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Studies of Molybdenum Sulfide Catalysts: Effects of Pretreatment on Sintering, Stoichiometry, and Oxygen Chemisorption

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The effects of various pretreatments on total area, oxygen chemisorption, and S/Mo ratio have been studied on unsupported molybdenum sulfide, prepared by *in situ* decomposition of ammonium tetrathiomolybdate (ATTM) in helium. The initial catalyst contains excess sulfur (S/Mo = 2.3–2.4), has high surface area, and shows little O_2 chemisorption. Temperature-programmed reduction (TPR) in H_2 shows two H_2S peaks, centered at about 180 and 380°C. Negligible sintering occurs during removal of sulfur corresponding to the first TPR peak; sintering does occur during the second TPR peak and increases when the sample is maintained in H_2 at 450°C. Specific O_2 chemisorption increases with increasing reduction temperature. The properties of the resulting sulfide depend both on the heating schedule during the original decomposition of ATTM and on the sample size. Pretreatment in H_2S/H_2 rather than in H_2 results in much less sintering and much lower specific O_2 chemisorption. © 1985 Academic Press, Inc.

INTRODUCTION

The catalytic sites in the sulfide form of Mo/Al_2O_3 catalysts are believed to consist of coordinatively unsaturated Mo ions and the associated anion vacancies (*1, 2*). These sites adsorb various probe molecules, for example, O_2, NO, CO. The selective chemisorption of O_2 has been widely used to characterize promoted and unpromoted Mo/Al_2O_3 catalysts in the oxide and sulfide forms (*3–31*). The amount of O_2 chemisorption has been found to correlate with the catalytic activity for hydrosulfurization (*9–21, 25, 26*), hydrogenation (*19, 22, 23*), and dehydrogenation (*6*). Other studies have shown the absence of such correlations (*8, 9, 21*).

Since the sulfide form of the Mo/Al_2O_3 catalyst may consist of patches of MoS_2 crystallites (*1, 32*), it is useful to study unsupported MoS_2. Such a study is important for two reasons: (a) development of a rational methodology for application of O_2 chemisorption to supported catalysts requires proof of the method for unsupported MoS_2 and for computation of the factor which relates molybdena area to O_2 chemisorption, and (b) the nature of the active sites on Mo sulfide catalysts is more directly studied on the unsupported sulfide relatively free from complications introduced by the support.

In the present study, unsupported nonstoichiometric molybdenum sulfide with S/Mo = 2.3–2.4 was prepared *in situ*, by thermal decomposition of ammonium tetrathiomolybdate (ATTM) in helium. The *in situ* preparation ensures an oxygen-free catalyst; the sulfur content of the catalyst can be decreased by reduction in H_2 or H_2S/H_2. Variations in the ratio, total (BET) area per chemisorbed oxygen molecule, were studied as a function of pretreatment. Oxygen chemisorption, by a pulse method at −78°C, and total (BET) area, by a continuous flow method, were measured *in situ* after the desired pretreatment.

EXPERIMENTAL

Apparatus

An integrated apparatus (shown in Fig. 1) was used to measure temperature-programmed reduction (TPR) profiles, reaction rates, chemisorption uptake, and BET area

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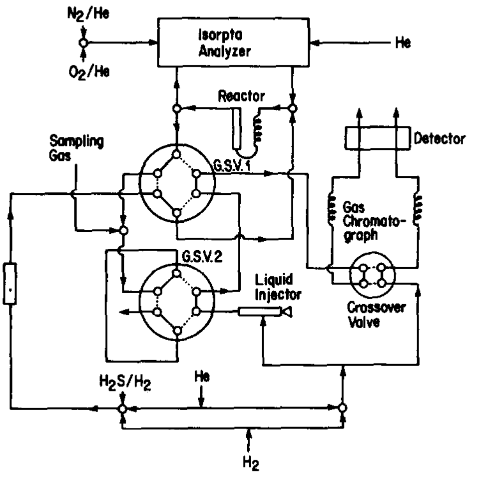

FIG. 1. Apparatus for *in situ* preparation of catalyst and measurement of TPR/TPD spectra, reaction rates, selective chemisorption, and BET area.

on a catalyst sample prepared *in situ* and subjected to a desired pretreatment. The apparatus consisted essentially of a microreactor (diameter, 4.5 mm) equipped with a preheating coil and connected through two six-port gas sampling valves to a HP-5754 gas chromatograph. The reactor was also connected to an Engelhard Isorpta-3A analyzer for measurement of adsorption isotherms by continuous flow.

