Mo-silicalite-2 (MoS-2): characterization and catalytic applications

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Abstract

Microporous molybdenum containing silicalite-2 (Mo-MEL) has been synthesized hydrothermally, under aluminium free alkaline conditions. Physicochemical characterization of the sample (XRD, FTIR, UV–visible spectra, TG/DTA) revealed the possible incorporation of molybdenum ions in the zeolite framework. Redox properties of the Mo species present in the sample has been studied by cyclic voltammetric technique. Mo-MEL was active in the oxidative dehydrogenation of ethanol to acetaldehyde with a maximum selectivity of ∼ 90% at about ∼ 40% conversion. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Mo-silicalite-2; Molybdenum silicate; Ethanol oxidation; Cyclic voltammetry of metallosilicate

1. Introduction

Incorporation of transition metal ions such as Ti, V, and Cr into the zeolite framework has been a subject of recent interest due to the unusual catalytic properties of the isomorphs [1–3]. Extensive work has been carried out on the application of Mo supported zeolite/oxide catalysts for several industrially important reactions [4,5]. However, reports available on the incorporation of molybdenum in the zeolite framework are scarce. In our earlier publication we have shown the incorporation of Mo in the MFI framework and the resulting isomorph being active in selective oxidation reactions [6]. In

the present study, the oxidative dehydrogenation of ethanol is used as the test reaction to compare the catalytic activity of the Mo-silicalite-2 samples with Mo-impregnated and Mo supported catalysts from literature. A number of reports are available for the above reaction over Mo supported catalysts. Tatibouet et al. has carried out ethanol oxidation over MoO_3 crystals prepared by sublimation [7]. They have proved that the $-M=O$ sites were responsible for acetaldehyde formation. It has been established by Iwasawa and Tanaka that the Mo dimers were the active centers for ethanol oxidation over MoO_3/SiO_2 [8]. The reaction proceeds through the formation of an ethoxide type intermediate [9]. Recently, the formation of two types of intermediates over $-M=O$ and Mo–O–Mo sites were reported using in situ laser

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Raman technique [10]. The transformation of ethanol has been used to evaluate the nature of the active sites in Mo-silicalite sample.

2. Experimental

The typical procedure for the synthesis of MoS-2 is outlined below.

The silica source (tetraethyl orthosilicate, Aldrich; 30 g) was mixed with the template (tetrabutylammonium hydroxide, Aldrich; 28 g, 40% solution in water) and stirred for 15 min. Then, the Mo source (sodium molybdate, LOBA, India; 0.98 g) dissolved in water (60 g) was added and stirred for 15 min to get a clear solution (pH = 11.21). The contents were transferred to a teflon lined autoclave, and kept at 453 K for 2 days. The as-synthesized material was separated, dried at 383 K for 12 h and calcined at 783 K for 8 h in a flow of air and labeled as MoS-2.

Powder X-ray diffraction data for the calcined samples were collected using a computer automated diffractometer (Rigaku; Model D-MAX III VC). Data were recorded in the 2θ range of 5 to 50° at a scan rate of 0.5° per minute using silicon as the internal standard. Infra-red spectra were recorded in a Nicolet FTIR spectrometer (Model 60 SXB). Thermal analysis (TG/DTA) was carried out in the temperature range 300 K to 1273 K with a heating rate of 10 K per minute (Setaram, Model 92), in a flow of air. UV–visible spectra were recorded in the range 200 to 800 nm using $BaSO_4$ as standard for baseline correction (Shimadzu, Model-ISR-260).

MoS-2 carbon paste electrodes used in cyclic voltammetric studies were prepared by mixing 100 mg zeolite with 50 mg graphite. The polystyrene solution in tetrahydrofuran (10 mg/3 ml) was added in drops to form a paste. The paste was then coated on a graphite disc electrode of area 0.063 cm^2. Cyclic voltammetric experiments were carried out in a computer controlled potentiostat (EG and G Model 283) using a Pt foil counter electrode and Hg/Hg_2SO_4 reference electrode in 0.5 M H_2SO_4. The solution was deoxygenated before the measurements by purging with argon.

The oxidative dehydrogenation of ethanol over MoS-2 was carried out in a fixed bed glass reactor (1.9 cm i.d., down flow mode), followed by a spiral condenser and a gas–liquid separator. Proper mass balance was done after analyzing both the gas and the liquid products using HP-5880A gas chromotograph fitted with a capillary column (50 m × 0.2 mm). The reactor was charged with 2.0 g of the catalyst (12–14 mesh, ASTM). Ceramic beads were used in the pre-heating zone. The experiment was carried out at different temperatures and space velocities. The alcohol/oxygen ratio was maintained well below the explosion limit (1.52 vol %). A small amount of CO_2 (0.5%) was produced which increased to ∼ 1.2% at very high conversion levels. Under experimental conditions, only a negligible amount of CO_2 was produced.

