Vanadium oxide supported on mesocellulous silica foams (MCF): An efficient and reusable catalyst for selective oxidation of sulfides

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Abstract

A green, efficient and selective approach for the oxidation of sulfides to sulfoxides and sulfones with UHP at room temperature is reported. The reaction is performed in the presence of vanadia catalyst supported on mesocellular silica foam (MCF) with a V content ranging from 2% to 10% as heterogeneous and reusable catalyst. The structural and textural characterization of this catalyst was done using FTIR, X-ray diffraction, and N_2 adsorption. This catalyst was found to be effective for selective oxidation of sulfides to sulfoxides and the 5.6% V/MCF catalyst showed the highest activity.

Keywords: Supported vanadia catalyst; impregnation method; oxidation of sulfides; mesocellular silica foams (MCF).

Introduction

Oxidation of sulfides is the most straightforward method for the synthesis of sulfoxides and sulfones [1], both of which are important as commodity chemicals and, in some cases, as pharmaceuticals [2].

This transformation has been performed in various ways [3-7]. However, the reported methods rarely offer the ideal combination of simplicity of method, rapid and selective reactions, and high yields of products and often suffer from a lack of generality and economical applicability.

Both supported noble metals [11,12] and metal oxides [13,14] are currently employed for the total oxidation of hazardous organic

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air pollutants. The former, though more active, are too expensive and undergo deactivation by chlorinated compounds in gas stream [11]. The latter, though not expensive, are far less active. All these are despite literature ports that vanadium-based catalysts are effective towards the catalytic oxidation of several volatile organic compounds [15–18]. V-containing mesoporous silicas (e.g. V-SBA-15, V-MCM-41, V-MCM-48, V-MCF, etc.) with uniform pores size and high surface area are interesting catalysts for oxidation reactions, allowing a large concentration of accessible and well-defined active centers (VO$_x$), often incorporate in the silica framework [19–23]. Although such catalysts are usually prepared by impregnation, it has been observed that V-SBA-15 materials prepared by direct synthesis exhibit larger surface area, better dispersion and reducibility of V pecies and superior catalytic performances in both selective and total oxidation reactions [20,21].

Herein, we describe the successful use of the MCF-supported vanadium catalyst for the selective oxidation of sulfides to sulfoxides (Scheme 1). The series of sulfides selected for these studies is shown in Scheme 2. The series include aliphatic and aromatic sulfides (a-h), olefinic sulfides (i), ester (j),

ketosulfides (k), alcohol (l) and olefinic sulfides (m, n).

Scheme 1. Reagents and conditions: (i) UHP (8 mmol), V-MCF (2 mol%), CH$_3$OH, r.t.; (ii) UHP (8 mmol), V-MCF (3 mol%), CH$_3$CN, r.t.

Scheme 2. The structures of the used sulfides

Experimental

All materials were commercial reagent grade. Infrared spectra (400–4000 cm^{-1}) were recorded from KBr pellets on a Nicolet *Impact 400 D* spectrometer. Reaction courses and product mixtures were monitored by thin layer chromatography. The X-ray powdered diffraction patterns were performed on a Bruker-D8 advance with automatic control. The patterns were run with monochromatic

Cu Kα (1.5406 Å) radiation with a scan rate of 2° min^{-1}. The BET specific surface areas and pore volumes of the catalyst were determined by the adsorption/desorption of nitrogen at liquid nitrogen temperature with a Micromeritics Bel sorp mini instrument. The pore sizes of the catalyst were obtained from the peak positions of the distribution curves determined from the adsorption branches of the isotherms.

Preparation of V-MCF

MCF-supported vanadia catalyst was prepared by an alcoholic impregnation method as described previously [23]. A methanol solution of NH_4VO_3 to achieve a final V content of 1.4–5.6 wt% of V atoms was contacted with the MCF carrier at 60 C, and the methanol was rotaevaporated until complete dryness. Then the catalyst was dried overnight in air at 120 C, followed by calcination at 600 C for 4 h in air.