Catalysts

Ammonium tetrathiomolybdate, mol. wt. = 260.28, was prepared in crystalline form as described in Ref. (*33*). A slightly different preparation method (*34*) was used for some of the earlier runs, but the two methods for ATTM preparation both yield an ultimate catalyst with the same BET area and O_2 chemisorption.

Thermal decomposition of ATTM in He produces molybdenum sulfide containing excess sulfur (S/Mo between 2 and 3).

$$(NH_4)_2MoS_4 \rightarrow 2NH_3 + H_2S + (3 - y)S + MoS_y, \quad (1)$$

The ATTM was supported between glass-wool plugs and decomposed in the reactor. Two heating schedules were used during ATTM decomposition in flowing He: flash-heating (done by lowering the reactor into a preheated oven) or programmed heating (10°C/min). The final temperature of 450°C was maintained for 60 min. In flash-heating, the final temperature of 450°C was attained in about 6 min, compared to about 40 min in 10°C/min heating.

Pretreatment

The molybdenum sulfide catalyst prepared by ATTM decomposition in He was cooled to room temperature and subjected to one of the following pretreatments.

(*A*) *Temperature-programmed reduction.* The catalyst was heated at a constant rate (15°C/min) in a H_2 stream, and H_2S evolution was monitored by passing the reactor effluent continuously through the sample side of the GC detector. The "standard" final temperature of 450°C was maintained for 60 min.

(*B*) *Reductive-sulfiding.* The catalyst was heated at 15°C/min in 15% H_2S/H_2 to 450°C and maintained at 450°C for 60 min. After the sample was purged with He at 450°C for 60 min, it was cooled to room temperature and then subjected to TPR as in (A).

Pulse Adsorption Measurement

The low-temperature oxygen chemisorption (LTOC) at −78°C was determined by a pulse method. Pulses of 1.5% O_2 in He were injected into the He carrier gas (about 25 cm^3/min) which passes through the catalyst bed (at −78°C) and then into the gas chromatograph for detection of unabsorbed O_2. The catalyst was considered to be saturated when successive outlet pulses do not differ by more than 1%. The pulse volume was adjusted so that the sample was saturated after 2–10 pulses.

BET Area

The Isorpta analyzer was used to determine the BET area by N_2 adsorption at −195°C. The N_2 partial pressure can be changed by changing the total pressure of a 7% N_2 in He stream flowing over the catalyst.

H_2S Evolution and S/Mo Ratios

The H_2S evolved during TPR was absorbed in zinc acetate solution and measured by iodometric titration. The cumulative H_2S evolution was also determined from the total area under the TPR profile and the H_2S calibration constant. The two values did not differ by more than 10–15%. The S/Mo ratio was determined from the weight loss in oxidizing the sulfide to MoO_3 in a muffle oven at 550°C for 60 min.

RESULTS AND DISCUSSION

Measurement of LTOC by Pulse Method

The results of the pulse method (used to measure LTOC in this study) were compared to those from continuous-flow two-isotherm method (*5*) and the static volumetric two-isotherm method (*3*). A commercial catalyst, Amocat 1-B (15% $MoO_3/\gamma\text{-}Al_2O_3$, BET area = 170 m^2/g, average pore diameter = 120 Å), was tested after the following pretreatment steps, all at 500°C: 15% H_2S/H_2, 2 h; He, 1 h; H_2, 4 h; and He, 1 h. The value of LTOC obtained by the pulse method was 1.42 cm^3 (STP)/g. This compares well with the value of 1.83 cm^3 (STP)/g obtained by the continuous-flow method (*30*) for an identical pretreatment, and with the value of 1.28 cm^3 (STP)/g obtained by the static volumetric method (*31*) for an essentially similar pretreatment (reduction period of 6 instead of 4 h). This agreement is in conflict with the finding of Bodrero and Bartholomew (*19*) that the pulse method of −78°C gives values of LTOC that are at most half of those from the static volumetric method at −78°C.

