

Selective catalytic oxidation of thioethers to sulfoxides over Mo-silicalite-1 (MoS-1) molecular sieves

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Abstract

Mo-containing silicalite-1 (MFI) samples with Si/Mo (mole) ratios in the range 80 to 300 have been synthesized hydrothermally and were characterized by different physico-chemical techniques such as SEM, XRD, BET, TG/DTA, FTIR, XPS, UV-visible spectra. The catalyst was found to be active for the chemoselective oxidation of various thioethers to the corresponding sulfoxides, without generation of sulfones, using 30% H₂O₂ as the oxidant.

Keywords: Mo-MFI; Mo-silicalite; Sulfoxidation; Thioethers; Sulfones

1. Introduction

Isomorphous substitution of Si⁴⁺ ions in aluminium free silicalite framework with ions such as Ti⁴⁺, V^{4+/5+}, and Sn⁴⁺ has been reported to result in novel molecular sieves with selective oxidation properties [1–5]. Many research groups have attempted the synthesis of molybdenum containing zeolites by a variety of techniques [6–8]. Though the direct hydrothermal synthesis of Mo-ZSM-5 from alkaline and fluoride media has already been reported [9,10], detailed characterization and catalytic activity are not well documented. In this paper, we report the hydrothermal synthesis of Al free Mo-silicalite-1 samples (Si/Mo = 80–297) and

their selective oxidation properties towards thioethers.

2. Experimental

In a typical synthesis, the silica source (tetraethylorthosilicate, Aldrich) was added to the organic template (tetrapropyl ammoniumhydroxide, Aldrich) with stirring. After 15 minutes, molybdenum source (ammonium heptamolybdate, LOBA, India) dissolved in water was added dropwise to the above mixture with continuous stirring for 30 minutes. The final clear solution was transferred to a stainless steel autoclave with teflon lining and kept in a static air oven maintained at 443 K for 24 h. The crystalline material was separated by centrifugation. The as-synthesized material was calcined

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at 783 K for 8 h and labeled as MoS-1(*n*), where *n* represents its Si/Mo ratio. The calcined material was characterized by various techniques. The chemical analysis was carried out by AAS/EDX and the results are presented in Table 1. Silicalite-1 was synthesized according to the procedure reported earlier [11]. The typical composition of the synthesis gel used in the synthesis of MoS-1(80) sample is given below.

SiO ₂	Template	MoO ₃	H ₂ O
1	0.326	0.02	24.33

Scanning electron micrographs of the samples revealed spherical crystallites of nearly uniform size in the range of 0.2–0.3 μm. Powder X-ray diffraction data for the calcined samples were collected on a computer automated diffractometer (Rigaku; Model D-MAX III VC). Data were collected in the 2θ range of 5 to 50 degrees at a scan rate of 0.5° per minute. Silicon was used as an internal standard. Infra-red spectra were recorded in a Nicolet FTIR spectrometer. Thermal analysis (TG/DTA) was carried out in the temperature range 300 K to 1273 K with a temperature program rate of 10 K per minute (Setaram, Model 92), in a flow of air. XPS were recorded (ESCA-3-MK II, VG Scientific) using Mg Kα radiation. UV-visible spec-

tra were recorded in the range of 200 to 400 nm using BaSO₄ as standard for baseline correction (Shimadzu, Model-ISR-260).

3. Results and discussion

The XRD profiles of the calcined MoS-1 samples (Fig. 1) match well with that of silicalite-1 (MFI) structure [11]. No impurity phase of MoO₃ was observed. The interplanar spacings 'd' (nm) were corrected with respect to silicon and used for the calculation of unit cell parameters and then further refined by least square fitting (ca. 30 reflections). There was an increase in the unit cell volume (*V*_{UC}; Table 1) compared to silicalite (blank) as the Mo content increased. At high Mo loading in the sample, the corresponding increase in the unit cell volume was not linear, suggesting that only a part of the Mo has been substituted in the framework position and the remaining part probably occupying non-framework positions. The surface areas of MoS-1 samples obtained by the BET method were found to be higher than that of silicalite-1 (Table 1).

