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# Preparation and characterization of molybdenum disulphide catalysts

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Molybdenum disulphide has been prepared by atmospheric-pressure hydrogen reduction of molybdenum trisulphide in the temperature range 400–750 °C for 4 h and characterized. Chemical analysis of the product confirmed the S to Mo ratio 2.00 as desired for $MoS_2$, consistent with its thermogravimetric analysis data in an air atmosphere. $MoS_2$ prepared under these reducing conditions possessed a hexagonal structure with n-type diamagnetic semiconducting behaviour and a lower surface area. The catalytic activity of the $MoS_2$ was studied for liquid-phase hydrogenation of nitrobenzene. X-ray studies on $MoS_3$ when reduced at 750 °C for 48 h indicated that $MoS_2$ so formed is unstable, resulting in the formation of its over-reduced products $Mo_2S_3$ and Mo.

## 1. Introduction

Layered transition metal dichalcogenides of groups IVB, VB and VIB constitute structurally and chemically a well-defined family of compounds whose physical and chemical properties have stimulated a considerable amount of interest during the past few years [1–3]. The most striking feature of these compounds is that they crystallize in a quasi-two-dimensional layer type of structure which imparts substantial anisotropy to most of their physical properties. In addition, this layer structure facilitates the process of intercalation to form stoichiometric and non-stoichiometric compounds with metal atoms, organic and inorganic molecules [4]. These layered transition metal dichalcogenides and their intercalation compounds are useful materials in the field of catalysis [5], high temperature–high pressure lubricants [3] and in solar energy conversion [6], etc.

Molybdenum disulphide, $MoS_2$, is representative of these materials and is most promising for modern uses [7–13]. It crystallizes in a layered structure. There exists a trigonal prismatic coordination between molybdenum and sulphur atoms within each layer and bonding is primarily covalent. The structure is characterized by the presence of $Mo^{4+}$ and $S^{2-}$ sheets where each $Mo^{4+}$ sheet is sandwiched between two $S^{2-}$ sheets. The sandwiched sheets are held together by weak van-der Waals forces. Molybdenum disulphide is also used as a catalyst for hydrogenation in those cases where the raw materials are not pure and contain catalytic poisons, particularly sulphur compounds [5, 14–17]. However, not much information is available about kinetic and mechanistic features of the hydrogenation of nitrobenzene over $MoS_2$ and the change if any in the catalyst system.

The present paper deals with the preparation of $MoS_2$ by atmospheric pressure reduction of $MoS_3$ and characterization by various physico-chemical methods. Attempts have also been made to assess the suitability of this material as a catalyst in hydroxygenation reactions like the hydrogenation of nitrobenzene to aniline. Further, the $MoS_2$ catalyst used has also been characterized and the results have been utilized to explain the catalytic activity of $MoS_2$ for this reaction.

## 2. Experimental procedure

### 2.1. Sample preparation

The base material $MoS_3$ was prepared by solid–state reaction of $MoO_3$ and thiourea at 130 °C [18]. The reduction of 5 g of $MoS_3$ was carried out in an electrically heated furnace by passing a stream of hydrogen with a flow rate of 60 $cm^3 min^{-1}$. Different samples of $MoS_2$ were prepared at 400, 500, 600 and 750 °C for 4 h and at 750 °C for 48 h. The furnace was then switched off but the flow of hydrogen was continued through the system until it cooled down to room temperature. Finally, the sample was taken out.

### 2.2. Characterization

$MoS_2$ was analysed by the conventional chemical analytical method [19]. Molybdenum was estimated by the oxime method and sulphur as $BaSO_4$.

X-ray diffractograms of the samples were obtained with a Philips 1720 diffractometer using $CuK_\alpha$ radiation ($\lambda = 0.15418$ nm). Each pattern was recorded in the range $5° < 2\theta < 60°$ with a scan rate of $1°/2\theta\ min^{-1}$ and a chart speed of $0.1°\ mm^{-1}$. The particle size for each specimen was calculated using the Scherrer formula

$$t = k\lambda/\beta \cos \theta_0$$

where $t$ is the particle size as measured perpendicular to the reflecting plane, $k$ is the Scherrer constant (taken as unity, assuming the particles to be spherical in shape), $\lambda$ is the wavelength of the X-ray radiation, $\beta$

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is the half-intensity width measured in radians and $\theta_0$ is the Bragg angle.