X-Ray Diffraction

The diffraction pattern of the initial catalyst prepared by flash decomposition of ATTM in He (Run 41, Table 1) consists of broad peaks characteristic of a poorly crystalline material. Reflections corresponding to the 002, 100, 103, and 110 planes of hexagonal MoS_2 (*36*) were identified. The rag-

TABLE 1

Effect of Reduction Temperature[a,e]

Run	Temperature (°C)	Time at final temperature (min)	H_2S evolution[b] (cm^3(STP)/g)	LTOC (cm^3(STP)/g)	BET area (m^2/g)	$Å^2/O_2$	S/Mo[c]
41	—	—	—	0.133	63.9	1783	2.31[d]
29	250	60	14.9	1.53	63.4	154	2.20
30	400	60	27.5	1.75	37.7	80.1	2.10
31	450	60	35.1	1.30	26.3	75.3	2.05
28	500	60	34.8	0.544	6.92	47.3	2.05
27	500	1	31.7	1.26	39.3	116	2.07
39[f]	450	60	36.2	1.45	28.0	71.7	2.05

[a] In all tables, H_2S evolution (during TPR), LTOC and BET area are expressed per gram of hypothetical MoS_2 formed. The ATTM was decomposed in He (flow rate 100 cm^3/min for 0.8-g samples, 40 cm^3/min for 0.3-g samples) at 450°C for 60 min, and then cooled to ambient temperature. The TPR was performed at 15°C/min in pure H_2 (flow rate 80 cm^3/min for all runs in Tables 1 and 6, 35 cm^3/min for runs in Tables 2–5, except Run 31).

[b] The values of H_2S evolution in this table were calculated from GC signal. The corresponding values in other tables (except Run 31) were obtained by titration of the H_2S.

[c] The values of S/Mo were calculated (except when indicated) from the S/Mo ratio for the initial catalyst (prepared by ATTM decomposition in He) and the corresponding H_2S evolution.

[d] The S/Mo ratios for the initial catalyst and others as indicated were calculated from the loss in weight in oxidizing the sulfide to MoO_3.

[e] ATTM (0.85 g) flash-decomposed in He; cooled in H_2 after TPR except Run 39.

[f] He purge at 450°C for 15 min after TPR.

like MoS_2 synthesized by Chianelli *et al.* (*37*) shows the same four main reflections. An additional reflection corresponding to the 003 plane (*39*) appears in the pattern of the present catalyst.

The same reflections appear in the pattern after heating the initial catalyst in H_2 at 450°C for 60 min (Run 31, Table 1); the peaks remain diffuse, indicating no measurable increase in crystallinity after this pretreatment. However, there is an appreciable increase in the intensity of the 003 reflection.

A similar diffuse peak pattern with all the same reflections (except 003) is obtained for a catalyst prepared by gradual decomposition (10°C/min) of ATTM, indicating no significant difference in crystallinity between flash-decomposed and 10°C/min-decomposed samples. The 003 reflection appears upon heating the initial 10°C/min-decomposed sample in H_2 at 450°C for 60 min (Run 115, Table 2); there is no significant change in the other reflections.

Effect of Reduction Temperature

The molybdenum sulfide formed by thermal decomposition of ATTM in He at 450°C contains excess sulfur (S/Mo = 2.3); it exhibits a low LTOC value but high BET area as shown in Table 1. (It should be noted that in all tables, the values of H_2S evolution, LTOC and BET area are expressed per gram of hypothetical MoS_2 formed, in order to avoid the effect of variable catalyst stoichiometry.) Heating in H_2 is required to remove excess sulfur and generate O_2 chemisorption sites. The H_2S evolution during TPR (in H_2) shows two peaks centered at about 180 and 380°C. Analysis of the TPR profiles will be considered later.

