JOURNAL OF CATALYSIS 63, 515–519 (1980)

Structure and Properties of Molybdenum Sulfide: Correlation of O_2 Chemisorption with Hydrodesulfurization Activity*

The chemisorption of oxygen has been used in a dynamic mode for the characterization of a number of samples of molybdenum disulfide. Their hydrodesulfurization activities (for dibenzothiophene) had previously been determined. Surface areas of the activity-tested catalysts gave little or no correlation with catalytic activity. However, a clear, linear relationship emerged when activities were plotted against O_2 chemisorption capacities of the activity-tested catalysts. These results are discussed in terms of the anisotropic nature of molybdenum disulfide.

The structural nature of the layered transition metal dichalcogenides is intimately related to their practical uses. Thus, the lubricity of MoS_2 stems from the weak bonding between adjacent basal planes. The intercalative properties of TiS_2, which has been exploited in nonaqueous battery applications (*1*), are likewise the consequence of the weak interlayer forces.

Another important application of transition metal dichalcogenides occurs in the area of heterogeneous catalysis. MoS_2 and, to a lesser extent WS_2 are the active components in catalysts currently in large-scale use for the removal of sulfur and nitrogen from a variety of petroleum feedstocks. In this report, we consider the question of whether the basal plane or edge plane is the source of this activity.

A previous report from this laboratory has described the low-temperature precipitation of amorphous MoS_2 (*2*). Another recent communication has dealt with the highly disordered rag-like morphology that develops when this material is annealed in H_2S/H_2 at 400°C (*3*). The high surface/volume ratio of this substance is suitable for catalytic studies, as well as ancillary techniques such as chemisorption. In the present investigation we have attempted to exploit this by the combined study of *selective* chemisorption (using a plane-specific adsorbate) and catalytic activity.

The literature does not indicate a suitable chemisorption agent. However, an account by Bahl *et al.* (*4*) is suggestive. They investigated single crystals of MoS_2 at 500–600°C and found that the edge plane oxidized much more rapidly than did the basal plane. This points to the possible use of O_2 as a plane-specific adsorbate for MoS_2, but a problem is posed by its strength of reaction with catalysts of this type. Well-dispersed, sulfided, molybdena-containing catalysts react vigorously with oxygen, even at ambient temperature, and such uncontrolled, exothermic adsorption will lead to a process that is no longer surface selective.

In order to obtain valid edge-plane area measurements, we have employed O_2 chemisorption in a *dynamic* mode; pulses of O_2 are added to a carrier gas stream and thus rapidly traverse the catalyst bed. The brief and intermittent adsorbate–catalyst contact leads to results which indicate that subsurface oxidation has been effectively suppressed.

Using O_2 chemisorption in this manner, we have characterized a number of MoS_2 catalyst samples after these had been tested for the hydrodesulfurization of dibenzothiophene. The total (BET) surface areas

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* Presented at AIChE National Meeting, San Francisco, November 1979.

0021-9517/80/060515-05$02.00/0

of the activity-tested catalysts were also measured. This enabled a comparison of the relative correlatabilities of O_2 chemisorption and total surface area with catalytic activity.

EXPERIMENTAL

Preparation of Catalysts

Catalysts were prepared by one of three basic routes, designated A, B, or C in Table 1. (A) Metathetical reaction of $MoCl_4$ with a stoichiometric amount of LiS_2. After solvent washing (ethyl acetate) to remove LiCl, the dried precipitate was treated in 15% H_2S/H_2 at a temperature indicated in Table 1. (B) $MoCl_5$ was dissolved in methanol to give $MoOCl_3$ and this solution was added to a solution containing excess $(NH_4)_2S$. After solvent washing (MeOH or H_2O) the dried precipitate was treated in 15% H_2S/H_2 at 400 or 800°C as indicated in Table 1. (C) Decomposition of ammonium thiomolybdate, yielding MoS_3 and $(NH_4)_2S$. Heat treatment of MoS_3 (e.g., under hydrodesulfurization reaction conditions) converts it to MoS_2. Variations of these three basic preparative routes will be pointed out either in the discussion of Table 1 or in its footnotes.