Room-temperature magnetic susceptibility was measured by using the Guoy method in a field strength of about 30.06 G. The balance was initially calibrated using $Hg[Co(SCN)_4]$ as a standard. The type of conductivity was determined by simple thermoelectric power experiments. The conductivity measurements were made using a two-probe technique on compressed pellets in the temperature range 25–350 °C. Thermogravimetric analyses were performed in an air atmosphere with a programmed heating rate of 10 °C $\text{min}^{-1}$ up to 1000 °C. The surface area for $MoS_2$ samples was measured by the BET method.

The catalytic activity of $MoS_2$ in the hydrogenation of nitrobenzene was tested in a high-pressure autoclave, details of which are given elsewhere [20]. The products were analysed by gas–liquid chromatography using an SE-30 column.

## 3. Results and Discussion

### 3.1. Characterization

The chemical analysis of the product confirmed the sulphur to molybdenum ratio of 2.00 for $MoS_2$.

The X-ray diffractograms of molybdenum disulphide prepared by reducing $MoS_3$ at 400, 500, 600 and 750 °C for 4 h each are shown in Fig. 1a–e respectively. The absence of any peak for $MoS_3$ confirmed its amorphous character. However, the *d*-values for its reduced product were found to be in good agreement with the data reported for hexagonal $MoS_2$ [21]. The diffractograms showed a strong orientation of the 0 0 2 peak along the *c* axis. It is also evident from Fig. 1 that the increase of intensity of the 0 0 2 reflection with increasing reduction temperature was more pronounced in comparison to other 0 0 *l* reflections. The intensity of other reflections such as 1 0 *l*, 1 1 *l* also improved but to a lesser extent. The lattice parameters were also calculated for $MoS_2$ (Table I) and were in agreement with the values reported by Al-Hilli and Leonard [22]. The X-ray diffractograms of $MoS_3$ when reduced at 750 °C for 48 h showed that the 0 0 2 line of maximum intensity in $MoS_2$ had disappeared and a few new sharp lines were present (Fig. 1f). These closely corresponded to $Mo_2S_3$ and metallic molybdenum. In addition, some lines of weak intensity due to unreduced $MoS_2$ were also observed.

Our results show that $MoS_3$ is reduced to metallic molybdenum via the following steps:

$$2MoS_3 + H_2 \longrightarrow Mo_2S_3 + H_2S$$

$$\tfrac{1}{3}\,Mo_2S_3 + H_2 \longrightarrow \tfrac{2}{3}Mo + H_2S$$

Calculation of the particle size for $MoS_2$ showed that there is slight anisotropy along the *a* and *c* axes, which diminishes with increasing reduction temperature (Table II).

Room-temperature magnetic susceptibility measurements and thermoelectric power experiments indicated that $MoS_2$ prepared by different methods is diamagnetic and possessed n-type conductivity (Table III). Conductivity ($\sigma$) measurements on $MoS_2$ in the temperature range 303–573 K confirmed its semiconducting behaviour (Fig. 2). From the plot of $\ln\sigma$ versus $10^3/T$, the value of activation energy, $E_a$, was calculated using the expression