3. Results and discussion

The chemical analysis of the final solid samples were carried out by EDX analysis and the

Table 1
Physico–chemical characterization of MoS-2 and silicalite samples

Sample no.	Sample (input Si/Mo ratio)	Si/Mo (sample)	Crystallinity (XRD, %)	V_{UC} (Å^3)	Mo_{Oh}/Mo_{Td} [a]
1.	MoS-1 (35)	50.1	85	5292.0	0.072
2.	MoS-1 (100)	199	92	5287.9	0.069
3.	MoS-1 (200)	301	96	5275.6	0.018
4.	Silicalite-2	−	100	5269.8	−

[a]Ratio of intensities of band at ∼ 300 nm (Mo_{Oh}) and ∼ 230 nm (Mo_{Td}).

results are presented in Table 1. The powder X-ray diffraction pattern of the calcined MoS-2 sample with different Si/Mo ratios was found to be similar to that of silicalite-2 and are given in Fig. 1. Absence of peaks at $2\theta = 9.05, 24.05°$ confirms the MEL structure [11]. A shoulder at $2\theta = 45°$ indicates the presence of a small amount of MFI impurity. The crystallinity of the MoS-2 samples were found to less compared to silicalite-2 and are given in Table 1. The crystallinity of MoS-2 samples were found to decrease as the Mo content was increased in the initial gel. The unit cell parameters and the unit cell volume (V_{UC}) were calculated after correcting 'd' values with respect to silicon (internal standard) using commercially available software (PDP11). The unit cell volume was found to increase with Mo content (Table 1). As the Mo content in the sample was increased, the V_{UC} increases and becomes constant. The excess Mo should be deposited/fixed at the surface which does not lead to increase in the cell volume. The thermal analysis showed (figure not given) that the Mo ions present in MoS-2 was found to be thermally stable up to 1273 K, associated with a structure collapse at around 973 K.

The FTIR spectra of silicalite-2 and MoS-2 samples are shown in Fig. 2. A band at around 965 cm^{-1}, assigned to Si–O–H stretching at defect sites [12]. The intensity of this band was

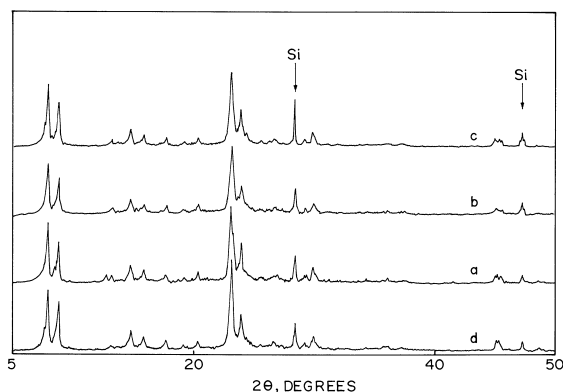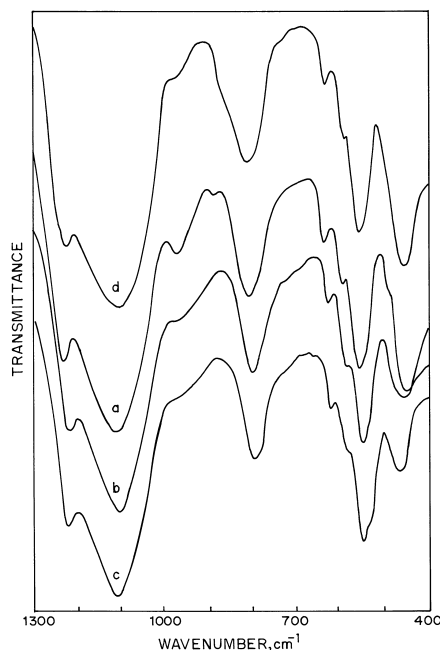Fig. 2. FTIR spectra of (a) MoS-2 [50] (b) MoS-2 [199] (c) MoS-2 [301] and (d) silicalite-2.

more pronounced for the MoS-2 sample with low Si/Mo ratio, which indicates the increase defect sites with the increase in Mo content. Moreover, this band position was shifted towards a lower wavenumber (964 cm^{-1}) for MoS-2 compared to silicalite-2 (970 cm^{-1}), indicating the weakening of the Si–O bond by the electropositive Mo ions (present at the de-

