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The Assay of Sulfided Molybdena–Alumina Catalysts

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Sulfided catalysts were characterized by measuring the comsumption of O_2 on reoxidation. The S/Mo, O_s/Mo, and *e*/Mo ratios could be evaluated. Most of the sulfur was removed and measured as SO_2; some SO_3 was formed and trapped by the alumina as SO_4^{-2}. This was released as SO_2 on reduction with H_2. The average extent of reduction, *e*/Mo, was calculated after correcting the oxygen consumed for that required to oxidize and replaced the sulfur. The oxygen removed by reduction and sulfiding was measured as H_2O, i.e., as W_R and W_S, respectively. This oxygen removed was mostly compensated by the addition of sulfur. Reduction occurred by breaking bonds between bound molybdena and the alumina surface. The results obtained show that usually S/Mo $\leq$ 2 and that *e*/Mo $\geq$ 2. It was concluded, therefore, that valence states below Mo^{4+} are common in these preparations. Parallel infrared studies were helpful in validating the procedures used.

INTRODUCTION

The purpose of the present work was twofold. First, it was desired to devise a simple analytical method for the characterization of sulfided molybdena–alumina catalysts which would be independent of any model of the catalyst surface. Second, we wished to learn whether or not valence states below Mo^{4+} exist in reduced or sulfided preparations. Several kinds of evidence suggest that they may. For reduced catalysts, measurements of the *average* extent of reduction (*1, 2*) are easy to make and sometimes values lower than Mo^{4+} are found. In addition, our own recent evidence (*3*) had suggested that the active catalytic centers are Mo^{2+}.

A number of reviews (*4–13*) have been written concerning the surface chemistry of these catalysts. Despite variations effected by preparation and pretreatment procedures, a consistent picture has evolved for the raw catalyst showing small patches of molybdena bound to the surface of alumina by replacement of the surface hydroxyl groups (*11, 14–16*). On reduction or sulfiding, Mo–OAl bonds are broken, the surface OH population being partially restored (*16, 17*).

Evidence for formation of submicrocrystalline MoS_2 in sulfided catalysts has been reported (*14, 15*). The active molybdena surface sites of both reduced and sulfided (*3, 17*) catalysts may be titrated by the chemisorption of O_2 (*18–23*) or NO (*2, 3, 24–28*). The uncovered alumina surface, on the other hand, may be distinguished spectroscopically after the chemisorption of CO_2 (*3, 17*) and by either ir or NMR from the terminal hydroxyl groups (*16*). In these respects the present authors have shown that sulfided catalysts (*3*) are quite similar to those which have simply been reduced (*17*). Hall and LoJacono (*1*) showed that such reduction–oxidation cycles could be carried out reproducibly many times over the same catalyst sample. The average extent of reduction could then be calculated directly from the oxygen consumed, [O_2], in the reoxidation process and the number of molybdenum atoms in the sample, i.e.,

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$$e/\mathrm{Mo} = 4[\mathrm{O_2}]/\mathrm{Mo} = 2[\mathrm{O}]/\mathrm{Mo}. \quad (1)$$

Moreover, an anion vacancy concentration, $\square/\mathrm{Mo}$, was calculated from the H_2O produced during reduction, W_R, and found to be a useful correlating parameter (*18, 24, 25*), i.e.,

$$\square/\mathrm{Mo} = W_R/\mathrm{Mo}. \quad (2)$$

Clearly, $\square/\mathrm{Mo}$ is the average number of oxygen atoms per MoO_3 unit removed during reduction. Its interpretation based on an epitaxial monolayer model was straightforward (*1*). More recent work (*11, 14–16*), however, has lead to the idea that small clusters of molybdena, possibly a couple of layers deep, become bound to alumina. Hence, the meaning of this parameter is now less clear, especially if a recrystallization occurs during the reduction or sulfiding treatment. Nevertheless, since it increases monotonically with e/Mo and may be determined without reoxidizing the catalyst, it has been used many times instead of e/Mo for studies of reduced catalysts as a qualitative measure of the extent of reduction.

In the present work, we have extended the use of mass balances for the characterization of sulfided catalysts. The analytical scheme developed permits estimation of e/Mo, $\mathrm{S/Mo}$, and $\mathrm{O_s/Mo}$, where $\mathrm{O_s}$ is the portion of the original three reducible oxygens associated with molybdena (MoO_3) which is retained by the catalyst after sulfiding. Equation (1) will still be valid, but correction must be made for the oxygen consumed in removing sulfur from the catalyst as SO_2 or SO_3 (measured volumetrically). Thus we write

$$\begin{aligned} e/\mathrm{Mo} &= 2\{2[\mathrm{O_2}]/\mathrm{Mo} - 3[\mathrm{SO_2}]/\mathrm{Mo}\} \\ &= 2\{[\mathrm{O}]/\mathrm{Mo} - 3[\mathrm{SO_2}]/\mathrm{Mo}\}, \quad (3) \end{aligned}$$

where as before $2[O_2]$ is the total oxygen (as atoms) consumed and $3[SO_2]/\mathrm{Mo}$ takes into account the removal of S as SO_2 and its replacement with an atom of oxygen. A further minor correction for SO_3 will be added later.

