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Studies of Molybdenum Sulfide Catalysts

I. Oxygen Chemisorption on Unsupported and Supported MoS_2

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The use of low-temperature oxygen chemisorption (LTOC) to characterize molybdenum sulfide catalysts has become common, but the values of LTOC are very sensitive to details of catalyst pretreatment. For unsupported MoS_2, the previously reported values for the ratio of BET surface area to LTOC, expressed as $Å^2/O_2$, have varied over a 10-fold range. Three samples of MoS_2, prepared by different routes in three laboratories, have now been shown to give values for this ratio which fall in the narrow, and low, range of 84 to 103 $Å^2/O_2$, provided that a common pretreatment in H_2 at 450°C precedes the LTOC measurement. (Prereduction is standard practice for characterization of Mo oxide catalysts by LTOC.) Application of the same methodology to a sulfided molybdena-alumina sample gives values for LTOC which are much higher than those previously reported for similar (but not H_2-pretreated) samples. LTOC on the sulfide is about 20% lower than that on the same sample in the oxide (reduced-only) condition, and the values after a given pretreatment—reduced-only, or sulfided and reduced—are quite reproducible when the supported catalyst is cycled at 450°C.

INTRODUCTION

Characterization of unsupported and supported molybdenum oxide by oxygen chemisorption at low temperature (LTOC) has become rather widely used in the last few years; the methodology has been recently reviewed (*1*). Application of LTOC to sulfided catalysts was first published by Tauster *et al.* (*2*) and has since been studied by Massoth and co-workers (*3, 4*), Bartholomew and co-workers (*5, 6*), and Burch and Collins (*7*). The values for LTOC on MoS_2 turn out to be very sensitive to details of the pretreatment. For unsupported MoS_2, the ratio of LTOC value to total surface area may vary over a 10-fold range, depending on the temperature of purge (or evacuation) after presulfiding, and on whether prereduction is employed after presulfiding and before LTOC (*1, 2*). The large range of values obtained by Tauster *et al.* was attributed to variation in the ratio of edge plane to basal plane sites. Equally plausible is the hypothesis that the LTOC values vary as a function of surface chemistry, which in turn depends on details of the high-temperature pretreatment.

Whatever methodology is used for pretreatment and LTOC measurement, it has become customary to use the ratio of LTOC and BET surface area on unsupported MoS_2 as a conversion factor with which to multiply LTOC values on supported MoS_2 in order to deduce an apparent specific surface area of MoS_2 in the supported catalysts. The presence of other reducible cations (Ni, Co) may complicate this procedure.

This paper represents a contribution toward a standardized methodology for unsupported MoS_2, and application of the technique to sulfided molybdena-alumina catalysts.

EXPERIMENTAL

Catalyst Preparation

Unsupported catalysts. Catalysts 1 and 3

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(see Table 1) were prepared by the comaceration method of Hagenbach *et al.* (*8*). For catalyst 1, the MoO_3 was digested in an aqueous ammonium sulfide solution for 6 hr at 70°C. The dried solid so obtained was then heated under H_2S–Ar for 4 hr at 400°C before evacuation. For catalyst 3 a hot solution (60–70°C) of ammonium heptamolybdate was poured into a hot solution (60–70°C) of 20% ammonium sulfide under vigorous stirring. The slurry was continuously stirred until all water was evaporated and only a dried product remained. This was heated in flowing 2% H_2S/H_2 (1.5°C/min) to 400°C and kept at 400°C for 4 hr. After cooling to room temperature, the sample was flushed with 0.1% O_2/N_2 for passivation before exposure to air.

Catalyst 2 was prepared according to the method of Naumann *et al.* (*9*). Ammonium thiomolybdate (ATM) was placed in the adsorption cell and thermally decomposed in flowing H_2 (220 cm^3/min) at 450°C for 2 hr. The cell was then purged with flowing He (150 cm^3/min) for 1 hr and sealed in the absence of air.

Supported catalysts. Gamma alumina (Girdler; area 188 m^2/g; pore volume 0.39 cm^3/g; ground and sieved to 1.19–0.86 mm) was impregnated with aqueous ammonium heptamolybdate. Excess water was evaporated at 80°C and 0.27 atm in a rotary evaporator. The dried samples were heated in a muffle furnace (flowing air) for 2.5 hr at 380°C, then at 550°C for 4.5 hr. The Mo loading was 8 wt% (based on Mo); BET area of the finished catalyst was 189 m^2/g, and the average pore diameter was calculated to be 83 Å.