The quantities in millimoles per gram of water, n-hexane and cyclohexane sorbed by silicalite-1, MoS-1 and Mo-impregnated samples

Table 1
Physico-chemical characterization of MoS-1, silicalite-1 and Mo-impregnated samples

Sl. No.	Sample	Si/Mo (gel) ^a	Si/Mo (sample)	<i>V</i> _{UC} (Å ³)	<i>S</i> _{BET} (m ² /g)	Sorption (mmoles/g) ^b			FTIR ^c	UV-Vis ^d	B.E. (eV)
						H ₂ O	n-C ₆	Cyclo C ₆			
1	MoS-1	35	80	5336.9	524	3.33	1.54	0.88	2.45	0.56	233.5
2	MoS-1	75	157	5335.5	525	2.31	1.61	0.89	2.38	0.52	232.1
3	MoS-1	100	202	5332.5	524	2.23	1.57	0.85	1.66	0.41	–
4	MoS-1	200	297	5332.2	523	2.28	1.52	0.80	1.45	0.40	–
5	Mo-impreg.	55	55	–	373	2.28	1.51	0.47	–	–	231.7
6	Silicalite-1	–	–	5323.5	384	2.22	1.49	0.79	1.00	–	–

^a The Si/Mo ratios of the samples are expressed in moles.

^b Gravimetric adsorption conditions: *p*/*p*₀ = 0.5; 298 K; equilibration time = 3 h.

^c Ratio of intensities at ca. 960 cm⁻¹ between MoS-1[*n*] and silicalite-1 samples.

^d Ratio of intensities of absorption bands at 285 and 230 nm from UV-visible spectra.

are presented in Table 1. The amounts of n-hexane and cyclohexane sorbed by MoS-1 samples is similar to that of silicalite-1, suggesting that the pore system is clear. Adsorption of water in MoS-1 samples increases with Mo content, due to increased hydrophilicity with increase in Mo content. The FTIR spectra for MoS-1 and silicalite samples are given in Fig. 2. A band at around 960 cm^{-1} was observed for all the samples including silicalite-1 (blank) sample. Earlier workers [12–14] have assigned this band to Si–O⁻ stretching associated with defect centres containing the incorporated metal (such as Ti, V, Sn and Mo in this case). Appearance of this band in silicalite-1 (blank) is due to the presence of defect sites as reported by Cambor and coworkers [12]. Even though, this band appears in all samples, the intensity of this band was enhanced in MoS-1 samples (the ratios of the intensities of this band between MoS-1 and silicalite-1 are given in Table 1). Thermal analysis revealed a small weight loss in the temperature range of 1138 and 1237 K for the Mo-impregnated sample which is attributed to the loss of Mo species from the silicalite surface. In the case of the MoS-1 samples, no Mo loss was

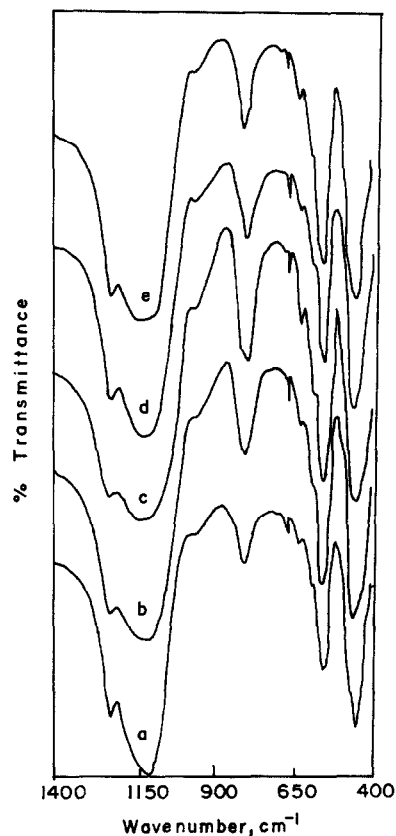


Fig. 2. FTIR spectra of (a) silicalite-1, (b) MoS-1 [80], (c) MoS-1 [157], (d) MoS-1 [202], and (e) MoS-1 [297].