TABLE 1

Surface Areas, O_2 Chemisorption Capacities, and Hydrodesulfurization Activities of MoS_2 Catalysts

#	Preparation method	Surface area (m^2/g)	O_2 adsorption (μmole/g)	Desulfurization rate constant[a]
1	A (400)[b,c]	40	17	10
2	A (400)[b,c]	27	11	9
3	A (400)[b]	18	20	11
4	A	—	17	11
5	A (700)[b,c]	15	6	3
6	B (400)[b]	—	13	13
7	B (800)[b]	—	1	2
8	C[e]	112	31	22
9	C[c]	87	27	16
10	C	112	19	11
11	C	108	41	35
12	C	108	37	36
13	C[d]	14	31	22
14	C	120	35	20
15	C	23	37	24

[a] Rate constant for hydrodesulfurization of dibenzothiophene at 350°C, 450 psig; molecules DBT per gram catalyst per second (× 10^{16}).

[b] Treated *ex situ* in flowing 15% H_2S/H_2 at indicated temperature.

[c] Pretreated *in situ;* heated under 15% H_2S/H_2 from 25 to 400°C over 90 min, then cooled to 25°C under H_2S/H_2.

[d] Pretreated *in situ* under 15% H_2S/H_2at 100°C, 1 hr, then cooled under H_2S/H_2 to 25°C.

[e] Catalyst charged as a powder, instead of usual 20/40-mesh particles.

Hydrodesulfurization Runs

Catalytic activity was studied in a stirred autoclave modified so as to permit hydrogen flow and liquid sampling. The autoclave was fitted with a condenser so that despite hydrogen flow, all organic materials were retained and the reactor was static in this sense. The reaction studied was the hydrodesulfurization of dibenzothiophene (DBT), at 350°C and 450 psi pressure.

The catalyst (1 g, 20/40-mesh pressed powder, diluted with $\frac{1}{16}$-in. porcelain beads) was placed in a 10-cm^3 basket. In several cases it was pretreated *in situ* with flowing H_2S/H_2 as indicated in Table 1. With the reactor at ambient temperature, a flow of H_2 at 100 cm^3/min was established and the reactor charged with 5 wt% DBT/decalin. The pressure was adjusted to 450 psi and the temperature raised to 350°C. Liquid sampling commenced when 350°C was reached and was repeated at hourly intervals. Samples were analyzed with a Perkin–Elmer 900 gas chromatograph, using a flame ionization detector and a 10% SP 2100 column. In order to obtain rate constants, the concentrations of the two products (biphenyl and cyclohexylbenzene) which result from the hydrodesulfurization of DBT were summed and plotted against time. Conversions of DBT $\leq$30% were used. In this regime, essentially linear concentration vs time plots will be obtained even if first-order dependence on DBT concentration prevails. Thus, even in the absence of knowledge of the true reaction order under our conditions, the slopes of the linear concentration vs time plots which we obtained sufficed to provide relative rate constants for these catalysts.

Characterization of Activity-Tested Catalysts

The activity-tested catalysts were recovered and their surface areas were determined by the BET method using N_2 at 195°K. In addition, their capacities for O_2 chemisorption were determined in a flow apparatus, with argon (99.996%) carrier gas and a thermal conductivity detector. As discussed above, a dynamic technique was utilized in order to kinetically suppress subsurface penetration by the adsorbate. The catalysts were treated *in situ* with 14% H_2S/H_2 at 350°C for 30–60 min, cooled to ambient temperature under H_2S/H_2, and purged there with argon for ~15 min. In many experiments with MoS_2 catalysts, we have found that varying the duration of this purge over a wide range does not influence the results. O_2 chemisorption was then measured at ambient temperature by the addition, at 2- to 3-min intervals, of 5-cm^3 pulses of 10% O_2/argon (20.5 μmole O_2/pulse) into the carrier gas just upstream of the catalyst with a microvolume value. Effluent O_2 peaks increased to constant size, signifying saturation of the catalyst, and the total uptake was calculated.