Procedure

Bulk MoS_2 samples were reduced with H_2 (static, 300 mm Hg) at 450°C for 4 hr and pumped at 500°C overnight (15 hr). The extent of oxygen chemisorption was then determined by difference between two oxygen isotherms at −195°C, with intermediate pumping at −78°C for 1 hr to remove physically adsorbed oxygen. Finally, the samples were reduced again as described above, and their BET surface areas were determined with nitrogen at −195°C. Duplicate experiments were performed for each sample.

Sulfidation of the oxidic form of the supported catalysts was accomplished *in situ* by passing 15% H_2S/H_2 (150 cm^3/min) through the sample cell for 5 hr at 450°C, purging with He for 1 hr, and reducing with H_2 (300 mm Hg) for 4 hr at 450°C. The sample cell was then sealed, pumped at 500°C overnight, and oxygen chemisorption performed as for unsupported catalysts. (Low-temperature oxygen chemisorption was found to be the same after evacuation for 1 hr at 500°C as after overnight evacuation.) Cycling of the samples (see Table 2) was carried out by oxidation of the samples in pure O_2 at 450°C for 2 hr, purging with He for 1 hr, pumping for 2 hr, reduction with H_2 for 16 hr at 450°C, and final pumping at 500°C overnight.

RESULTS AND DISCUSSION

Unsupported Catalysts

Three samples of unsupported MoS_2, prepared by different routes (see Experimental section), were studied; their surface areas varied from 4 to 20 m^2/g. Table 1 summarizes the extent of oxygen chemisorption, the BET surface area, and the area

TABLE 1

Oxygen Chemisorption at −196°C on Unsupported MoS_2 Samples

Sample	O_2 uptake (mg/g)	S_{BET} (m^2/g)	(A^2/O_2)
MoS_2—1[a]	1.17	21.3	97
	1.15	20.2	94
MoS_2—2[b]	0.51	10.1	102
	0.45	9.0	103
MoS_2—3[a]	0.26	4.1	85
	0.26	4.0	83

[a] Prepared according to Ref. (*8*).

[b] Prepared by flash thermal decomposition of $(NH_4)_2MoS_4$ at 450°C in a hydrogen flow.

covered by an oxygen molecule (calculated from the ratio of the first two quantities). Duplicate samples of each preparation showed good reproducibility. Of particular interest is the area per O_2 molecule, for several reasons: (1) the relatively small variation between the three samples—from 83 to 103 Å^2/O_2, (2) the lower mean value relative to those reported by Tauster *et al.* and by Bodrero and Bartholomew, and (3) comparison of the mean value with that characteristic of LTOC on Mo oxide.

The pioneering work of Tauster *et al.* (*2*) reported areas per molecule varying from 75 to 978 Å^2/O_2; the mean value for eight different samples was 472 Å^2/O_2 (*1*). Voorhoeve and Stuiver (*10*) had elaborated a model in which the edge-plane in MoS_2 or WS_2 is the active center of hydrodesulfurization activity. Their model of pseudointercalation of Ni^{2+} ions at the WS_2 edge-plane was supported by the TEM analyses of Farragher and Cossee (*11*). On this basis, Tauster *et al.* interpreted their chemisorption results, with high values of the area per molecule, as a measurement of the edge-plane area; they attributed the large range in area per molecule to the variable relative amount of edge-plane area when different preparation methods are used.

Bodrero and Bartholomew (*6*) very recently reported LTOC measurements on four samples of unsupported MoS_2 having BET areas ranging from 18 to 68 m^2/g. Their ratios of BET area to oxygen chemisorbed correspond to values of 231 to 316 Å^2/O_2, with a mean value of 287 Å^2/O_2. Although this mean is much lower than that of Tauster *et al.*, Bodrero and Bartholomew also deduce that the selective adsorption of oxygen occurs on edge or corner sites.

The three samples of unsupported sulfide listed in Table 1 differed in substantial detail in their preparation before measurement of LTOC. Sample 1 was sulfided after exposure to air. Sample 2 was never exposed to air after its preparation by decomposition of ATM. Sample 3 was reductively sulfided and exposed to air before LTOC. Their BET areas varied by a factor of 5. Nevertheless, the area per O_2 molecule falls within a quite narrow range, and the mean value of 94 Å^2/O_2 is lower by a factor of 3 than that of Bodrero and Bartholomew and is lower by a factor of 5 than that of Tauster *et al.*