Synthesis of sulfoxides and sulfones

To a stirred suspension of the selected sulfide (10 mmol) and the heterogeneous catalyst V-MCF (0.019 g, 2 mol%) in methanol (10 mL), urea hydrogen peroxide (UHP, 8 mmol) was added in one portion. The slurry was stirred at room temperature for 20 min. The catalyst was filtered off and washed with methanol (10 mL). Ethyl acetate (10 mL) was added and resulting solution was dried with anhydrous sodium sulphate and evaporated in vacuo to afford the crude product which was purified by column chromatography on silica gel (10% EtOAc in hexane) to afford the pure sulfoxide. Similar method was utilized to produce sulfones. In this case, 3 mol % of V-MCF in CH_3CN were utilized.

Selected spectroscopic data

Dibutyl sulfoxide (2a)

Mp 34-35 C. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 0.97 (t, 6H, *J*=7.4 Hz), 1.41-1.57 (m, 4H), 1.72-1.79 (m, 4H), 2.60-2.73 (m, 4H). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 13.64, 22.05, 24.56, 52.13.

Methyl phenyl sulfoxide (2b)

Mp 30-31 C. IR (ν_{max}, KBr, cm^{-1}): 530, 690, 751, 957, 1037, 1431, 1647, 2922, 3004; ^{1}H NMR (400 MHz, CDCl$_3$, δ): 2.73 (s, 3H), 7.49-7.57 (m, 3H), 7.61-7.67 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 43.95, 123.47, 129.33, 131.00, 145.72.

Diphenyl sulfoxide (2c)

Mp 72-73 C. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.42-7.49 (m, 6H), 7.63-7.66 (m, 4H). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 124.77, 129.30, 131.03, 145.61.

Benzyl 4-bromobenzyl sulfoxide (2d)

Mp 139-140 C. IR (ν_{max}, KBr, cm^{-1}): 1028; ^{1}H NMR (500 MHz, CDCl$_3$, δ): 3.78(d, 1H, *J*= 13.1 Hz), 3.89(d, 1H, *J*= 13.09 Hz), 3.95 (s, 2H), 7.2 (d, 2H, *J*=8.3 Hz), 7.32-7.33 (m,

2H), 7.40-7.44 (m, 3H), 7.54(d, 2H, *J*=8.3 Hz).

4-Nitrobenzyl phenyl sulfoxide (2e)

Mp 161-163 ^{o}C. IR (ν_{max}, KBr, cm^{-1}): 1026, 1345, 1515; ^{1}H NMR (200 MHz, CDCl$_3$, δ): 4.04 (d, 1H, *J*= 12.0 Hz), 4.24 (d, 1H, *J*= 12.0 Hz), 7.13 (d, 1H, *J*= 6.5 Hz), 7.40-7.51 (m, 5H), 8.12 (d, 2H, *J*= 6.5 Hz).

Methyl 2-(phenylsulfinyl)acetate (2j)

Isolated as yellow oil. IR (ν_{max}, KBr, cm^{-1}): 487, 691, 749, 1045, 1444, 1736, 2927; ^{1}H NMR (400 MHz, CDCl$_3$, δ): 3.72 (s, 3H), 3.68(d, 1H, *J*= 13.6 Hz), 3.86 (d, 1H, *J*= 13.6 Hz), 7.52-7.59 (m, 3H); 7.66-7.73 (m, 2H).

Dibutyl sulfone (3a)

Mp 46-47 C. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 0.97 (t, 6H, *J*=7.4 Hz), 1.44-1.53 (m, 4H), 1.78-1.86 (m, 4H), 2.93-2.97 (m, 4H). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 13.53, 21.78, 23.93, 52.46.

Methyl phenyl sulfone (3b)

Mp 89-90 C. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 3.06 (s, 3H), 7.56-7.60 (m, 2H), 7.65-7.69 (m, 1H), 7.95-7.97 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 44.67, 127.32, 129.34, 133.67, 140.58.

Diphenyl sulfone (3c)

Mp 128-129 C. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.48-7.59 (m, 6H), 7.94-7.97 (m, 4H). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 127.65, 129.26, 133.15, 141.61.

2-Hydroxyethyl phenyl sulfone (3k)

^{1}H NMR (400 MHz, CDCl$_3$, δ): 2.04 (br, 1H), 3.35 (t, 2H, J. 5.2 Hz), 4.01 (t, 2H, J.5.2 Hz), 7.60 (t, 2H, J.7.6 Hz), 7.68-7.72 (m, 1H), 7.95 (d, 2H, J.7.6 Hz). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 56.33, 58.24, 127.95, 129.47, 134.07, 138.94.