Table 1 contains data on flash-decomposed samples heated in H_2. The series of runs 29, 30, 31, and 28 were performed to

TABLE 2

Effects of Decomposition Heating Rate and Sample Size[a–g]

Run	ATTM (g)	Decomposition heating rate	H_2S evolution[b] (cm³(STP)/g)	LTOC (cm³(STP)/g)	BET area (m²/g)	Å²/O_2	S/Mo[c]
41	0.85	Flash	—	0.1333	63.9	1783	2.31[d]
118	0.3	Flash	—	0	56.2	—	2.42[d]
109	0.3	10°C/min	—	0	35.6	—	2.40[d]
31	0.85	Flash	35.1	1.30	26.3	75.3	2.06
115	0.85	10°C/min	39.5	0.315	11.6	137	2.03
87	0.3	Flash	50.2	0.710	12.9	79.1	2.06
111	0.3	10°C/min	48.8	0.270	8.95	123	2.05

[a] In all tables, H_2S evolution (during TPR), LTOC and BET area are expressed per g. of hypothetical MoS_2 formed. The ATTM was decomposed in He (flow rate 100 cm³/min for 0.8 g sample 40 cm³/min for 0.3 g samples) at 450°C for 60 min, and then cooled to ambient temperature. The TPR was performed at 15°C/min in pure H_2 (flow rate 80 cm³/min for all runs in Tables 1 and 5, 35 cm³/min for runs in Tables 2–4, except Run 31). Runs 41, 118, and 109 are for ATTM samples decomposed in He but not treated in H_2.

[b] The values of H_2S evolution in this table were calculated from G.C. signal. The corresponding values in other tables (except Run 31) were obtained by titration of the H_2S.

[c] The values of S/Mo were calculated (except when indicated) from the S/Mo ratio for the initial catalyst (prepared by ATTM decomposition in He) and the corresponding H_2S evolution.

[d] The S/Mo ratios for the initial catalyst and others as indicated were calculated from the loss in weight in oxidizing the sulfide to MoO_3.

[e] ATTM (0.85 g) flash-decomposed in He; cooled in H_2 after TPR except Run 39.

[f] He purge at 450°C for 15 min after TPR.

[g] TPR to 450°C, 450°C for 60 min, He purge at 450°C for 10 min (no He purge in Run 31), cool to ambient temperature.

evaluate the effect of final reduction temperature, and Run 27 to determine the effect of short holding time at the final temperature. The following conclusions may be drawn:

(a) There is no decrease in BET area during reduction at 250°C, i.e., evolution of H_2S corresponding to the first peak in the TPR spectrum (see Fig. 2). The BET area decreases with increasing reduction temperature beyond 250°C, i.e., evolution of H_2S in the second TPR peak. This sintering phenomenon occurs at fairly low temperatures in a H_2 atmosphere. Contrary to this, Ratnasamy and co-workers (*39, 40*) found that the surface area of the molybdenum sulfide obtained by reduction of amorphous MoS_3 in H_2 increased with temperature, reaching a maximum at 550°C. The difference in composition of the initial catalysts may explain the opposite trends in surface area. Ratnasamy's initial catalyst was MoS_3 which, upon heating in H_2, loses excess amorphous sulfur blocking the pores, thus increasing the surface area; at maximum surface area, poorly agglomerated crystallites are formed (*40*). The initial catalyst in the present study was poorly crystalline sulfide with S/Mo = 2.3. The removal of sulfur from this material increases the extent of lattice rearrangement and decreases the surface area.

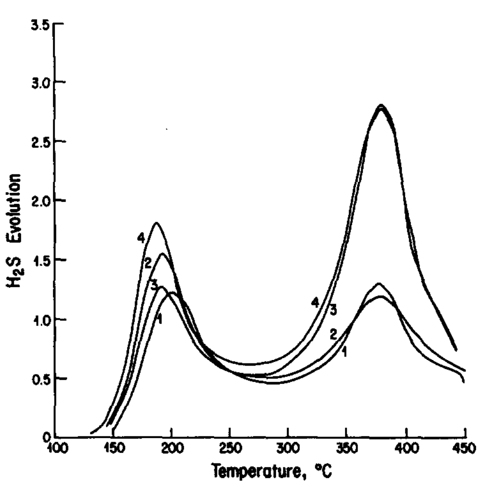

FIG. 2. TPR spectra of molybdenum sulfide prepared by decomposition of ATTM at 450°C. ATTM (0.8 g) samples: (1) flash-decomposed; (2) 10°C/min-decomposed. ATTM (0.3 g) samples: (3) flash-decomposed; (4) 10°C/min-decomposed.