In some cases, BET surface areas and O_2 adsorption capacities were determined for catalysts prior to activity testing. As compared with these values, those obtained with the activity-tested materials were substantially lower. The catalytic data gave no evidence of deactivation once the catalyst had been brought to 350°C and sampling commenced. Thus, loss in BET surface area and O_2 adsorption capacity must occur during the first moments of contact with the feed, i.e., before the reaction temperature is established. Accordingly, the activity-tested sample provides a much better representation of the working catalyst.

RESULTS AND DISCUSSION

Table 1 compiles the rate constants, surface areas of the activity-tested catalysts, and O_2 chemisorption capacities of the activity-tested catalysts.

Turning first to the preparations following Method A (metathetical reaction of $MoCl_4$ and Li_2S) we observe that treating the dried precipitate *ex situ* in 15% H_2S/H_2 at 400°C has no discernible effect on the resultant catalytic activity, but if this treatment is carried out at 700°C (No. 5) the activity is substantially lowered. This is not surprising since treatment at the lower temperature leads to a poorly crystalline product (*3*) whereas the higher temperature gives well-crystallized MoS_2. A similar observation applies to a comparison of runs Nos. 6 and 7.

Runs Nos. 8–12 pertain to preparations in which ammonium thiomolybdate was decomposed with aqueous, excess HCOOH at ambient temperature, followed by digestion at 50°C, filtering, washing of the precipitate, and vacuum drying at 150°C. The resultant activities vary over a threefold range despite approximately constant surface area. The catalyst in run No. 14 arose via the *in situ* decomposition of amonium thiomolybdate, while in runs Nos. 13 and 15, thermochemical decomposition was effected *ex situ* at 350–400°C. This is seen to have led to a large decrease in surface area, whereas catalytic activity was apparently unaffected.

The above observations make it plain that the correlation between hydrodesulfurization activity and surface area is poor. This is manifest upon inspection of Fig. 1, which presents this correlation for 12 catalysts listed in Table 1. In addition to the absence of linearity, the scatter of the data around any curve is very large.

A vastly improved correlation emerges if catalytic activity is plotted versus O_2 chemisorption capacity, as shown in Fig. 2. The relationship, despite some scatter, is seen to be linear and furthermore appears to pass through the origin.

Voorhoeve and Stuiver (*5*) have proposed that the edge plane in MoS_2 and WS_2 is the site of their hydrodesulfurization activity, based on ESR studies of NiS/WS_2 catalysts. Their model of pseudointercalation by Ni^{2+} at the WS_2 edge plane was supported by electron micrographs obtained by Farragher and Cossee (*6*). The

