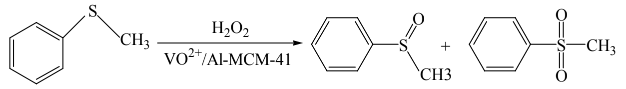
Table 1 Texture parameters of samples taken from XRD and nitrogen adsorption studies

Catalyst	XRD *d* value (nm)	Lattice parameter (nm)	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
Al-MCM-41	3.878	4.478	1455	1.0740	1.972
VO-Al-MCM-41	3.803	4.391	1202	0.9735	1.950

Table 2 FT-IR band assignments corresponding to the wavenumbers obtained for Al-MCM-41 and immobilized vanadyl ions within the nanoreactors of Al-MCM-41

Catalyst	υOH (Si-OH)/cm^{-1}	υ_{as}(Si-O-Si)/cm^{-1}	υ_{as}(Si-O-Si)/(Si-O-V)/cm^{-1}	υ_s(Si-OSi)/cm^{-1}
Al-MCM-41	3422	1080, 1223	960	802
VO-Al-MCM-41	3424	1091, 1223	968	805

Table 3 Effect of time on the oxidation of phenyl methyl sulfide in acetonitrile in the presence of VO^{2+}/Al-MCM-41



Entry	Time (min)	Conversion (%)	Sulfoxide selectivity (%)	Sulfone selectivity (%)
1	10	58	48	52
2	20	75	56	45
3	30	87	85	15
4[a]	30	66	80	20
5	60	87	84	16
6[b]	30	14	59	41

Reaction conditions: catalyst 0.05 g, substrate 20 mmol, H_2O_2 24 mmol, room temperature. [a]Catalyst 0.10 g. [b]A blank reaction.

substrate with 30% aqueous H_2O_2 was carried out using VO^{2+}/Al-MCM-41 as a catalyst. To obtain the optimum reaction time, the oxidation reactions were carried out over different times. The results are presented in Table 3. As seen in Table 3, about 87% of the methyl phenyl sulfide was converted into sulfoxide and sulfone with 85% and 15% selectivities, respectively, during 30 min of reaction time.

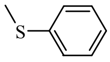
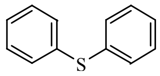
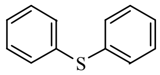
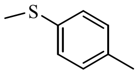
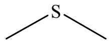
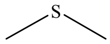
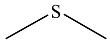
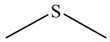
Furthermore, the use of about 0.05 g catalyst was shown to give a substrate conversion of 85%. A further increase in the amount of catalyst by 0.10 g led to a decrease in conversion to 66%. Increasing the amount of catalyst to beyond the optimum amount increases the available catalyst surface area and thus creates a suitable medium for the adsorption of guest molecules (either substrates or products). This in turn may result in a decrease in the total conversion.

A blank reaction under similar conditions with methyl phenyl sulfide resulted in a 14% conversion with 59% and 41% selectivity for the sulfoxide and sulfone, respectively. Thus, running the oxidation reaction in the presence of VO^{2+}/Al-MCM-41 as a catalyst not only enhances the methyl phenyl sulfide conversion but also improves its selectivity toward the formation of sulfoxides.

We then examined a range of sulfides having various R groups that were either aromatic or aliphatic and were attached to the sulfur atom under oxidation conditions. The results are listed in Table 4. Table 4 reveals that dimethylsulfide with 99% conversion and diphenyl sulfide with 4% conversion show the most and the least oxidation reactivity, respectively, at room temperature but the conversion of diphenyl sulfide increased to 98% under reflux conditions.

The recyclability of VO^{2+}/Al-MCM-41 as a catalyst was investigated for the dimethylsulfide reaction in a typical experiment where the reaction mixture was filtered and the catalytic reaction was repeated under similar conditions after activating the catalyst by washing with acetonitile and drying at 100 °C. No appreciable loss in catalytic activity was observed and this suggests that the active species is still present in the Al-MCM-41 nanopores. On the other hand, the filtrate did not show any activity when it was subjected to another 30 min reaction with fresh oxidant and substrate. An ICP determination of the vanadium catalyst found 1.660% and 1.559% before and after the reaction, respectively. The vanadium content of the filtrate solution was found to be below the ICP detection limit. These results clearly demonstrate the heterogeneous nature of the sulfoxidation reaction.

Table 4 Oxidation of aryl alkyl sulfides with H_2O_2 in the presence of VO^{2+}/Al-MCM-41

Substrate	Conversion (%)	Sulfoxide selectivity (%)	Sulfone selectivity (%)	TON[a]
	87	85	15	1088
	4	84	16	1025
	84[b]	100	—	50
	98	66	34	1225
	≈99	90	10	1238
	95[c]	90	10	—
	20[d]	100	—	—
	10[e]	100	—	—

Reaction conditions: catalyst 0.05 g, substrate 20 mmol, H_2O_2 24 mmol, solvent acetonitrile 10 ml, room temperature, 30 min.

[a]TON is the mmol of product to mmol of vanadium present in the catalysts. [b]Under reflux conditions for 3 h. [c]Used catalyst. [d]In the presence of Al-MCM-41 catalyst. [e]No catalyst was used.

We propose a mechanism based on the chemistry of peroxovanadium as reported previously [10]. The peroxo species is obtained in situ by the interaction of the catalyst with hydrogen peroxide. A subsequent transfer of electrophilic oxygen from the peroxometal species to the nucleophilic sulfide leads to the formation of sulfoxide with the eventual regeneration of the catalyst [20].

Compared with the reported procedures [14,15,21], the use of VO^{2+} without using any ligand plus the heterogeneous nature of the catalysis system free of metal ion leaching is the novelty of our method. The diversity of the sulfide used in this work and dimethyl sulfide in particular for the synthesis of dimethyl sulfoxide (DMSO) is of particular importance in this research.

3 Conclusions

We found that VO^{2+}/Al-MCM-41 promotes the sulfoxidation of methyl phenyl, dimethyl, tollyl methyl, and diphenyl sulfides towards sulfides and sulfones with ecofriendly oxidants under mild conditions. The reactivity of sulfides toward sulfoxidation increases by increasing the electron donating ability of the organic sulfide groups. The sulfoxidation of tollylmethyl and dimethyl sulfide occurred with 98% and 99% conversion, respectively, and the absence of leaching during the course of these reactions is of fundamental importance and should be emphasized.

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