Ratnasamy and Leonard (*39*) detected a new set of lines in the XRD pattern of MoS_2 reduced at 800°C. They attributed this to rhombohedral MoS_2, which is formed due to kinetic factors (the hexagonal form is more stable). However, Furimsky and Amberg (*41*) who used a similar preparation method attributed the new lines to metallic Mo formed by over-reduction of MoS_2. Wilderwanck and Jellinek (*38*) detected only hexagonal MoS_2.

(b) The area per chemisorbed O_2 molecule decreases with increasing reduction temperature; the effect is large. In contrast, Concha and Bartholomew (*18*) observed approximately constant ratio of area/chemisorbed O_2 for molybdenum sulfide pretreated in 10% H_2S/H_2 at temperatures of 400–600°C.

(c) BET area and area/chemisorbed O_2 also decreased with increasing time of reduction at 500°C; compare Run 27 (1 min at temperature) with Run 28 (1 h at temperature). The area per molecule is especially striking for Run 28: the value of 47 $Å^2/O_2$ is in the same low range as it is for MoO_2 after high-temperature reduction.

(d) In the series of Runs 28, 30, 31, and 28, the values of LTOC show a maximum at 400°C (Run 30) at which S/Mo = 2.1. This represents a balance between two opposing effects on LTOC. An increase in sulfur removal results in increasing anion vacancies. Opposing this is a loss of total surface area (sintering) and a possible annealing of the surface coordinative unsaturation.

(e) The excess sulfur content is reduced to almost zero (S/Mo $\simeq$ 2) after heating at temperatures 450°C and higher for sufficiently long time.

(f) A He purge at 450°C for 15 min (Run 39) following TPR does not cause any significant change in LTOC compared to cooling in H_2 after TPR (compare 72 $Å^2/O_2$ in Run 39 to 75 $Å^2/O_2$ in Run 31). This indicates that any sorbed H_2 present after cooling the catalyst in H_2 does not react with O_2 to increase the LTOC. Wright *et al.* (*44*) have shown that H_2 sorbed on MoS_2 is bonded to one or more sulfur atoms.

Effect of Decomposition Heating Rate

The heating rate during ATTM decomposition has a significant effect on the properties of the product. Two heating schedules were studied: flash-heating in a preheated oven and gradual heating (10°C/min). The results are shown in Table 2.

Flash-heating produces a starting material of higher surface area (compare Runs 41 or 118 with Run 109); this has been observed earlier by Naumann *et al.* (*35*). The difference in surface area persists even after heating in H_2 at 450°C for 60 min (compare Runs 31 and 115, or Runs 87 and 111). The value is lower (75–79 $Å^2/O_2$) for the flash-heated samples (Runs 31, 87) compared to that (123–137 $Å^2/O_2$) for the gradually heated samples (Runs 115, 111). This difference suggests that the two procedures for ATTM decomposition may result in different morphological properties of the product, even though the stoichiometries are similar. Tauster *et al.* (*10*) have proposed that O_2 is a selective chemisorbate for edge sites. If this speculation is valid, the flash-heated sample may exhibit a higher proportion of edge sites than the gradually heated sample.

Effect of Sample Size

Two different sample sizes (0.3 and 0.85 g) of ATTM were studied, as shown in Table 2. Both samples result in a decomposition product with approximately the same specific surface area (compare Runs 41 and 118), but the larger samples show a higher surface area after heating in H_2 at 450°C for 60 min (compare Runs 31 and 87, or Runs 115 and 111). The extent of sintering may be related to the excess sulfur content. The smaller samples contain a larger amount of excess sulfur (S/Mo = 2.4) than the larger sample (S/Mo = 2.3). This results in a higher specific H_2S evolution during TPR for the smaller samples; the ultimate value of S/Mo in both samples is 2.0. Similar values of $Å^2/O_2$ are observed for both sample sizes.