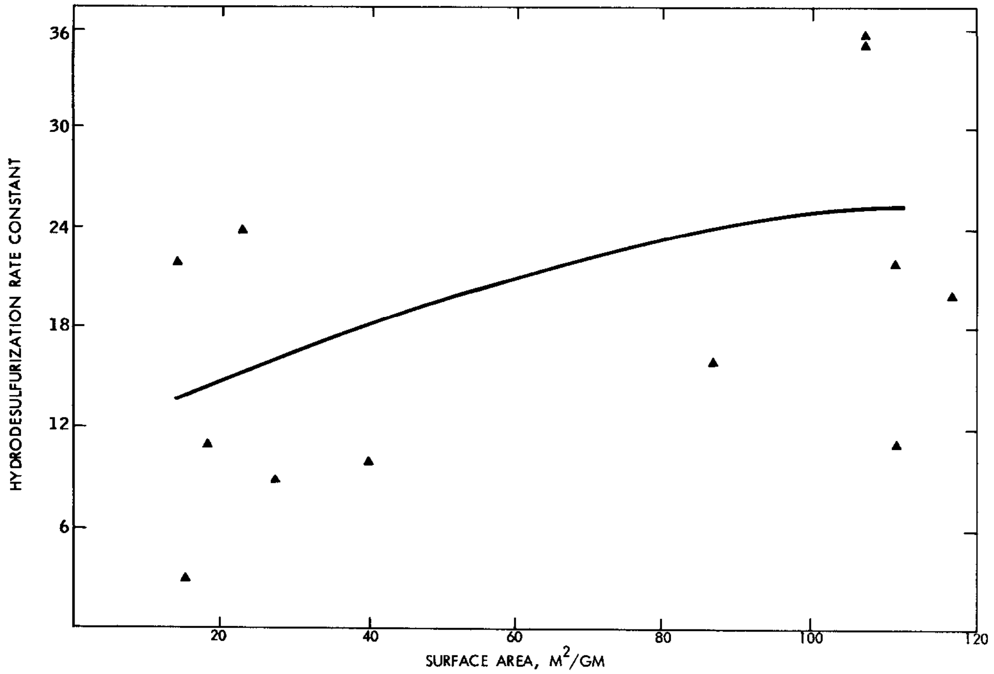

FIG. 1. Correlation of hydrodesulfurization rate constant with surface area.

present results support this hypothesis and demonstrate that the chemisorption of oxygen, when applied in a dynamic mode, is effective in determining the edge plane area of MoS_2. The poor correlation of activity with total surface area apparently reflects the fact that the edge plane/basal plane ratio is capable of wide variations among

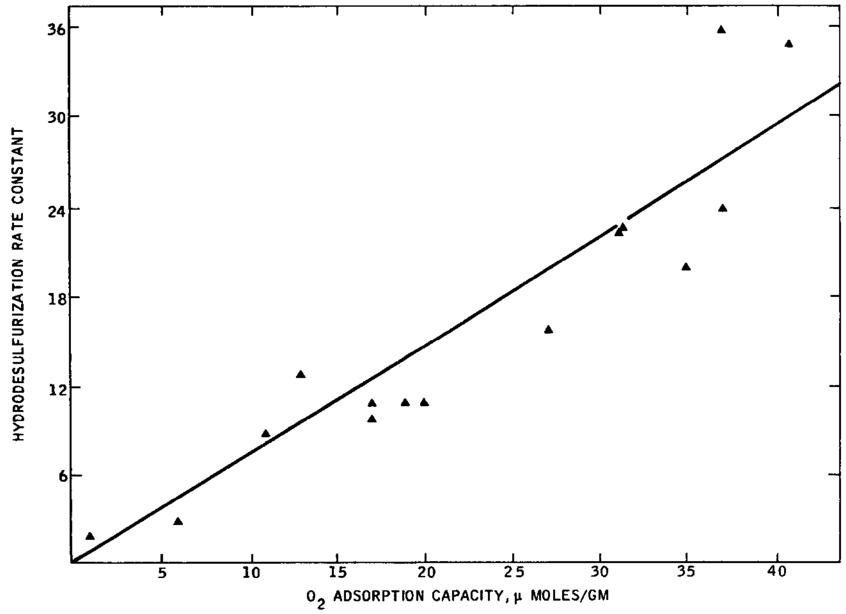

FIG. 2. Correlation of hydrodesulfurization rate constant with O_2 adsorption capacity.

preparations of MoS_2, sometimes for reasons that are difficult to identify or control.

REFERENCES

1. Whittingham, M. S., *Science* **192,** 1126 (1976).
2. Chianelli, R. R., and Dines, M. B., *Inorg. Chem.* **17,** 2758 (1978).
3. Chianelli, R. R., Prestridge, E. B., Pecoraro, T. A., and deNeufville, J. P., *Science* **203,** 1105 (1979).
4. Bahl, O. P., Evans, E. L., and Thomas, J. M., *Proc. Royal Soc. London Ser. A* **306,** 53 (1968).
5. Voorhoeve, R. J. H., and Stuiver, J. C. M., *J. Catal.* **23,** 228 (1971); **23,** 228 (1971).
6. Farragher, A. L., and Cossee, P., *in* "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), p. 1301. North-Holland, Amsterdam, 1973.

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Received November 29, 1979