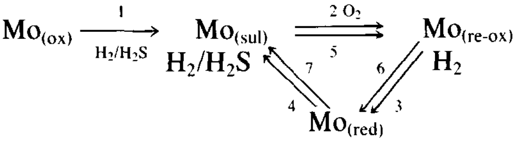
The explanation for these differences between different investigators is likely to reside in the details of pretreatment, rather than in variation of edge- to basal-plane site ratios. Our own studies of pretreatment variables will be separately published; for the present it may suffice to call out significant differences in the procedures used by different laboratories. Tauster *et al.* cooled their samples, after presulfiding, in flowing H_2S/H_2 and purged (for 15 min) only at room temperature; no high-temperature purge or hydrogen treatment was used before oxygen chemisorption. Bodrero and Bartholomew evacuated their samples at 350°C after presulfiding at 350°C; no subsequent exposure to H_2 at elevated temperature was employed. The samples summarized in Table 1, by contrast, received a 450°C treatment in H_2 after presulfiding, followed by pumping at 500°C. Chemisorbed H_2S should be removed by this treatment, and some change in valence of the surface Mo ions may occur. It is worth noting that when LTOC is applied to Mo oxide catalysts, unsupported or supported, pretreatment with hydrogen at elevated temperature immediately precedes the chemisorption determination.

The mean value of area/molecule for the samples listed in Table 1 for (H_2-pretreated) MoS_2, 94 Å^2/O_2, is still considerably higher than the 51 Å^2/O_2 found by Parekh and Weller (*10*) and the 47 Å^2/O_2 by Fierro *et al.* (*11*) for (H_2-pretreated) MoO_2. A major factor leading to this larger value may be the fact that the ratio of atomic volume for Mo in MoS_2 to that in MoO_2 is 33.4/19.8 = 1.69. The assumption that the areal density of Mo sites is proportional to the $\frac{2}{3}$ power of the atomic volume would lead to a prediction that the area per O_2 should be 40–45%

higher in MoS_2 than in MoO_2. This calculation does not presume that chemisorption occurs only on selected planes.

Reduced and Sulfided Mo/Alumina Catalysts

A series of oxygen chemisorption measurements was sequentially performed *in situ* on a Mo/alumina sample which underwent cycles of sulfidation, oxidation, and hydrogen reduction. The seven treatment steps in two complete cycles are represented schematically by



Detailed conditions for each step are given in Table 2. Steps 1, 4, and 7 are sulfidations, 2 and 5 are reoxidations, and 3 and 6 are reductions. Table 2 also summarizes the results of LTOC measurements after steps 1, 4, and 7 and after steps 3 and 6.

The chemisorption values listed in Table 2 are much higher than those reported recently by Zmierczak *et al.* (*4*) for a similar sulfided molybdena/alumina sample. As in the case of unsupported MoS_2, these differences among investigators may reside in the details of pretreatment. For example, Zmierczak *et al.* presulfided at 400°C and purged with He; no H_2 pretreatment preceded the LTOC measurement.

TABLE 2

O_2 Adsorption Measurements on Reduced and Sulfided MoO_3/Al_2O_3

Catalyst	Pretreatment	O_2 uptake (mg/g)
MoO_3/Al_2O_3 (fresh)	1. Sulfiding with 15% H_2/H_2S for 5 hr, purging with He for 1 hr, and reducing with H_2 for 4 hr	4.35
	2. Reoxidation of sample 1 with O_2 at 450°C for 2 hr, purging with He for 1 hr	
	3. Reduction of sample 2 (after outgassing at 10^{-2} mm Hg for 2 hr) with H_2 at 450°C for 16 hr	5.62
	4. Resulfiding as in 1	4.09
	5. Reoxidation as in 2	
	6. Reduction as in 3	5.05
	7. Resulfiding as in 1	4.18

The following conclusions may be drawn:

(1) Oxygen uptake on the sulfided form of Mo/alumina is significantly lower than that on the oxide. This decrease may result from (a) a real difference in dispersion of Mo ions in MoS_2 and MoO_2, and (b) incremental plugging of pores in the support when the sulfide is present, because of the difference in molar volumes between sulfide and oxide.

(2) LTOC values for the sulfided-reduced and reduced-only forms of the MoO_3/Al_2O_3 sample are very similar in two successive sulfiding-oxidation–reduction cycles; i.e., the O_2 uptake after resulfiding the reoxidized sample was quite similar to that of the fresh sulfided sample. By implication, cycling the sample does not result in deterioration of the distribution of the supported Mo species.

(3) It is not possible from these results to deduce anything about an appropriate model for the supported MoS_2 or the MoO_2 (e.g., monolayer and/or microcrystallites). Reoxidation of either reduced species presumably regenerates a monolayer of the trioxide on the alumina; the thermodynamic driving force for monolayer formation is responsible for the stability of the Mo dispersion during the cycling treatment. The chemisorption data provide insufficient basis for discriminating between models for the reduced-only oxide and the reductively sulfided material supported on alumina.

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