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

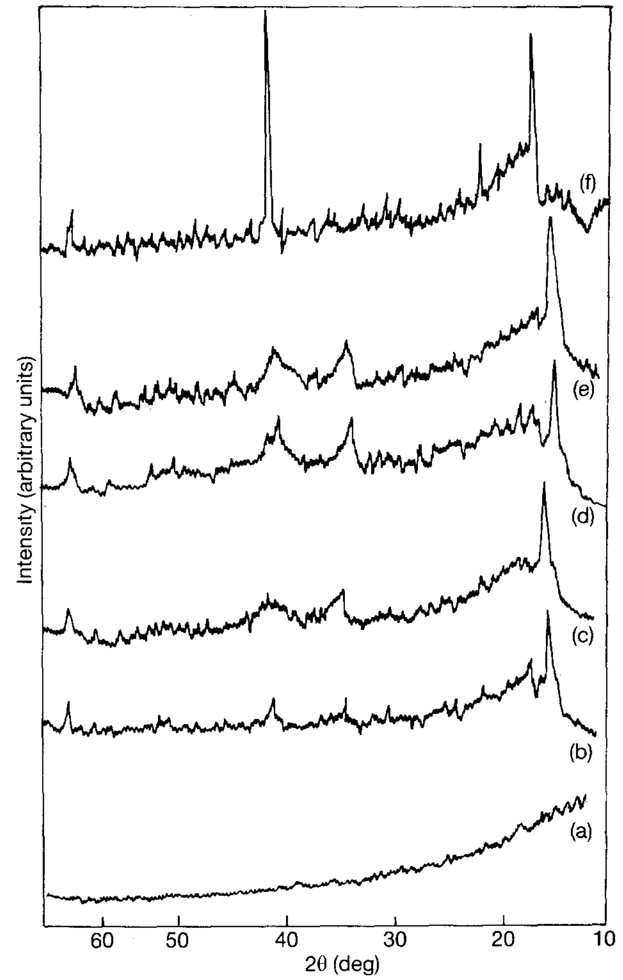

*Figure 1* X-ray diffractograms for (a) $MoS_3$ and when reduced for 4 h at (b) 400 °C, (c) 500 °C, (d) 600 °C and (e) 750 °C, and at (f) 750 °C for 48 h.

TABLE I Unit cell dimensions of $MoS_2$

| Reduction temperature (°C) | *a* (nm) | *c* (nm) | *c*/*a* | *V*(nm)$^3$ |
|---|---|---|---|---|
| 400 | 0.3162 | 1.2271 | 3.890 | 0.1065 |
| 500 | 0.3162 | 1.2273 | 3.881 | 0.1062 |
| 600 | 0.3160 | 1.2274 | 3.884 | 0.1061 |
| 750 | 0.3163 | 1.2276 | 3.880 | 0.1063 |

TABLE II Particle size distribution for $MoS_2$

| hkl | Partical size (nm) | | | |
|---|---|---|---|---|
| | 400 °C | 500 °C | 600 °C | 750 °C |
| 100 | 11.51 | 12.23 | 12.94 | 13.42 |
| 103 | 13.72 | 12.93 | 13.46 | 14.80 |
| 110 | 13.53 | 14.10 | 14.60 | 15.63 |
| 008 | 17.00 | 16.23 | 17.04 | 17.94 |

TABLE III Room-temperature magnetic susceptibility ($\chi$), Seebeck coefficient ($S$), conductivity ($\sigma$) and activation energy ($E_a$) data for $MoS_2$

| Reduction temperature (°C) | $(\chi_{300\ \mathrm{K}}$ ($10^{-6}$ e.m.u.) | $S°_{300\ \mathrm{K}}$ ($\mu$V °C$^{-1}$) | $\sigma_{300\ \mathrm{K}}$ ($\Omega^{-1}$ cm$^{-1}$) | $E_a$ (eV) | Surface area (m$^2$ g$^{-1}$) |
|---|---|---|---|---|---|
| 400 | − 0.158 | − 410 | $2.14 \times 10^{-5}$ | 0.22 | 2.50 |
| 500 | − 0.065 | − 390 | $1.88 \times 10^{-5}$ | 0.17 | 2.89 |
| 600 | − 0.720 | − 255 | $1.67 \times 10^{-5}$ | 0.18 | 3.30 |
| 750 | − 0.503 | − 274 | $4.1 \times 10^{-6}$ | 0.27 | 3.50 |

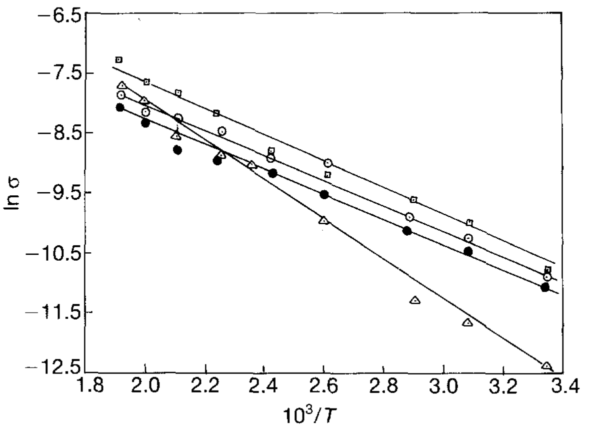

*Figure 2* Temperature dependence of electrical conductivity ($\sigma$) for $MoS_2$ prepared at different reduction temperatures: (□) 400 °C, (○) 500 °C, (●) 600 °C and (△) 750 °C,

The smaller values of $E_a$ (Table III) probably refer to extrinsic (impurity) conduction process. However, the changes in the values of $\sigma_{RT}$ and $E_a$ may be a result of changes in the time and temperature of $MoS_2$ preparation, or due to small changes in stoichiometry or imperfections which act as scattering centres.