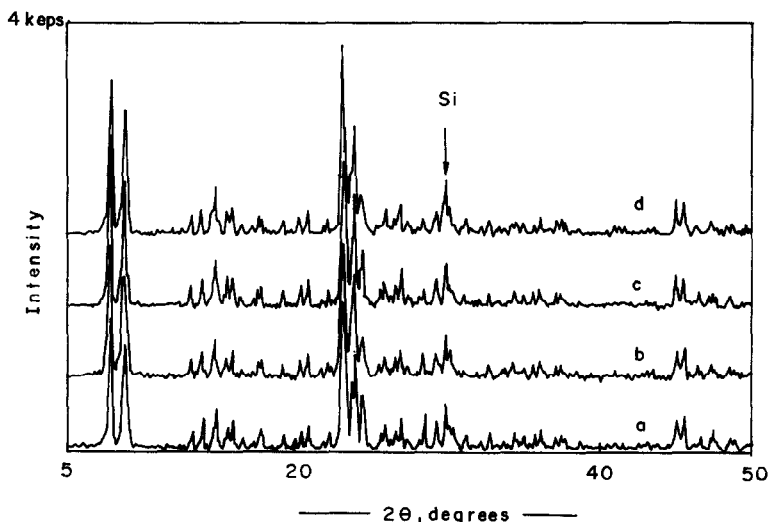


Fig. 1. X-ray diffraction patterns of (a) MoS-1 [80], (b) MoS-1 [157], (c) MoS-1 [202], and (d) MoS-1 [297] samples.

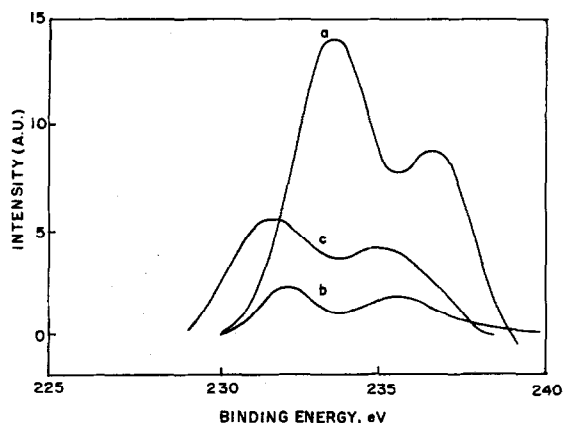


Fig. 3. X-ray photoelectron spectra of (a) MoS-1 [80], (b) MoS-1 [157], and (c) Mo-impregnated silicalite-1 [55] samples.

observed up to 1273 K indicating that the Mo present in MoS-1 is strongly bound to the surface/framework and does not sublime. The binding energy values (using C1s peak as the internal standard) obtained by XPS analysis for MoS-1 samples are given in Table 1 (Fig. 3). In general, the B.E. values of Mo ions in 4+, 5+ and 6+ oxidation states are not very different, the typical values being, respectively, 230.9 eV (MoO_2), 231.0 eV (MoCl_5) and 232.5 (MoO_3) [15]. The values are found to be slightly lower for the lower oxidation states. The values obtained by us (Table 1) are in the range 231.7 to 233.5 eV, suggesting that the ions are mostly in the 6+ oxidation state. The results, however, do not preclude the presence of a small amount of Mo in other oxidation states such as 5+. The differences in the values observed (± 0.9 eV) are probably due more to the differences in