Analysis of TPR Data

The TPR profiles contain information which provides clues to the nature of the starting catalyst. The TPR profiles of the flash-decomposed and 10°C/min-decomposed samples are shown in Fig. 2 (0.3- and 0.8-g samples). For both sample sizes, the 10°C/min-decomposed and flash-decomposed samples show about the same H_2S evolution in the first TPR peak. Since the 10°C/min-decomposed sample has a lower surface area (Table 2) but a larger first peak area, the area per H_2S molecule evolved in the first peak is lower for this sample than for the flash-decomposed sample.

The relevant data are tabulated in Table 3 for flash-decomposed and 10°C/min-decomposed ATTM samples subjected to TPR. The H_2S evolution in the first TPR peak, the ratio of the two peak areas, the BET area of the initial catalyst (before TPR), and the ratio of BET area of H_2S evolved in the first peak are tabulated. The values of $Å^2/H_2S$ molecule evolved in the first TPR peak for the flash-decomposed and 10°C/min-decomposed samples differ by a factor of 2, which suggests a difference in catalyst morphology.

Comparison of the TPR profiles of the 0.3- and 0.8-g flash-decomposed samples in Fig. 2 shows that the first peak is roughly the same size in all samples. The second peak, however, is considerably higher in the 0.3-g samples; compare curves 1 and 2 with 3 and 4.

It is possible to estimate the activation energies for the reduction processes corresponding to the two peaks in the TPR spectrum. This has been done for the 0.3-g flash-heated and gradually heated samples (Runs 87 and 111, Table 2). The calculation is based on an analysis of the detailed shape

TABLE 3

H_2S Peaks during TPR[a-g]

Run	ATTM (g)	Decomposition heating rate	$H_2S(1)$[h] (cm^3(STP)/g)	$\frac{H_2S(2)}{H_2S(1)}$[i]	BET area[j] (m^2/g)	$Å^2/H_2S(1)$
99	0.3	Flash	9.72	3.11	55	21
108	0.8	Flash	9.20	1.74	63	26
111	0.3	10°C/min	12.3	2.66	36	11
115	0.8	10°C/min	13.3	1.87	36	10

[a-g] Footnotes same as in Tables 1 and 2.

[h] H_2S evolution in the first TPR peak calculated from the GC signal.

[i] Ratio of H_2S evolutions in the second and first TPR peaks.

[j] BET area of initial catalyst (before TPR).

of the TPR peaks 42); the method is indicated below.

The total area under a peak, Q_T is proportional to the corresponding total amount of sulfur. The area under the curve, ΔQ, up to temperature T is proportional to the amount of sulfur lost to that point. The difference, $Q = Q_T - \Delta Q$, is proportional to the amount of removable sulfur remaining. Since the height, dQ/dt, of the curve at temperature T is proportional to the rate of sulfur loss, H_2S evolution should be fitted by an Arrhenius expression of the form

$$-\frac{dQ}{dt} = A \exp(-E/RT)Q^m, \qquad (1)$$

where E is the activation energy, m is the apparent order of the sulfur removal process, and A is constant that contains the preexponential factor and the calibration factor for H_2S.

Equation (1) implies that the data should be rectified by a plot of $\ln[-(dQ/dt)/Q^m]$ vs $1/T$. The rectifying plots for the two peaks in Run 111 with $m = 1$ and $m = 2$ are shown in Figs. 3 and 4. For both peaks, the data are better fitted if m is taken as 2, i.e., if the process is second-order. Linear regression of $\ln[-(dQ/dt)/Q^2]$ vs $1/T$ showed a correlation coefficient exceeding 0.995. The calculated values of the activation energies for the two TPR peaks are in good agreement for the two runs as shown in Table 4. The values in brackets are calculated from the half-peak width with the assumption of second-order desorption (*43*). The activation energies calculated from the rectifying plots and those from the half-peak-width method are in good agreement.

Change in Properties along the TPR Profile

It is of interest to determine the instantaneous values of LTOC and BET area at various stages of the TPR profile. This was studied on a 0.3-g, 10°C/min-decomposed sample by purging with He at the final temperature to end the TPR. The results are shown in Table 5.