EXPERIMENTAL

Catalysts. The 8% Mo on Ketjen-γ-alumina (CK-300) catalyst was that used in most of our earlier work (loc. cit.). The catalyst was made by the incipient wetness impregnation method and contained $4.6 \pm 0.3 \times 10^{20}$ Mo/g (an average of five analyses made by the Galbraith Laboratories). The remaining catalysts were prepared by the equilibrium adsorption method of Wang and Hall (*29*), which was designed primarily to make uniform preparations for spectroscopic work. The loading and surface chemistry of these were controlled by variation of pH. The coverage varied from about 1 to 7×10^{20} Mo/g, so that the *average* surface area per Mo varied from 200 to 40 Å^2. The assumption of uniform coverage with monomeric units is of course untrue (*11, 14, 15*), but nevertheless these figures show that in all cases at least half of the alumina surface remained uncovered. Most of the ir spectroscopic work was done with a loading of 5×10^{20} Mo/g made at pH 1.95, which is thought to consist of polymolybdate clusters containing seven or so molybdenum atoms (*29*).

Gases. Airco tank O_2 (nominal purity 99.6%) was dried by passage through a column filled with Linde-5A sieves and over anhydrous $CaCl_2$ followed by $Mg(ClO_4)_2$. Airco He (nominal purity 99.995%) was passed through a −195°C trap containing about 25 g of activated charcoal; ultrapure H_2 and D_2 were obtained by passing Airco and Matheson products, respectively, through Pd–Ag alloy thimbles. The H_2S was an Airco product of 99.5% purity; it was used as received. The O_2 used for the reoxidation measurements was condensed and distilled between liquid nitrogen traps before bulb storage. Similarly, Matheson SO_2 (anhydrous minimum purity 99.98%) was also given the usual freeze–pump–thaw distillation treatment before it was introduced into the BET system.

Reduction and sulfiding procedures. Approximately 1-g aliquots of catalysts were precalcined overnight at 500°C in a stream of flowing O_2 (~100 ml/min) followed by a 20-min purge with He at the same temperature. In some cases, they were then reduced with H_2 (~70 ml/min) for 1 h at 500°C and again purged with pure He before sulfiding. The H_2O formed during the reduction was collected in a glass bead trap at −78°C placed downstream from the catalyst. This could be measured volumetrically in the attached BET system. As shown previously (*30*), these reduction conditions resulted in average values of e/Mo ≈ 1.3. In other cases, the calcined catalysts were sulfided directly without this reduction step.

The preparations were sulfided at 350°C in a stream of 10% H_2S in H_2 for 4 h at a total flow rate of ≈77 ml/min. This mixture was prepared by controlling the flow rate of the pure gases using Moore regulators. Following this treatment, the catalyst was purged with He as the temperature was gradually raised to 500°C, where it was maintained for an additional hour. The H_2O formed during sulfiding, W_s, was collected downstream in a trap thermostated at −78°C and measured as before.

Reoxidation of sulfided catalysts: An analytical procedure. As outlined above, the same techniques devised earlier (*1*) for reduced catalysts were employed with appropriate modification. An all-glass recirculation system, consisting of the catalyst, a pump, a liquid-nitrogen trap, and an attached BET system for manometric and volumetric measurements, was used. A measured quantity of pure O_2 was circulated at ~100 Torr over the catalyst and through the trap at −195°C which removed the oxidation products. The consumption of O_2 could be followed by observing the decrease in pressure. The catalyst was first exposed to O_2 at about 25°C and the temperature was gradually raised to 200°C as the gas was recirculated. At the latter temperature, the consumption of O_2 was rapid; conditions were maintained constant until the O_2 uptake became immeasurably slow. The catalyst was then heated to 500°C to ensure complete reoxidation. The total consumption of O_2 was measured and the unused O_2 was removed from the system by evacuation through the trap. The trap contained both H_2O and SO_2, but no SO_3 could be detected by mass spectrometric analyses. The SO_2 was separated from the H_2O by raising the temperature of the trap to −78°C and distilling the SO_2 into another trap at −195°C, leaving behind the H_2O. The amounts of the separated gases could then be determined volumetrically in the BET system.