Fig. 1. XRD patterns of (a) MoS-2 [50] (b) MoS-2 [199] (c) MoS-2 [301] and (d) silicalite-2.
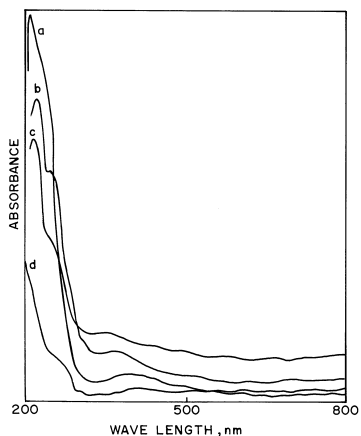

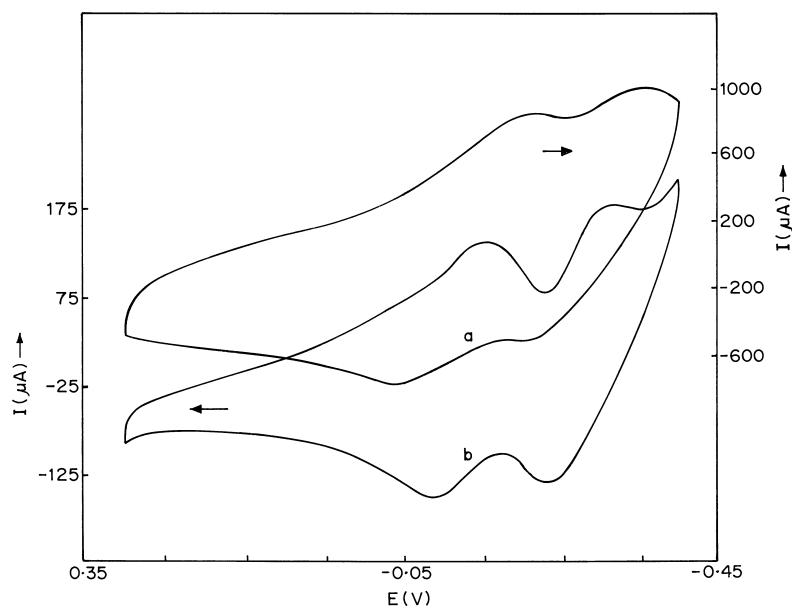Fig. 3. UV–visible spectra of (a) MoS-2 [50] (b) MoS-2 [199] (c) MoS-2 [301] and (d) silicalite-2.

Fig. 4. Cyclic voltammogram of (a) MoS-2—scan rate 200 mV/s (b) MoS-2—scan rate of 20 mV/s.

fect sites), thereby substantiating the incorpora-
tion of Mo. An additional band, observed around
900 cm^{-1} for MoS-2 can be assigned to the
symmetric stretching vibration of the terminal
–Mo=O of a monomeric molybdate species
[13].

The UV–visible spectra of the sample exhib-
ited an absorption at around 230 nm indicating
the presence of isolated MoO_4^{2-} in tetrahedral
coordination (Fig. 3) [14]. A shoulder around

260 nm can be assigned to Mo–O–Mo bridging
group of polyanionic species probably present at
the external surface [15]. Another prominent
absorption band was observed ∼ 300 nm repre-
sents Mo^{6+} in octahedral coordination [16]. An
increase in the ratio of Mo_{Oh}/Mo_{Td} with the
increase in the Mo content was observed (Table
1). This infers qualitatively, the formation of
octahedral species at higher concentration of
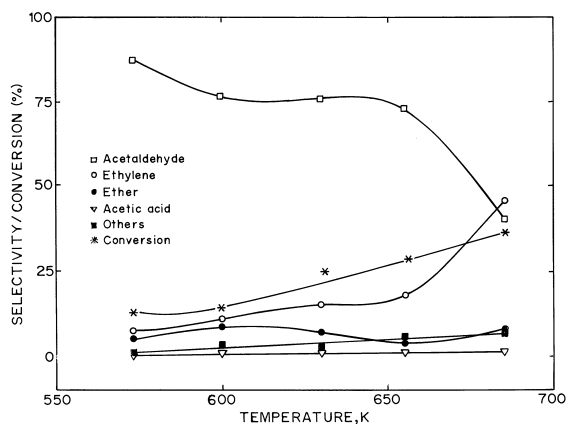Mo, possibly forming defect sites at the surface.