As discussed earlier, there is no sintering

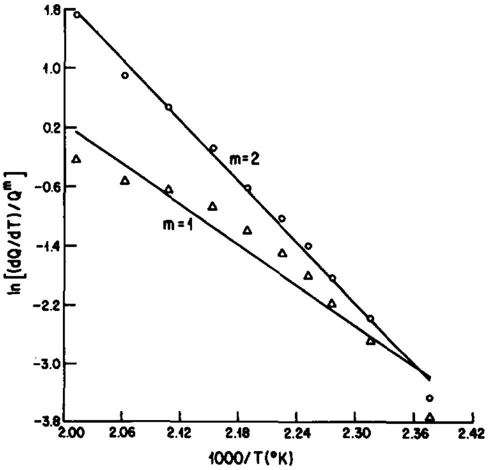

FIG. 3. Rectifying plots for TPR spectrum: 0.3 g ATTM flash-decomposed, peak 1.

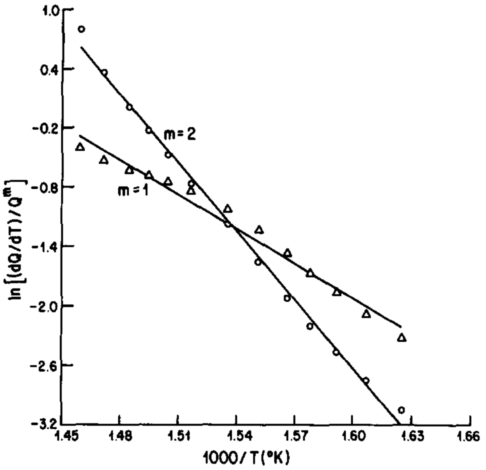

FIG. 4. Rectifying plots for TPR spectrum: 0.3 g ATTM flash-decomposed, peak 2.

during the first TPR peak (Run 121), whereas sintering occurs during the second peak (Run 106). Further sintering occurs upon holding the temperature at 450°C for 60 min (Run 111).

The value of LTOC increases from zero for the initial catalyst, to an appreciable (though low) value after the first TPR peak, and to a maximum after the second TPR peak; the LTOC value decreases upon holding the temperature at 450°C for 60 min. The value of the ratio $Å^2/O_2$ reaches a minimum of 82 after the second TPR peak and increases to 123 after continued heating at 450°C for 60 min.

TABLE 4

Activation Energies for TPR Peaks (kcal/mole)

Sample	Peak 1	Peak 2
10°C/min-decomposed	27 (25)	46 (43)
Flash-decomposed	26 (20)	41 (41)

Removal of sulfur during the second TPR peak causes a decrease in the $Å^2/O_2$ value. This decrease is similar to the decrease in $Å^2/O_2$ with increasing reduction temperature for the flash-decomposed samples listed in Table 1. The increase in $Å^2/O_2$ upon holding at 450°C for 60 min indicates a rearrangement of the surface caused by sintering.

Effect of H_2S/H_2 Pretreatment

Table 6 contains the results of experiments to investigate the effect of a H_2S/H_2 pretreatment. Since hydrodesulfurization catalysts are continually exposed to H_2S in practice, the H_2S/H_2 pretreatment may lead to results more representative of processing conditions than reduction in pure H_2. A final He purge at high temperature has been shown necessary to remove adsorbed H_2S (*23*).

If the final pretreatment step is H_2S/H_2 instead of pure H_2, the value of $Å^2/O_2$ is much higher (compare Runs 36 and 31, Ta-

TABLE 5

Variation in Properties along TPR Profile[a–j,k]

Run	Final Temperature (°C)	Time at final temperature (min)	H_2S evolution[b] (cm^3(STP)/g)	LTOC (cm^3(STP)/g)	BET area (m^2/g)	A^2/O_2	S/Mo[c]
109	—	—	0	0	35.6	—	2.40
121	250	0[l]	11.6	0.442	39.8	335	2.32
106	450	0[l]	39.7	0.634	13.9	81.5	2.10
111	450	60	48.8	0.270	8.95	123	2.03

[a–j] Footnotes same as in Tables 1, 2, and 3.

[k] ATTM (0.3 g) decomposed at 10°C/min; TPR to indicated temperature, He purge at final temperature for 10 min.

[l] Sample purged with He as soon as indicated final temperature was reached.