Despite the care taken, not quite all of the sulfur was removed from the catalyst by this treatment. A small amount was retained as SO_4^{2-}, presumably on the uncovered alumina surface. It was found, however, that this could be removed by treatment in flowing H_2 at 500°C for 4 h. The reduction products, H_2O and SO_2, were collected and measured as before. At this point, the removal was complete as judged by both chemical analysis by Galbraith and by ESCA determinations,[3] both of which showed extremely low levels of S equivalent to those found in blank determinations using the unsulfided catalyst. The oxygen consumption values were corrected for this additional sulfur (SO_2) by subtracting 4 SO_2/Mo from the right-hand member of Eq. (3). Implicit was the assumption that this sulfur had been oxidized to SO_3, which was then "gettered" by the alumina surface. The effect of this correction was to ensure that minimum possible values of e/Mo were deduced, i.e., the total sulfur was calculated as the sum of the SO_2 and the SO_3 and

$$e/\mathrm{Mo} = 2\{2[O_2]/\mathrm{Mo} - 3[SO_2]/\mathrm{Mo} - 4[SO_3]/\mathrm{Mo}\}. \quad (4)$$

Some supplemental ir studies were made to firmly establish the surface chemistry and, in particular, to define conditions for

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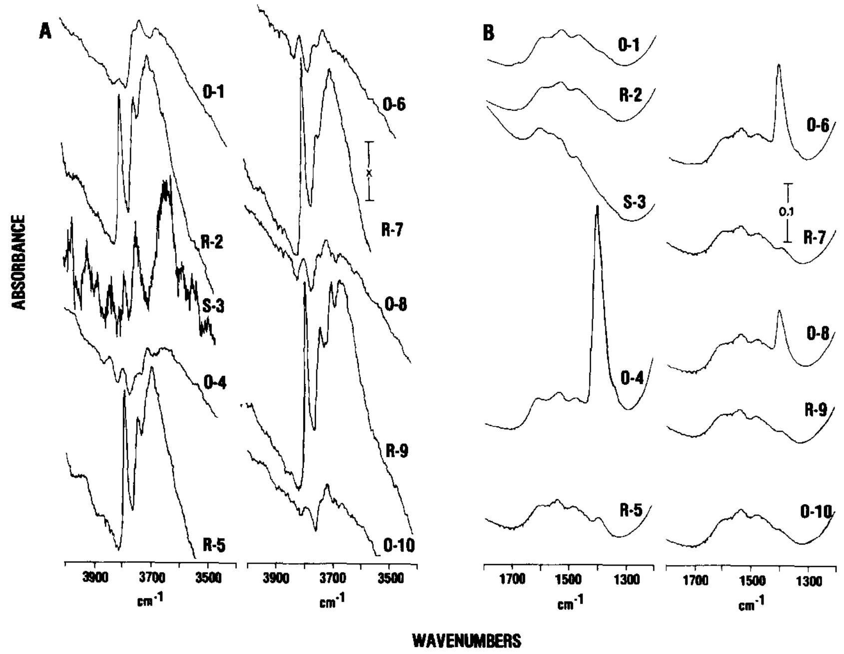


FIG. 1. Spectra from a molybdena–alumina catalyst in the OH (A) and the sulfate (B) regions after various treatments. The catalyst had been prepared by the equilibrium absorption method (Refs. (*11*, *29*)); the platelet had a thickness of ~10 mg/cm^2. Treatment in O_2 is denoted by O-*n*, reduction in H_2 by R-*n* and sulfiding in 10% H_2S/H_2 by S-*n*, where *n* is an integer denoting the step number. Oxidations and reductions were carried out at 500°C. Originally the catalyst was calcined in flowing dry O_2 overnight at 500°C (O-1). Subsequent reduction and reoxidation steps were carried out for periods of 1 h at 500°C followed by evacuation with the same conditions. Sulfiding was also for 1 h, but at 350°C followed by evacuation with the final temperature raised to 500°C. The scale factor x was 0.1 for S-3 and 0.04 for all of the other spectra of the OH region.

complete removal of sulfur from the surface. A Nicolet MX-1 FT-IR spectrometer operating in the absorbance mode was used in these experiments. The resolution was about 2 cm^{-1} at all wavelengths studied. The self-supporting wafers had a thickness of about 10 mg/cm^2; they were mounted on a quartz rack which could be moved from the heated portion of the tube into the optical cell fitted with KBr windows as described previously (*17*). The assembly was vacuum tight and the catalyst wafer could be treated in various atmospheres and temperatures.

EPR measurements were made on a few selected samples after reduction in H_2 and then again after sulfiding. The spectra were recorded using a Varian E-115 spectrometer operating at X band (9.15 GHz). The EPR tube was sealed as a side arm on the sample treatment tube as in the experiments of Cirillo *et al.* (*16*) so that the samples could be pretreated, evacuated, reduced, and sulfided, as well as removed to the EPR apparatus, all without exposure of the catalyst to air.