Benzyl 4-bromobenzyl sulfone (3d)

Mp 176-178 ^{o}C. IR (ν_{max}, KBr, cm^{-1}): 1116, 1299; ^{1}H NMR (400 MHz, CDCl$_3$, δ): 4.02 (s, 2H), 4.14 (s, 2H), 7.17-7.60 (m, 9H).

4-Nitrobenzyl phenyl sulfone (3e)

Mp 204-205 C. IR (ν_{max}, KBr, cm^{-1}): 1140, 1302, 1341, 1519; ^{1}H NMR (400 MHz, CDCl$_3$, δ): 4.44 (s, 2H), 7.10 (d, 2H, *J*= 6.5 Hz), 7.40-7.70 (m, 5H), 8.18 (d, 2H, *J*= 6.5 Hz).

Results and discussion

Physico-chemical characterization

FTIR

Figure 1 presents the FTIR spectra in the skeletal region of 4000–400 cm^{-1} for the V-loaded MCF materials. As shown in the spectrum of the parent MCF silica, the typical bands due to siliceous Si–O–Si material are observed: a main band at 1070 cm^{-1} with a shoulder at 1200 cm^{-1}, due to asymmetric Si–O–Si stretching modes, the corresponding symmetric stretch at 810 cm^{-1}, and Si–O– or Si–OH at 972 cm^{-1} [19]. In the

spectra of the V-containing samples, an additional band at ca. 915 cm^{-1}, indicative of Si–O–V species [21], is well developed for the samples with V content up to 5.6 wt%. Coupled with the significant spectral changes in the hydroxyl region, these phenomena further confirm the perturbed silica vibrations due to the incorporation of vanadium into the MCF silica framework; other researchers have reported similar trends in the IR spectra of their catalytic vanadia-silicas [19-23].
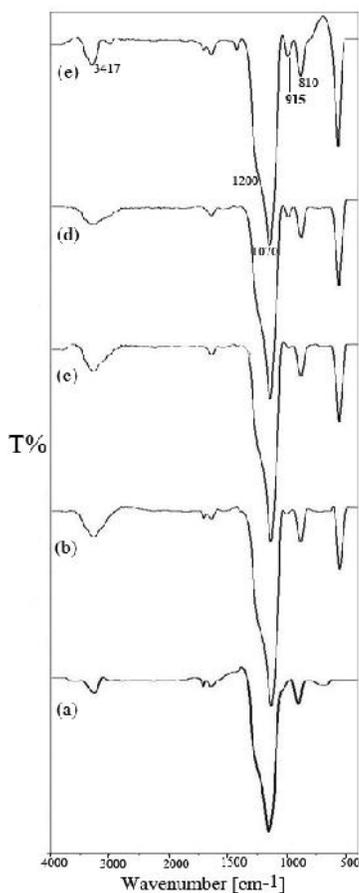
Figure 1. FTIR spectra of (a)MCF; (b) 1.4V-MCF; (c)2.8V-MCF; (d)4.2V-MCF; (e)5.6V-MCF

XRD

Wide-angle XRD patterns of the V/MCF samples with various V content are shown in Figure 2. No diffraction peaks corresponding to vanadium oxides were detected in the V/MCF catalyst with a V content of up to 5.6% suggesting the vanadium species in these samples are highly dispersed on the surface. As the V content was increased to 8%, weak diffraction peaks of crystalline V_2O_5 appeared indicating the formation of bulk vanadia at a high V content. Figure 3 shows wide-angle XRD patterns of the V/MCF samples with V content about 18%. An increase in V content further on the MCF support results in an increase in the peak intensity.
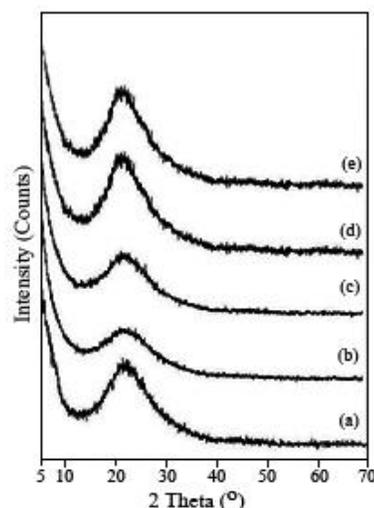
Figure 2. XRD patterns of (a)MCF; (b)1.4V-MCF; (c)2.8V-MCF; (d)4.2V-MCF; (e)5.6V-MCF
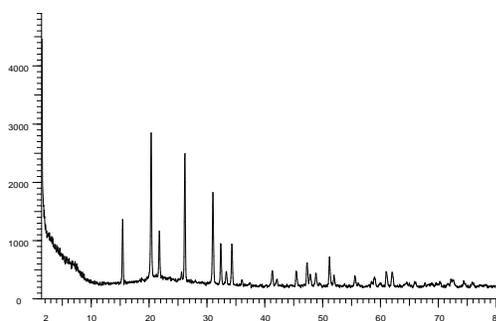
Figure 3. XRD patterns of 18% V-MCF