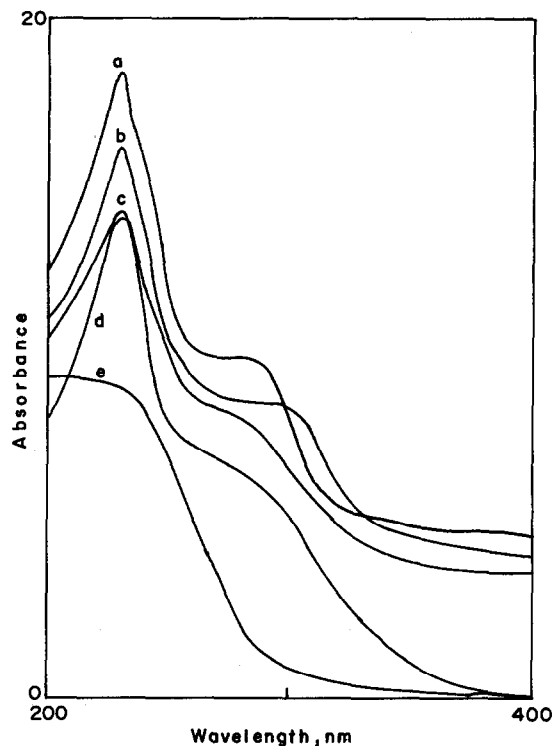


Fig. 4. UV-visible spectra of (a) MoS-1 [80], (b) MoS-1 [157], (c) MoS-1 [202], (d) MoS-1 [297], and (e) Mo-impregnated silicalite-1 [55].

the location of Mo ions than to differences in Mo oxidation states.

The UV-visible spectra of MoS-1 samples consist of two broad absorption bands, one at around 285 nm and another at around 230 nm (Fig. 4). The absorption at 285 nm has been assigned by earlier workers to octahedral Mo species, and 230 nm to both octahedral and tetrahedral Mo species [16]. The ratio of intensi-

Table 2
Sulfoxidation of various thioethers with H_2O_2 as oxidant over MoS-1 [80] catalyst

Sl. No.	Substrate	Time (h)	Conversion (%)	Selectivity (%) (towards sulfoxide)
1	Me_2S	2	96	94
2	$(\text{N-Bu})_2\text{S}$	3	98	93
3	PhS-Me	3	93	90
4	Ph_2S	8	80	75
5	$(\text{PhCH}_2)_2\text{S}$	3	90	85
6	$\text{Ph-S-CH}_2\text{C}=\text{CH}_2$	7	89	85
7	$\text{Ph-S-CH}_2\text{C}\equiv\text{CH}$	7	98	84
8	Tetrahydrothiophene	2	98	94

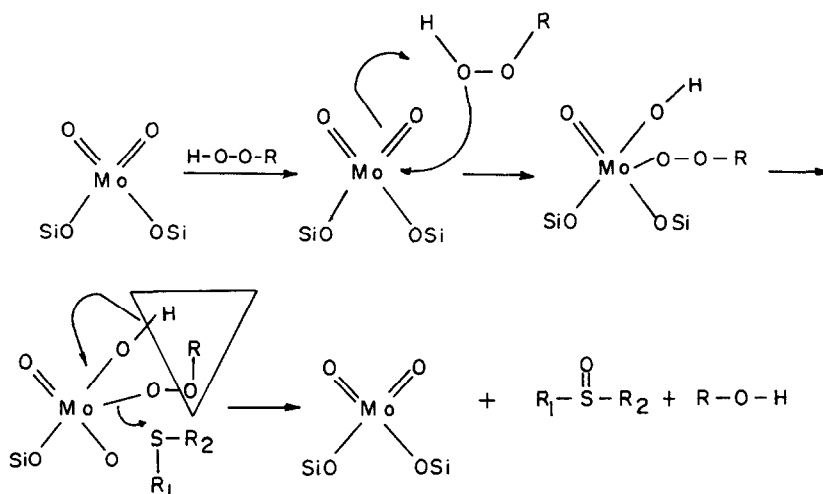


Fig. 5. Mechanism for the activation of thioethers by Mo species in MoS-1.

ties of these bands (285 and 230 nm) increases with increase in Mo content. As the absorption at 230 nm could arise from both tetrahedral and octahedral Mo^{6+} species, it is not possible to know if Mo is present in tetrahedral coordination in the samples. In any case, more Mo ions are likely to be present as octahedral species. These species are probably associated with defect sites. Earlier workers have shown that the isomorphous substituents such as Ti, and V are associated with defect sites [1,4,5], and V is present in tetrahedral, octahedral, and square-pyramidal coordinations. The Mo-impregnated sample gave a broad absorption over a wide range of wavelength.