RESULTS

Infrared spectroscopy. Spectra taken in the oxidized, reduced, sulfided, and reoxidized states of the catalyst are presented in Fig. 1, where the OH and sulfate regions may be compared in A and B, respectively. The OH bands were weak after the initial calcination at 500°C (O-1), but they appeared again strongly when the catalyst was reduced (R-2). On sulfiding, this region became very noisy; the spectrum (S-3) was

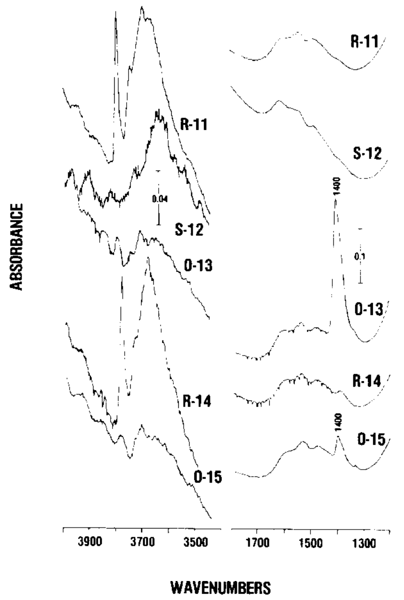
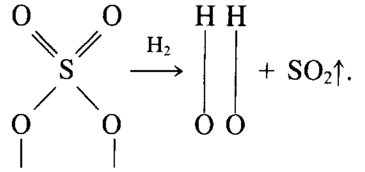


FIG. 2. Continuation of the experiment in Fig. 1 through another sulfiding, oxidation–reduction cycle.

recorded at a sensitivity lower than that used for the others to obtain better resolution, i.e., $x = 0.1$ for S-3 and 0.04 for all of the others. Interestingly, on reoxidation (O-4) the OH region was returned nearly to its initial condition showing that the alumina OH groups, which were formed as surface molybdate bonds were broken during reduction (*16*) (and were retained during subsequent sulfiding (*17*)), were removed (as H_2O) on reoxidation. These features were further confirmed with two more oxidation–reduction cycles on the same spectroscopic platelet (compare O-4, O-6, O-8, and O-10 with each other and with O-1; also, compare R-5, R-7, and R-9 with R-2).

The corresponding spectra in the sulfate region are particularly significant to the present work. All spectra were essentially identical except for the strong band near 1395 cm^{-1} which appeared (O-4) when the sulfided catalyst (S-3) was reoxidized. This was greatly reduced in intensity by reduction in H_2 (R-5 and O-6), and in parallel experiments with larger amounts of catalyst it was observed that SO_2 was released by this treatment. Interestingly, this process appears to be analogous to the reduction of the alumina-bound molybdena, i.e.,



(5)

An additional reduction–oxidation cycle (R-7 and O-8) removed more sulfur. In this way it was determined that a 4-h reduction would remove most of this sulfur. These experiments were continued through another cycle and the results are presented in Fig. 2. Because the spectrum in the OH region after sulfiding was so noisey, the OD region was examined with a deuterated catalyst. These results are presented in Fig. 3. The reduced catalyst was first exchanged with D_2 [60 cm^3 (NTP)] at 150 Torr for 90 min at 350°C followed by a 1-h purge with He. The spectrum from this preparation is shown as Spectrum A; the OH region showed no detectable bands. The catalyst was then sulfided in the usual way and exchanged with D_2 yielding Spectrum B. Because the noise level was greatly diminished in this region of the spectrum, it can be clearly seen that the relative intensity of the several bands is different than with the

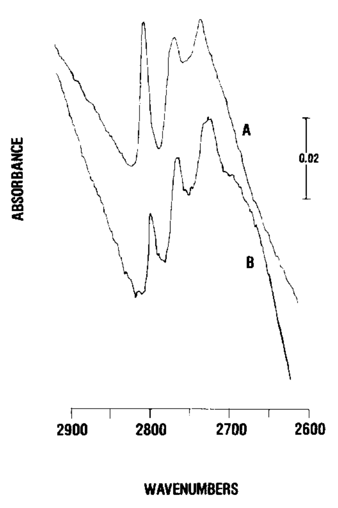


FIG. 3. Spectra of the deuterated reduced catalyst (A) and the sulfided catalyst (B) in the OD region.

reduced catalyst. The high-frequency band was most affected by sulfiding as was also observed by Topsoe (*28*). The strong decrease in the relative intensity of the high-frequency band on sulfiding suggested that this hydroxyl might have been replaced by SH. However, in agreement with Topsoe, we could not detect any S–H vibration, possibly because of its low concentration and/or its low extinction coefficient. This sulfur might correspond to that which appears as sulfate on oxidation. If this actually occurred, then we have overcorrected the oxygen consumption values, thus lowering the *e*/Mo values.

"Sulfate-like species" have been reported (*31–33*) to appear on the alumina surface when it is heated in SO_2. We confirmed these experiments spectroscopically. SO_2 was adsorbed on our calcined support at room temperature. Bands appeared at 1149 and 1336 cm^{-1} corresponding to the antisymmetric and symmetric stretching vibrations of SO_2, respectively (*31*). On evacuating and heating, a strong band was evolved at 1377 cm^{-1} resembling the one at 1395 cm^{-1} on the molybdena–alumina catalyst. The corresponding symmetric sulfate stretching vibration at about 1130 cm^{-1} cannot be seen because of the alumina cutoff. According to Chung and Massoth (*34*), the surface sulfate is stable under vacuum up to 800°C, but can be removed in 3 hr at 400°C in H_2. The present experiments confirm this observation. A likely source of the surface sulfate, however, is from any SO_3 formed in the reoxidation process. This would become selectively chemisorbed on the alumina part of the surface, and be released as SO_2 on reduction (Eq. (5)). We make this assumption in treating the data for these experiments, *vide infra*.