Table 1. Characteristics of the mesoporous silica

Entry	Sample	BET, surface area (m²/g)	Pore volume (cm³/g)	Pore diameter (nm)	Pore size (nm) BJH adsorption
1	MCF, silica	720	1.76	9.8	7.99
2	5.6% V/MCF	244	1.89	30.94	7.99

BET

The maintenance of the well-defined MCF frameworks after introduction of vanadium is further supported by the nitrogen sorption data. For both of MCF and V-MCF samples, the nitrogen adsorption/desorption isotherms (Figure 4) are of type IV and show steep hysteresis of type H_1 at high relative pressures. The pore size distribution of the 5.6 V-MCF shown in the inset of Figure 4b unambiguously reveals that the 3D mesocellular structure of the support has been preserved. Structural properties of MCF samples are listed in Table 1. MCF showed BET surface area of 720 m²/g and pore volume of 1.76 cm³/g. After Vanadium modification, the nitrogen adsorption isotherm became an even line and the volume adsorbed decreased distinctly, suggesting the occupation of the pore by Vanadium. BET surface area and pore volume of V-MCF decreased which confirms that Vanadium have occupied the channels in MCF.

Catalytic activity

Oxidation to sulfides

In order to check the feasibility of UHP-V-MCF system in an organic medium, we performed the oxidation in methanol, *n*-hexane, dichloromethane, acetonitrile, ethanol, H_2O and ethanol:H_2O (1:1). In agreement with our studies, solvents of high hydrogen bonding capacity, such as methanol and water, favour the formation of sulfide with high chemoselectivity. Afterwards, we performed a set of preliminary experiments on benzyl phenyl sulfide to examine the effects of different amounts of UHP and V-MCF in acetonitrile at 25 C. It is noteworthy that in a blank experiment, no significant oxidation was observed in the absence of V-MCF, and only a low yield of sulfoxide was obtained in the presence of 2 equiv of UHP after 6 h.

(a)

(b)
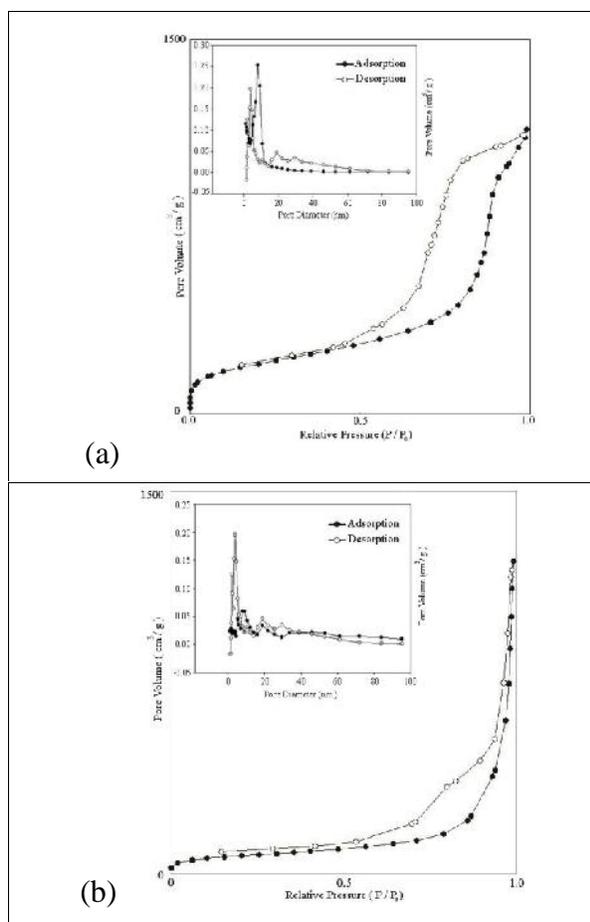
Figure 4. N_2-adsorption-desorption isotherms of (a) MCF; (b) V-MCF