Fig. 5. Oxidative dehydrogenation of ethanol over MoS-2: selec-
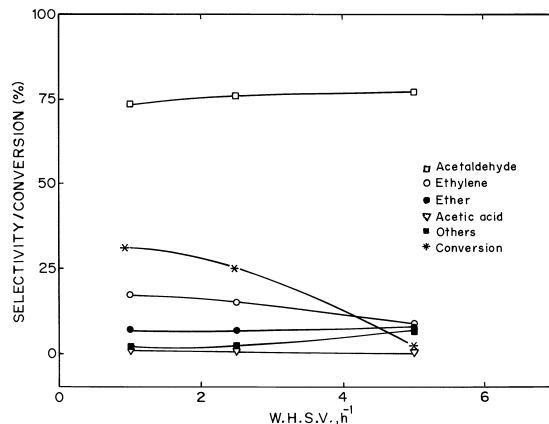tivity of products at different temperatures.

Fig. 6. Oxidative dehydrogenation of ethanol over MoS-2: selec-
tivity of products at different space velocities.

Table 2
Oxidation of ethanol

Sample no.	Sample	MoO_3 (wt.%)	T (K)	Selectivity (%)				Conversion (%)	E_A (kJ mol^{-1})
				C_2H_4	CH_3CHO	$(C_2H_5)_2O$	CH_3CO_2H		
1.	MoO_3/SiO_2 [a]	1.00	575	3	81	14	2	2.4	54
2.	MoO_3/SiO_2 [a]	9.00	563	4	72	7	4	42.7	92
3.	MoS-2	4.47	573	7.3	87.4	4.9	–	19.4	83

Product distribution over MoS-2 and MoO_3/SiO_2 at different temperatures.
[a] Values taken from Ref. [10].

Similar observation was made in the case of Mo in silicalite-1 (MoS-1) system [6].

Cyclic voltammetry of MoS-2 (calcined) modified electrode at scan rates of 200 mV/s and 20 mV/s in 0.5 M H_2SO_4 as the electrolyte with Hg/Hg_2SO_4 as the reference electrode are shown in Fig. 4a and b, respectively. The electrode was dipped in the electrolyte for 1–2 h prior to scan. The voltammogram of MoS-2 clearly shows two peaks with $E_{1/2}$ value at -0.136 V/Hg/Hg_2SO_4 (-0.24 V/SCE) and -0.281 V/Hg/Hg_2SO_4 (0.09 V/SCE). The reversibility of the two peaks was found to be good ($EP_1 = 44$ mV, $I_{pa}/I_{pc} = 1.055$, $EP_2 = 72$ mV, $I_{pa}/I_{pc} = 0.73$). A comparison of the literature values for electrochemical oxidation shows that peak at -0.281 V (0.09 V/SCE) corresponds to $Mo^{6+/5+}$ couple [17]. The second peak with $E_{1/2} = -0.24$ V/SCE corresponds to the transition of Mo^{6+} ions in molyb-

date species (MoO_4^{2-}) to Mo^{5+} ions. Thus, two different types of Mo^{6+} species can be inferred to be present in MoS-2. Under identical conditions Mo-impregnated silicalite-2 did not showed the above features. It has been already established by earlier workers [18], that the extraframework metal ions, deposited at the surface will not show any activity for cyclic voltammetry. They have also concluded that the peak current was proportional to the metal ions present in the framework of the zeolite.

3.1. Oxidative dehydrogenation of ethanol

Fig. 5 shows the product distribution and conversion at different temperatures during the ethanol oxidation over MoS-2 (Si/Mo = 50). Four major components were observed in the product stream viz., acetaldehyde, ethylene, diethyl ether, acetic acid. With increase in temperature, the selectivity of acetaldehyde was de-
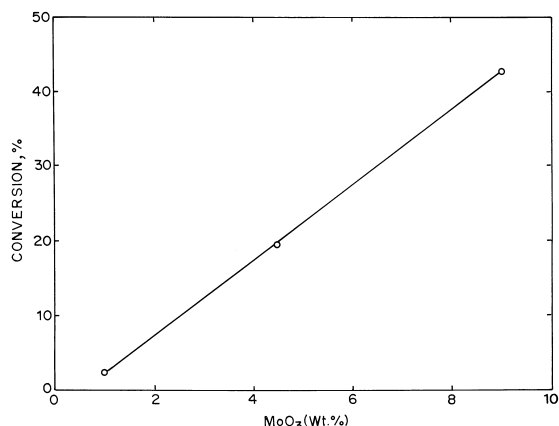

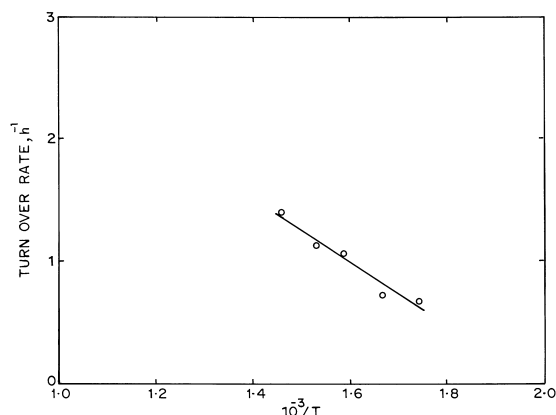Fig. 7. Oxidative dehydrogenation of ethanol over MoS-2: a plot of %MoO_3 vs. conversion.