Stoichiometric experiments. Data were obtained to determine the average extent of reduction by Eq. (4); these are listed in Table 1. The oxygen consumptions (Column 3) required to reoxidize the sulfided catalysts were much larger than for reduced catalysts. According to Eq. (1), the corresponding [O]/Mo ratios for reduced catalysts having *e*/Mo = 2 or 3 would be 1 or 1.5, respectively. The values listed in Table 1 fall in the range of 5.7 to 6.9, depending upon whether the catalysts were prereduced or sulfided directly. Part of this ([O]/Mo = 3 to 4) may be attributed to the oxygen required to remove and replace the sulfur, but after correcting for this (Eq. (4)) a substantial deficit was left attributable to reduction. The average valence state of molybdenum was evidently lowered below Mo^{4+} during sulfiding.

TABLE 1

Assay of a Sulfided Molybdena–Alumina Catalyst (Loading 4.6 × 10^{20} Mo/g Incipient Wetness Method) by Reoxidation Experiments

1 Expt No.	2 Treatment	3 $\frac{[O]}{Mo}$	4 $\frac{S}{Mo}$	5 $\frac{S_a}{Mo}$	6 $\frac{H_2O}{Mo}$	7 $\frac{e}{Mo}$
1	*a*	6.86	1.63	(0.1)	0.22	3.14
2	*a*	6.54	1.55	(0.1)	0.19	2.98
3	*a*	6.93	1.70	0.10	0.13	2.86
Average (1,2,3)		6.78	1.62	0.1	0.18	2.99
4	*b*	5.74	1.32	0.10	0.16	2.76
5	*b*	5.72	1.31	0.11	0.15	2.70
6	*b*	6.15	1.46	0.05	0.03	3.14
Average (4,5,6)		5.87	1.36	0.09	0.11	2.86
7	*c*	7.30	1.88	0.15	0.26	2.12

[a] Pretreatment conditions: Oxidized overnight followed by a 20-min purge in He at 500°C, then sulfided for 4 h in 10% H_2S/H_2 mixture at 350°C, and finally purged for 1 h with He at 500°C.

[b] Catalyst was oxidized overnight and then purged in He for 20 min at 500°C. It was then reduced in H_2 for 1 h and again purged with He at 500°C [$(e/MO)_R \approx 1.3$] before sulfiding as in footnote *a* with a final purge at 500°C.

[c] Same as footnote *b* except sulfiding in a 10% H_2S/He stream.

The sulfur content may be assayed directly as SO_2 (Columns 4 plus 5). These measurements should be accurate to within 1 or 2%. The values in Column 4 correspond to the SO_2 released by the circulating O_2 while those in Column 5 were estimated from the SO_2 released by H_2. The former was multiplied by 3 and the latter by 4; i.e.,

TABLE 2

Assay of Sulfided Molybdena–Alumina Catalysts of Various Loadings[a] by Reoxidation[b]

1 Expt. No.	2 Mo/g × 10^{-20}	3 $\frac{[\mathrm{O}]}{\mathrm{Mo}}$	4 $\frac{\mathrm{S}}{\mathrm{Mo}}$	5 $\frac{\mathrm{S_a}}{\mathrm{Mo}}$	6 $\frac{\mathrm{H_2O}}{\mathrm{Mo}}$	7 $\frac{e}{\mathrm{Mo}}$
1	1.14	8.21	1.68	0.24	0.83	4.42
2	3.3	7.22	1.74	0.05	0.34	3.60
3	4.3	7.28	1.73	(0.1)	0.23	3.38
4	4.3	7.36	1.81	0.10	0.14	3.06
5	4.6	8.28	2.26	0.09	0.36	2.28
6	4.6	7.45	2.01	0.13	0.40	1.80
7	4.6	7.22	1.84	0.08	0.36	2.76
8	5.0	7.34	2.01	0.05	0.39	2.22

[a] Catalysts were prepared by the equilibrium absorption method; loadings were varied by control of the pH.

[b] The catalysts were pretreated in flowing O_2 overnight and then purged with He for 20 min at 500°C. The catalysts were then sulfided in flowing 10% H_2S/H_2 at 350°C for 1 h and finally purged with He at 500°C.

it was assumed that all of the sulfur was released as SO_2 or SO_3 on treatment with O_2; the former was collected and measured directly while the latter was held up on the alumina surface and released in H_2 as described in the ir studies.