Several functionalized sulfides were selected to examine the scope and limitations of this procedure (Table 2). Aryl alkyl, aryl allyl, diaryl, dialkyl, cyclic and heterocyclic sulfides could be oxidized to the corresponding sulfoxides in excellent yields. Sulfides carrying either electron-withdrawing (Entries d and e) or electron-donating (Entry f) substituent gave the corresponding sulfides in excellent yields with high purity. Importantly, this method was compatible

with other functional groups such as ketone (Entry l), alkene (Entry i), ester (Entry j), and alcohol (Entry k). Typically, these oxidations could usually be stopped at the sulfoxide stage without over-oxidation to the sulfone.

Table 2. Oxidation of sulfides to sulfoxides and sulsones using the UHP/V-MCF system.

Sulfide 1	Sulfoxide[a] 2 Yield[c] (%) : Time (min)	Sulfone[b] 3 Yield[c] (%) : Time (h)
a	95 :65	95 :2.0
b	92 :45	98 :1.8
c	90 :60	98 :2.2
d	90 :100	95 :2.2
e	90 :100	95 :2.6
f	95 :120	95 :2.8
g	95 : 90	95 :3.8
h	90 :90	90 :3.5
i	85 : 65	90 :3.0
j	90 :80	90 :4.5
k	90 :90	80 :4.5
l	80 :90	80 :5.0
m	75 :260	85 :7.5
n	75 :180	65 :8.5

[a]Reaction conditions: Sulfide (1 mmol), UHP (8 mmol), 5.6% V-MCF (2 mol%), CH_3OH (5 mL), r.t.

[b]Reaction conditions: Sulfide (1 mmol), UHP (8 mmol), 5.6% V-MCF (3 mol%), CH_3CN (5 mL), r.t.

[c]**Isolated yields**

Oxidation to sulfones

In order to further demonstrate the efficiency and applicability of the UHP/V-MCF system, the chemoselective oxidation of sulfide to sulfones was also investigated. The reaction conditions specified in Table 2 was optimized for carrying out the reaction in CH_3CN at room temperature (sulfide/UHP/V-MCF ratio: 1: 8: 3). It was found that a wide variety of diaryl, dialkyl,

dibenzyl, aryl benzyl, alkyl aryl and cyclic sulfides were oxidized to their corresponding sulfones in excellent yields in CH_3CN at room temperature. The results are summarized in Table 2.

The recovery and reusability of the catalyst has been investigated. We have noticed that after the addition of $CHCl_3$ to the reaction mixture, this catalyst can be easily recovered quantitatively by simple filtration. The wet catalyst was recycled (the nature of the recovered catalyst has been followed by NAA, XRD and FT-IR spectra) and no appreciable change in activity was noticed after three cycles (Table 3).

Conclusion

A series of mesoporous V-containing mesocellular silica foam catalyst (V/MCF) were prepared by the wet impregnation method. The mesocellular arrangement of the MCF framework is retained upon vanadium incorporation at least up to a V loading of 5.6% and, therefore, high surface areas were obtained for the final catalyst. The V/MCF is an excellent heterogeneous system for promoting the highly chemoselective and rapid oxidation of functionalized sulfides with UHP under mild conditions. It is noteworthy that the reaction tolerates oxidatively sensitive functional groups and the sulfur atom is selectively oxidized.

Table 3. Investigation of the feasibility of reusing V-MCF in the oxidation of sulfides to sulfones with UHP in CH_3CN after 70 min.[a]

Run	Yield (%)[b]
1	98
2	98
3	92
4	57

[a]Reaction conditions: Diphenyl sulfoide (1 mmol), UHP (8 mmol), 5.6 % V-MCF (3 mol%), CH_3CN (5 mL), r.t.

[b]Isolated yields

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