3.1. Catalytic activity

The results of MoS-1 catalyzed oxidation of thioethers with 30% H_2O_2 at 293 K in methanol as solvent are presented in Table 2. In a typical reaction procedure, a mixture of phenyl allyl sulfide (0.50 g, 0.0034 mol), MoS-1 (50 mg, 10% w/w) and 30% H_2O_2 (0.69 ml, 0.0068 mol) in methanol (20 ml) was stirred at 293 K for 6 h. After the reaction was complete (thin layer chromatography), the catalyst was filtered off and the product purified by flash chromatography (SiO_2 , 50% ethyl acetate: pet. ether as

eluant) to afford the corresponding sulfoxide (0.47 g, 85%) which was characterized ¹.

Evidently, a variety of aromatic and aliphatic thioethers are smoothly oxidized to the corresponding sulfoxides in excellent yields and 100% selectivity (GLC) with MoS-1- H_2O_2 system. Even the sterically hindered thioethers (entries 2–5, Table 2) have been successfully converted to the corresponding sulfoxides in good yields. It is also remarkable that the unsaturated ethers (entries 6 and 7, Table 2) underwent oxidation very efficiently with the present catalytic system and the reaction is essentially chemoselective. Gall et al. have carried out the selective oxidation of thioethers to the corresponding sulfoxides (> 99%) over $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ in non-aqueous medium at room temperature [17]. They have used TBHP as the oxidant and the reaction was found to be inhibited by moisture. It should be noted here that TS-1- H_2O_2 combination failed to oxidize sterically hindered thioethers, e.g. diphenyl sul-

¹ IR (neat): 1620, 1480, 1450, 1220, 1085, 1050 (s), 1000, 940 and 760 cm^{-1} ; ¹H-NMR (200 MHz, CDCl_3): δ 3.55 (2H, m, CH_2), 5.25 (1H, d, $j = 14$ Hz, CH), 5.3 (1H, d, $j = 12$ Hz, CH), 5.65 (1H, m, CH) and 7.55 (5H, m, ArH); MS; m/z (rel. intensity) 166 (M^+ , 41), 149 (8), 135 (8), 125 (100), 118 (15), 117 (39), 109 (20), 97 (45), 77 (32) and 65 (8).

fide [18–20]. It is found that the choice of the solvent (methanol) for MoS-1 catalyzed oxidation of phenyl methyl sulfide with H_2O_2 is critical as the reaction fails when carried out in solvents such as dichloromethane and chloroform. While the sulfoxidation can also be carried out with 70% tert.-butyl hydroperoxide (TBHP) instead of 30% H_2O_2 as oxidant, the catalyst failed to activate molecular oxygen under the reaction conditions.

When the oxidation of allyl phenyl sulfide with 30% H_2O_2 was carried out with other catalysts such as TS-1 and Mo-impregnated silicalite-1, no significant formation of sulfoxide (< 5%) was observed even after stirring for 24 h at 293 K. The inability of Mo-impregnated silicalite-1 to catalyze the reaction demonstrates that the Mo species present in the framework (defect sites) of MoS-1 is responsible for its unique activity. Similar observations were made by Sen et al. during the catalytic oxidation of alkyl aromatics [4,5]. They have reported that V-incorporated silicalite-2 was active, while V-impregnated silicalite-2 was inactive for the reaction. A plausible mechanism for the oxidation of thioethers on the Mo species present in the framework (defect sites) is shown in Fig. 5.

4. Conclusions

The MoS-1 sample synthesized hydrothermally were found to be structurally similar (XRD) to silicalite-1. Expansion of the unit cell volume of the MoS-1 samples suggests the incorporation of Mo in the framework. These Mo ions are probably present in defect sites mostly in octahedral coordination. The MoS-1 samples were found to be more hydrophilic than silicalite-1 and stable towards thermal treatment. The catalytic activity results demonstrate that MoS-1 possesses an unique selectivity in the

oxidation of thioethers to the corresponding sulfoxides by H_2O_2 .

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