Measurement of H_2O in the BET system was the most inaccurate of the measurements made; the error was estimated to be ~5%. However, these measurements do not enter directly into the calculation of e/Mo by Eq. (1). The validity of these results therefore seems quite certain. The interesting conclusion is shown in Column 7. Even after the *maximum* possible correction for the amount of oxygen consumed in reoxidizing the sulfur was made, the reduced molybdenum had an *average* valence state of $2 < e/\mathrm{Mo} < 3$. Moreover, catalysts prereduced to $e/\mathrm{Mo} \sim 1.3$ at 500°C were further reduced to $e/\mathrm{Mo} \geq 2$ by sulfiding at 350°C (Column 7, Rows, 4, 5, and 6). The amounts of sulfur incorporated (the sum of Columns 4 and 5) were lower when the catalyst was prereduced than when it was sulfided directly, in agreement with a similar finding by Massoth (*35*). Indeed, where cross comparison could be made with his gravimetric data the actual S/Mo values of Tables 1 and 2 were in fair quantitative agreement. Finally, the sulfur was removed quantitatively as shown by both chemical analysis and ESCA determinations of randomly selected samples of catalyst.

An experiment was made in which He was substituted for H_2 in the sulfiding gas (Row 7). The sulfur level was a little higher than usual but still $S/\mathrm{Mo} \leq 2$. This catalyst had been prereduced, presumably to $e/\mathrm{Mo} \approx 1.3$. The data indicate that a further reduction had occurred. This chemistry is not fully understood, but H_2S appeared to react to form $H_2O + S$; some of the latter condensed in the cold part of the glass tube as the gas passed from the reactor. Overall, the results were quite similar to the ones obtained with H_2S/H_2 mixtures.

The results obtained from a series of catalysts with varying loadings are reported in Table 2. These data, together with those of Table 1, provide a basis for assessing the reproducibility of the overall results (including the reduction and sulfiding steps). The calculations indicate that valence states below Mo^{4+} are quite common. The catalyst with the lowest loading (Row 1, Table 2) was previously shown (*11*) to be very difficult to reduce with H_2; values of $e/\mathrm{Mo} \sim 1.2$ were obtained at 650°C. It is particularly interesting to note that this preparation, which contained predominantly tetrahedrally bound monomeric molybdena, was virtually destroyed by sulfiding. These data were checked and EPR determinations made to verify this finding. These data are listed in Table 3. The reduced sample (Row 1) contained nearly one EPR detectable Mo^{5+} for each Mo in the sample. Sulfiding, by increasing the extent of reduction, lowered the spin density by nearly an order of magnitude. A similar decrease was observed on sulfiding the catalyst containing 5×10^{20} Mo/g.

The oxygen removed as H_2O during prereduction, W_R, and sulfiding, W_S, was measured volumetrically after evacuation of the ambient gas phase, first through the catalyst and then through the collection trap at −195 or −78°C. These data are plotted in

TABLE 3

Properties of the Reduced and Reduced–Sulfided Catalysts (1.4 × 10^{20} Mo/g Cat) Data Determined Volumetrically by Reoxidation and by EPR Spectroscopy

1 Expt No.	2 $\frac{[O]}{Mo}$	3 $\frac{S}{Mo}$	4 $\frac{S_a}{Mo}$	5 $\frac{W_o}{Mo}$	6 $\frac{e}{Mo}$	7 g_{ave}	8 N^c
1	0.46	—	—	0.55[a]	0.93	1.9417	9
2	6.54	1.28	0.18	0.32[b]	3.96	1.9406	1

[a] The amount of H_2O, produced by reoxidation of the reduced catalyst.

[b] The amount of H_2O, produced by reoxidation of the sulfided sample.

[c] The relative number of spins in Experiments 1 and 2.

Fig. 4 from which the sum $(W_R + W_S)/Mo$ can be calculated. These sums were found to fall in the range between 1.5 and 1.8, regardless of whether the preparation was prereduced in H_2 or not. Thus, in agreement with Massoth (*35*), up to half of the reducible oxygen of the unreduced catalyst is retained after sulfiding.

DISCUSSION

The salient feature of the present work was the finding that $e/Mo \geq 2$ for the sulfided catalysts, i.e., that valence states lower then Mo^{4+} were almost invariably present. This was surprising insofar as these lower valence states have not so far been characterized by ESCA (*36*). This finding does, however, support the tentative conclusion of the present authors (*3*) that NO chemisorbs on Mo^{2+} centers as dinitrosyl or dimeric species. These sites are responsible for the dissociative adsorption of H_2 (*37*) and oxygen chemisorption (*3*) as well, and are therefore of direct interest to the catalytic chemists.