TABLE 6

Effect of H_2S/H_2 Pretreatment[a–l,m]

Run	Gas[n]	H_2S evolution[b] (cm^3(STP)/g)	LTOC (cm^3(STP)/g)	BET area (m^2/g)	Å^2/O_2	S/Mo[d]
36	H_2S/H_2, He	—	0.694	54.1	290	2.15
37	H_2S/H_2, He; then H_2, He	17.9	1.22	31.0	95.0	2.07
31	H_2	35.1	1.30	26.3	75.3	2.05

[a–l] Footnotes same as in Tables 1, 2, 3, and 5.

[m] ATTM (0.85 g) flash-decomposed in He.

[n] Samples heated in H_2S/H_2 or H_2 to 450°C, held at 450°C for 1 h, He purged at 450°C for 1 h, cooled to room temperature. Run 37: sample reheated in H_2 after first He purge.

ble 6). This value of 290 Å^2/O_2 is in excellent agreement with the value of 287 Å^2/O_2 reported by Bodrero and Bartholomew (*19*) for a similar pretreatment. The presence of H_2S in H_2 inhibits sulfur loss in H_2; this reduces the extent of sintering and also results in fewer anion vacancies and a higher value of Å^2/O_2.

However, if the H_2S/H_2 treated sample is reheated in H_2 to 450°C (Run 37, Table 5), the area decreases strongly to 31 m^2/g and the value of Å^2/O_2 decreases to 95. A final reduction in H_2 is necessary to generate a high value of LTOC.

CONCLUSIONS

1. Temperature-programmed reduction yields information about the nature of the initial catalyst prepared by thermal decomposition of ATTM in He. The TPR profile shows two peaks. The first TPR peak is about the same for a 10°C/min-decomposed sample and a flash-decomposed sample in spite of the smaller specific surface area of the former. The value of area per H_2S molecule evolved in the first peak is about 11 Å^2/H_2S for the 10°C/min-decomposed sample and 21 Å^2/H_2S for the flash-decomposed sample, suggesting that decomposition mode affects catalyst structure.

2. The flash-decomposed sample has a lower value of Å^2 per chemisorbed O_2 molecule (75–79) than the 10°C/min-decomposed sample (123–137) after heating in H_2 at 450°C for 60 min. In both samples, the value of S/Mo is about 2.0.

3. The initial catalyst prepared by ATTM decomposition in He contains excess sulfur (S/Mo = 2.3–2.4) and exhibits a high BET area but negligible O_2 chemisorption. Considerable O_2 chemisorption results after removal of excess sulfur corresponding to the first TPR peak, i.e., reduction at 250°C. The ratio S/Mo at this stage is 2.2–2.3 and decreases to 2.0 upon heating at 450°C for 60 min. The specific O_2 chemisorption increases with reduction temperature. The value of 47 Å^2/O_2 molecule obtained for a flash-decomposed sample after reduction at 500°C is comparable to the value obtained on reduced unsupported MoO_3.

4. Sintering starts after heating in H_2 beyond the first TPR peak, i.e., at temperatures above 250°C. Sintering is severe at temperatures above 450°C. The presence of H_2S during reduction dramatically reduces the extent of sintering at 450°C by limiting the amount of excess sulfur lost. Sample size affects the extent of sintering for both 10°C/min and flash-decomposed samples: smaller samples sinter more after reduction in H_2 than larger ones. This may be related to the larger excess sulfur content of the smaller samples, which lose more sulfur (per unit weight) and undergo a greater extent of lattice rearrangement. However, the Å^2/O_2 molecule after reduction is independent of sample size, depending only on its initial decomposition schedule.

5. A low value of specific O_2 chemisorption (274 Å^2/O_2 molecule) occurs upon reductive-sulfiding (15% H_2S in H_2) at 450°C for 60 min followed by He purge at 450°C. Reduction in pure H_2 is required to generate larger values of O_2 chemisorption. The Å^2/O_2 decreases to 95 upon heating in H_2 at 450°C for 60 min. A He purge at 450°C following reduction in H_2 at 450°C does not significantly affect the specific O_2 chemisorption. This indicates that any H_2 sorbed on the catalyst after cooling in H_2 does not react with O_2 to increase the amount of chemisorption.

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