### *3.2.1. Used catalysts*

Used catalysts were also characterized by chemical analysis, X-ray diffractometry and thermal analysis to establish the nature of the surface which has suffered deactivation.

Chemical analysis and X-ray diffraction pattern did not reveal any significant change in composition or any phase change of the used catalyst. Since $MoS_2$ catalyst is characterized by a very low surface area (2.86 m$^2$ g$^{-1}$), it appears that only a small amount of aniline accumulated on the surface will be sufficient to stop further hydrogenation of nitrobenzene. Such a small amount of aniline may not be able to effect any conceivable change either in the composition or any consequent changes in the unit cell dimensions. Intercalation of aniline in $MoS_2$, which is quite possible, is not likely to be detected by X-ray diffractometry, since no change in X-ray parameters has been observed with the intercalation compounds of $MoS_2$ with $NH_3$ [23]. These intercalated compounds are highly susceptible towards decomposition when exposed to air or moisture.

Differential thermal analysis of the fresh and used catalysts provided substantial proof in favour of accumulated aniline on the $MoS_2$ surface (Fig. 3). It is evident from the thermograms that the thermal behaviour of $MoS_2$ in air is significantly altered after being used in the reaction, although a common trend is retained. When heated in air, freshly prepared $MoS_2$ exhibited two distinct peaks, one highly exothermic, starting at 340 °C and ending at 665 °C with a peak at 425 °C, and another endothermic one starting at 750 °C and ending at 805 °C with a peak at 790 °C. The first peak is due to the oxidation of $MoS_2$ to $MoO_3$ and the second one to melting of $MoO_3$. With used $MoS_2$, the corresponding temperatures for the first thermal change are considerably shifted, while those for the second phase remain essentially the same. Additional differences that could be observed in the thermogram of the used $MoS_2$ catalyst are and a series of several endothermic peaks occurring at 180, 210, 270, 290 and 405 °C just before the onset of oxidative decomposition of $MoS_2$. Endotherms at 180 and 210 °C are easily identifiable as those due to imbibed aniline and nitrobenzene, respectively. Other endotherms beyond 210 °C are likely to be due to desorption of some of the products originating from oxidative decomposition of aniline and nitrobenzene or from their interaction with $MoS_2$ itself at higher temperature.

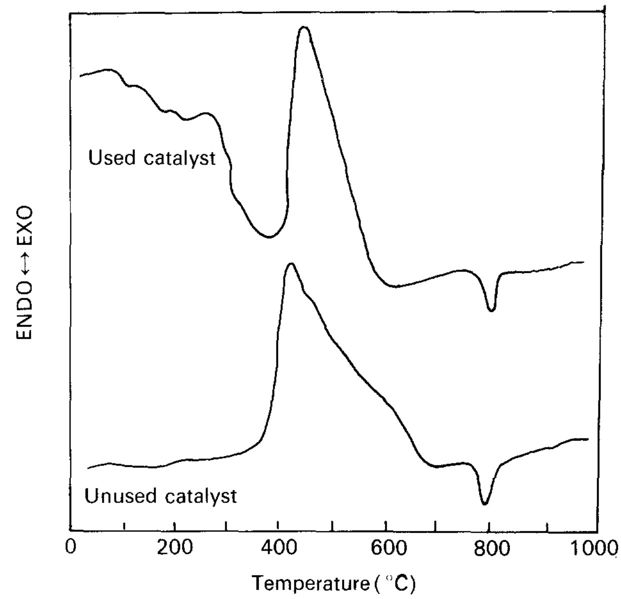

*Figure 3* Thermograms of pure and used $MoS_2$ catalyst.