The present paper may be considered complementary to an earlier paper by Massoth (*35*), who followed the weight changes on reduction and sulfiding and in addition made sulfur determinations on the final preparation by an analytical method. He was therefore able to characterize the S/Mo and the O_s/Mo ratios, where O_s is the portion of the original three reducible oxygens, which is retained on sulfiding. He could not, however, directly estimate the extent of reduction from these data. His catalyst was the same as used in our earlier work (*1*) and a duplicate of that used to collect the data of Table 1. However, he used generally lower H_2S/H_2 ratios and somewhat milder conditions. For comparison with the data for the directly sulfided catalysts of Table 1 (the present work) we interpolate from his Fig. 3 the following: S/Mo = 1.5, $O_s/Mo = 1.3$, and $(O_s + S)/Mo = 2.8$. For comparison with the prereduced values of our Table 1, we interpolate from his Fig. 4 corresponding values of 1.1, 1.7, and 2.8, respectively. His values of S/Mo (1.5 and 1.1) correspond to our "average values" (1.72 and 1.45) as well as may be expected. For further comparison we must deduce from our data values of O_s/Mo. First, maximum values may be calculated from

$$O_s/Mo = 3 - S/Mo. \qquad (6)$$

Here it was assumed that initially the unreduced catalyst contained three (3) reducible

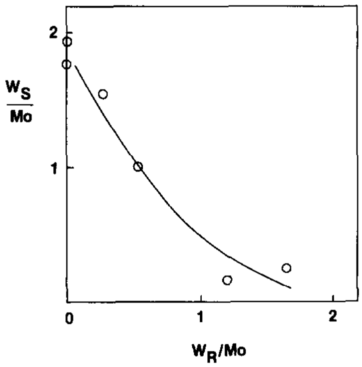


FIG. 4. Measurements of H_2O removed during sulfiding as a function of prereduction. W_S/Mo is the number of water molecules collected during the sulfiding step and W_R the number during the prereduction (when this was done). The accuracy of these points is estimated to be about ±5%. The line represents the least-squares fit of the data.

oxygens per molybdenum and that no oxygen is removed from the catalyst by reduction. These "average" results, $O_s/Mo = 1.28$ and 1.55, may be compared with Massoth's values of 1.3 and 1.7, respectively, for the directly sulfided and prereduced catalysts.

Another approach is to deduce values from the oxygen known to be removed from the catalyst as H_2O during reduction and sulfiding, W_R and W_S, respectively, i.e.,

$$O_s/Mo = 3 - W_R - W_S. \quad (7)$$

By selecting the appropriate values from Fig. 4, we obtained $O_s/Mo = 1.2$ and 1.5 as "averaged values" for the directly sulfided and prereduced catalysts of Table 1, respectively. The corresponding values of $(O_s/Mo + S/Mo)$ are 2.92 and 2.95, leading to the conclusion that little of the original reactive oxygen is removed form the catalyst without being compensated by the addition of an atom of sulfur. Thus, both our oxygen and sulfur balances are in substantial agreement with those of Massoth.

The finding that the $(O_s/Mo + S/Mo)$ values range from 2.7 (Massoth) to 2.9 (present work) suggests at first sight that the catalysts are very little reduced ($e/Mo = 0.2$ to 0.6). The determination of e/Mo by the reoxidation experiments show that this is far from true. Why? Evidently, the S and the O_s cannot both remain bonded to Mo as O^{-2} and S^{-2}. Recently, Huntley *et al.* (*38*) found that the EXAFS Fourier transform spectrum of a sulfided HDS catalyst was remarkably similar to that of amorphous MoS_2 prepared by the method of Chianelli *et al.* (*39*). Thus, the bonding between oxygen and molybdenum is evidently largely (although probably not entirely) eliminated by sulfiding. This conjecture is supported by the ir data shown in Figs. 1 and 2 where new alumina hydroxyl groups appear when the oxidized catalyst is reduced and sulfided. Similar earlier findings (*16*) for reduced catalysts were obtained by both ir and NMR. Based on this hypothesis, values for the reactive oxygen *remaining* bound to molybdenum may be estimated by reducing the O_s/Mo values by (1/2) e/Mo (as calculated from the reoxidation data. For the directly sulfided and prereduced catalysts of Table 1, the corresponding O_s/Mo values of 1.2 and 1.5 are thus lowered to −0.3 and +0.1, respectively. Correction for the small amount of H_2O generated during the reoxidation of the sulfided catalysts gives values of −0.04 and +0.23. Hence, within experimental error, these data may be satisfied by the assumption that bonding between the oxygens of the alumina lattice and the Mo ions is almost completely eliminated on sulfiding.

A further consistency test may be made by assuming no residual bonding between oxygen and molybdenum exists and that e/Mo is determined only by the electrons required to satisfy the sulfur present, i.e.,

$$e/Mo = 6 - 2(S/Mo). \quad (8)$$

Implicit is the further assumption that all of the sulfur is present as S^{-2}; the possible presence of SH^- and S_2^{-2} is ignored. The values of e/Mo calculated from Eq. (8) provide an upper limit for the extent of reduction provided only that this condition is satisfied. A comparison is made of the calculated and experimental values in Table 4 for all of the data from Tables 1 and 2. The values of e/Mo calculated from Eq. (8) were generally lower than those determined experimentally, suggesting that lower valence states of sulfur were actually present. Residual bonding to alumina oxygen was not included in the calculation. Had it been, the calculated values would be further lowered. The salient point is, however, that these calculations still generally yielded $e/Mo \geq 2.0$; i.e., they were consistent with the presence of valence states of molybdenum lower than Mo^{4+}.