Fig. 8. Oxidative dehydrogenation of ethanol over MoS-2: Arrhenius plot.

Table 3
Oxidation of ethanol

Sample no.	Sample	MoO_3 (wt.%)	T (K)	Selectivity (%)					Conversion (%)
				C_2H_4	CH_3CHO	$(C_2H_5)_2O$	CH_3CO_2H	Others	
1.	MoS-2	4.47	630	15.1	75.8	6.8	0.3	2.0	30.2
2.	Mo-impregnated	4.50	630	12.9	58.4	8.6	2.1	18.0	11.7

Product distribution over MoS-2 and Mo-impregnated silicalite-2.

creased and that of ethylene was increased. Earlier workers have concluded that the –Mo=O bond was responsible for the formation of acetaldehyde and weakening of this bond gives more selectivity [19]. Zhang et al. [10] have proved that the ethoxy intermediates formed on Mo–O–Mo was responsible for the formation of acetic acid, since, its selectivity increase with increase in Mo loading and Mo–O–R (R = Si, H) sites are responsible for the formation of ethers. The product distribution and conversion over MoS-2 at different space velocities are given in Fig. 6. It is from the figure that even though there was a decrease in conversion as the space velocity was increased, the product distribution was nearly the same.

A comparison of product distribution and conversion during the ethanol oxidation over MoO_3/SiO_2 and MoS-2 are given in Table 2. The conversion over MoS-2 falls well in the trend when plotted against %MoO_3 loading (Fig. 7). The selectivity of acetaldehyde over MoS-2 was found to be far better than that over MoO_3/SiO_2. In the case of MoS-2, the Mo=O bond is weakened due to the strong interaction between Mo and Si (zeolite framework), thus favoring the formation of acetaldehyde. On the other hand, in the case of MoO_3/SiO_2, a weak interaction between Mo and Si (–SiO_2) results in the formation of a strong Mo=O, thus suppressing the selectivity of acetaldehyde. The lower selectivity towards the formation of ether over MoS-2 compared to MoO_3/SiO_2 (both at low and high loading) proves absence of strong acid sites (Bronsted sites) in MoS-2. At the same time, absence of acetic acid in the product stream over MoS-2 indicates less amount of

poly anionic Mo–O–Mo species at the surface, even though negligible amount of acetic acid was formed at higher temperatures ($\sim$ 1%).

The turnover frequencies at different temperature over MoS-2 were calculated, assuming that all Mo sites are accessible for the reaction. Arrhenius plot is shown in the Fig. 8 and the activation energy was calculated to be 83 kJ (Table 2).

Under identical conditions the Mo-impregnated silicalite-2 (with Si/Mo = 50) was tested for its activity towards the reaction and the results are presented in Table 3. The low conversion of ethanol over Mo-impregnated silicalite-2 compared to MoS-2 clearly indicates the stronger interaction of Mo with silicalite framework in MoS-2. It is also possible that the MoO_3 in the Mo-impregnated sample might have blocked the pore system, thereby reducing the availability of Mo species for the reaction. The selectivity towards acetaldehyde was less on Mo-impregnated compared to MoS-2, suggesting that the –Mo=O is stronger in the former. In other words, Mo in Mo-impregnated is weakly bonded to silicalite-2.

4. Conclusions

Molybdenum containing silicalite-2 was synthesized hydrothermally under aluminium free alkaline conditions. Thermal analysis indicated the presence of a very stable Mo species in the sample. The cyclic voltammetric activity of MoS-2 substantiates the incorporation of Mo in MEL lattice. The characterization of the sample by spectral analysis has revealed the presence of

both tetrahedral and octahedral coordination of Mo. Presence of such a different types of Mo species were revealed through cyclicvoltammetric studies also. The excess Mo gets deposited at the surface forming polyanions with Mo–O–Mo bridging group. The oxidative dehydrogenation of ethanol over MoS-2 was found to be unique with good selectivity towards acetaldehyde, compared to MoO_3/SiO_2 and Mo impregnated silicalite-2.

Acknowledgements

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