The two distinct phases as observed in the time–conversion plots under different experimental conditions of temperature and pressure are now easily understood (Figs 4 and 5). The first phase, in which conversion rises steadily to a maximum value, corresponds to the slow accumulation of product aniline on

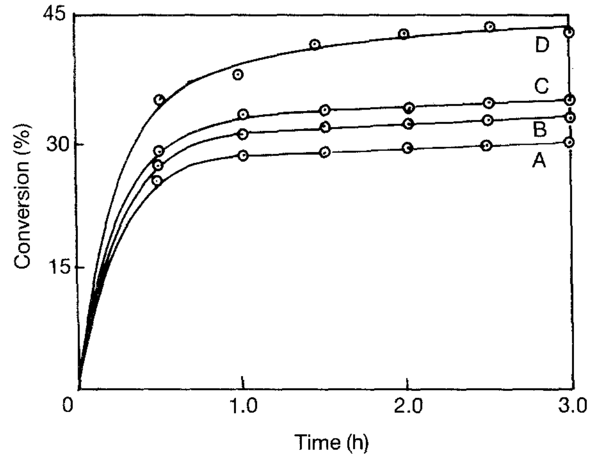

*Figure 4* Time–conversion plots for conversion of nitrobenzene in the presence of $MoS_2$ catalyst at (A) 110 °C, (B) 135 °C, (C) 150 °C and (D) 180 °C; catalyst amount 20 g $l^{-1}$, $H_2$ pressure $3.44 \times 10^6$ N $m^{-2}$.

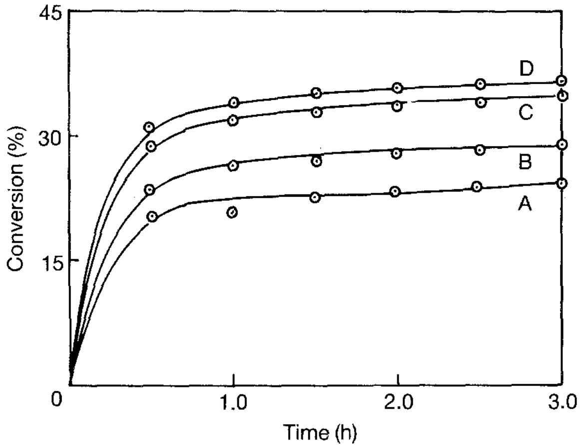

*Figure 5* Time–conversion plots for conversion of nitrobenzene in the presence of $MoS_2$ catalyst at $H_2$ pressure (A) $2.06 \times 10^6$, (B) $2.95 \times 10^6$, (C) $3.44 \times 10^6$ and (D) $4.13 \times 10^6$ N $m^{-2}$; catalyst amount 20 g $l^{-1}$, temperature 150 °C.

the $MoS_2$ surface up to a point of saturation. Beyond this, the second phase starts in which the reaction is virtually totally arrested and conversion remains almost constant, even up to 3 h.

## 3.2. Surface interaction between catalyst and product

Some secondary interactions between the catalyst and the product aniline appear to be theoretically very much favoured. Aniline being a proven base and $MoS_2$ an n-type semiconductor, a strong cumulative adsorption is predictable on the basis of Hauffe's electrical double layer theory [24]. Also, in view of the acidic character of $MoS_2$ a strong interaction between aniline and the catalyst is indicated. Furthermore, Mo(IV) is known to form stable amine complexes [25] which may effectively alter the surface characteristics of $MoS_2$.

## 4. Summary and conclusion

Molybdenum disulphide has been prepared by atmospheric pressure reduction of $MoS_3$in the temperature range 400–750 °C for 4 h. It was found to be an n-type diamagnetic semiconductor with a surface area varying in the region of 2.35 $m^2$ $g^{-1}$. $MoS_2$ has also been used as a catalyst in liquid-phase hydrogenation of nitrobenzene and then characterized. The reaction was found to be partially complete with aniline as the only product. Possibly the surface accumulation of aniline on the catalyst surface as a strongly adsorbed species or the formation of an intercalated compound makes the $MoS_2$ surface completely inactive against further hydrogenation. With all these possibilities taken together, it appears that the surface of the catalyst is progressively covered with aniline as the reaction progresses, debarring the nitrobenzene from further adsorption on the catalyst surface. Thus the observed second phase in the time–conversion plots (Figs 4 and 5) may be explained in terms of a situation where the surface of the catalyst is virtually unavailable to nitrobenzene for further hydrogenation.

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