The presence of SH groups in sulfided molybdena–alumina catalysts has not yet been demonstrated directly by spectroscopic measurements although Wright and co-workers (*40*) have presented evidence

TABLE 4

Comparison of Extents of Reduction Estimated by Eq. (8) with Those Experimentally Determined in Reoxidation Experiments

Data from Table 1				Data From Table 2			
Expt No.	S_T/Mo^a	$(e/Mo)_{calc.}$	$(e/Mo)_{expt.}$	Expt No.	S_T/Mo^a	$(e/Mo)_{calc.}$	$(e/Mo)_{expt.}$
1	1.73	2.54	3.14	1	1.92	2.16	4.42
2	1.65	2.70	2.98	2	1.79	2.42	3.60
3	1.80	2.40	2.86	3	1.83	2.34	3.38
Av.	1.72	2.56	2.99				
4	1.42	3.16	2.76	4	1.91	2.18	3.06
5	1.42	3.16	2.70	5	2.35	1.30	2.28
6	1.51	2.98	3.14	6	2.14	1.72	1.80
Av.	1.45	3.10	2.86				
				7	1.92	2.16	2.76
				8	2.06	1.88	2.22

[a] $(S_T/Mo) = (S/Mo) + (S_A/Mo)$.

obtained from inelastic neutron scattering data for S–H vibrations in MoS_2. However, such hydrogen should appear as H_2O during reoxidation. Indeed such H_2O was produced (Column 6 in Tables 1 and 2), but in quantities too small to account for the differences between the calculated and experimental values of *e*/Mo. Moreover, the ir spectra of Figs. 1 and 2 suggest that the origin of this H_2O should be associated with the removal of Al–OH groups concomitant with rebonding of molybdena to the alumina surface. The presence of terminal disulfide linkages remains a possibility, but the values of S/Mo ≤ 2.0 render this explanation suspect.

As shown previously for reduced catalysts (*1*), the hydrogen held as new OH groups (H_I) formed as the catalyst is sulfided is an important factor in measuring the extent of reduction (see Eqs. (1) and (2)). This factor could not be evaluated quantitatively in the present work. Massoth did not discuss this aspect in his paper (*35*), although he obtained a representative set of measurements of total hydrogen contents of the support, unreduced, reduced, and sulfided catalysts by exchange with D_2. We have found it instructive to reinterpret these data in the light of the findings of the present work. The following data have been extracted from his Table 2 (*35*). The 8% Mo/γ-Al_2O_3 catalyst after calcining and sulfiding, both at 400°C, contained 1.47 mmol H/g catalyst. The alumina support treated in the same way contained 1.71 mmol H/g. One gram of the catalyst contains 8% × 144/96 = 12% MoO_3 and therefore 0.88 g Al_2O_3. Hence, if the alumina is nearly completely freed of molybdena during sulfiding, it should supply $1.71 \times 0.88 = 1.50$ mmol H/g catalyst, in good agreement with the 1.47 mmol determined experimentally. Thus, the alumina surface was nearly completely freed from bonding with Mo.

As pointed out above, Massoth also found that most of the oxygen removed on sulfiding was compensated by the addition of sulfur. The resulting anion deficit (0.3) taken at face value would correspond to *e*/Mo = 0.6. Since we know that the composition of the sulfide approaches MoS_2, this value is obviously much too low. The reason is that H_I has been neglected. Going back to Massoth's Table 2 we find that the total hydrogen amounts associated with the sulfided and unreduced catalysts, pretreated in the same way, were H_T/Mo = 1.74 and 0.40, respectively. The difference, 1.34, is H_I/Mo. Thus, a value of *e*/Mo =

$1.34 + 0.6 = 1.94$ may be deduced. Similarly a value of $(e/\mathrm{Mo})_{\max}$ may be calculated using Eq. (8), i.e., $(e/\mathrm{Mo})_{\max} = 6 - 2 \times 1.75 = 2.50$. The true value undoubtedly lies in between 1.94 and 2.50. Hence, our results and those of Massoth are in substantial agreement when interpreted in this way. However, the physical picture evolved is very different from the monolayer interpretation which he presented. On sulfiding, the removed oxygen is mostly replaced by sulfur. Reduction occurs by hydrogenolysis of the Al–O–Mo bonds present in the unreduced catalyst. A sulfur-deficient molybdenum disulfide is formed containing valence states lower than Mo^{4+}. The submicroscopic crystallites (observed by EXAFS) of molybdenum sulfide probably remain bound to the alumina surface only at an edge (*41*). The catalytic properties of this system should therefore not differ much from those of MoS_2 (except in specific activity, not in turn-over number).

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