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Electron Spin Resonance and Microbalance Study of Sulfided Molybdena–Alumina Catalysts

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Sulfiding and reducing hexavalent Mo in the oxide form on an Al_2O_3 support produce pentavalent and tetravalent Mo, the former as oxide and the latter in the form of sulfide. Sulfiding favors the formation of tetravalent Mo at the expense of Mo(V), and the principal components of the system are Mo(IV) and Mo(V). The formation of polymeric paramagnetic sulfur is also indicated.

Molybdenum, and particularly pentavalent molybdenum, has been studied by ESR in several host materials (*1, 2*), and a number of correlations have been established between catalytic activity and ESR signal intensity (*2, 3*). In addition, molybdenum oxide and bismuth molybdate have been used to catalyze several reactions (*4–6*). During these reactions, the reduction of Mo(VI) and its subsequent oxidation are postulated with the formation of Mo(V) not excluded. Despite the considerable attention that molybdenum-containing catalysts have received, very little work has been reported on sulfided molybdenum oxide systems (*7*). This is particularly surprising in view of the widespread interest in hydrosulfurization catalysts and the utilization of molybdenum in such catalysts. The present paper reports on ESR and microbalance work on several molybdenum sulfided systems, and in particular on evidence for the existence of Mo(V) in sulfided MoO_3–Al_2O_3 catalysts.

EXPERIMENTAL METHODS

Pure molybdenum trioxide was obtained from Vitro Labs in the form of microspheres. Powdered molybdenum disulfide of high purity was supplied by the courtesy of Climax Molybdenum Corporation. Both materials analyzed less than 0.1% metal impurities by emission spectroscopy and gave good X-ray patterns for the respective compounds with no extraneous lines.

Supported molybdena catalysts were prepared by impregnating Filtrol Grade 86 alumina (290 m^2/g) with a solution of ammonium paramolybdate of the desired concentration. The incipient-wetted catalysts were oven dried at 125°C, followed by calcination in air at 540°C for 10 hr. The alumina catalysts contained about 1% sulfur in the form of sulfate derived from the original Al_2O_3 used. A silica catalyst, using Davison Grade 70 silica gel (312 m^2/g), was prepared in the same manner. All catalysts were ground to 20 to 40 mesh before sulfiding. All alumina-supported catalysts gave no lines attributable to Mo phases by X-ray diffraction analysis, except for the 16% Mo/Al_2O_3 sample in which small but definite lines for MoO_3 were detected. The silica catalyst exhibited a good pattern for MoO_3.

Catalyst sulfiding was performed in a conventional, flow tube reactor at atmospheric pressure employing a ceramic boat containing about 1 g of catalyst. Mixtures of hydrogen sulfide in hydrogen were used for the sulfiding to suppress possible disposition of free sulfur. Hydrogen sulfide and hydrogen flows were metered separately to obtain the desired partial pressure of H_2S. Flow rates of H_2S were sufficient to completely sulfide the sample within 0.5 min of reaction time. Several runs were also made in a flow spring balance microreactor of the

McBain type to follow the course of the reaction.

The sulfided samples were transferred in air to Pyrex glass tubes, evacuated under moderate vacuum, and sealed. The spin resonance spectra were obtained on a Varian V4500 spectrometer operating at 9.5 kMHz. The magnetic field was modulated by 100 kHz, and the first derivative of the spectrum was recorded. The sample tubes were filled with the sample to a height greater than the depth of the resonant cavity. The integrated intensities were taken to be proportional to the product of the signal amplitude and the square of peak-to-peak width. This method was adequate for the present purpose since the band shape of all the signals was identical. We have also measured the number of spins per gram in similar samples using the dual sample cavity and our results agree well with the results obtained by weight loss measurements by a microbalance technique. Bulk sulfided molybdenum oxide samples were diluted with the Al_2O_3 base in such proportion to give a mixture of at least 3.0% in Mo. The Al_2O_3 support did not have any paramagnetic impurities to interfere with the signal due to Mo(V) or polyatomic sulfur molecules present.

A series of $MoCl_5$–Al_2O_3 mixtures were prepared to obtain an absolute value of Mo(V) signal intensity in the range of interest. Figure 1 gives the calibration curve obtained from which Mo(V) in sulfided samples was estimated.

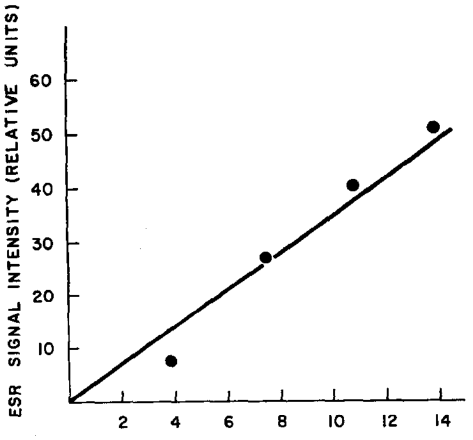

FIG. 1. Calibration curve for Mo(V) in a mixture of $MoCl_5$–Al_2O_3.

SULFIDING RESULTS

Sulfiding of bulk MoO_3 at temperatures between 300 and 500°C showed only the presence of MoO_2 and MoS_2 by X-ray analysis in agreement with the literature (*8, 9*). Runs in the microbalance showed a rapid weight loss to approximately MoO_2, followed by a slow weight gain, presumably due to slow formation of MoS_2. Thus, it appears that sulfiding of MoO_3 to MoS_2 in the presence of H_2S–H_2 mixtures occurs through MoO_2 as intermediate. Similar results (including X-ray confirmation) were obtained for the Mo/SiO_2 catalyst, indicating that the MoO_3 on a silica base behaves like bulk MoO_3.

Sulfiding of MoO_3 supported on Al_2O_3 occurred differently. A continuous weight gain was obtained throughout sulfiding, with a faster apparent sulfiding rate than for the bulk MoO_3 under similar conditions. The degree of sulfiding increased with time, temperature, and partial pressure of H_2S. Interestingly, the same degree of sulfiding ($\sim$55% to MoS_2) was obtained for all catalysts between 2 and 16% by weight of Mo at a given set of treatment conditions as shown in Table 1. This would seem to indicate that the basic Mo oxide particle size is the same for all the catalysts or that the Mo oxide is dispersed as a monolayer on the Al_2O_3 surface. Complete coverage of the Al_2O_3 surface is estimated at about 16% Mo.

ESR RESULTS

Since the alumina-supported catalysts gave no X-ray diffraction patterns, these samples were subjected to ESR analysis. The calcined catalysts, pure MoO_3 and MoS_2, gave no Mo(V) signal, nor did the sulfided MoO_3 and sulfided MoO_3/SiO_2 samples. However, the sulfided alumina catalysts gave intense Mo(V) signals. A typical ESR spectrum of a sulfided MoO_3–Al_2O_3 catalyst is shown in Fig. 2. A weak triplet structure around $g = 2.000$ is evident in addition to the intense line around $g = 1.930$. The latter has a g value which

TABLE 1

RESULTS OF SULFIDED Mo/Al_2O_3 CATALYSTS—VARIATION IN Mo CONTENT

Sulfiding conditions: 260°C; 9% H_2S in H_2; 2 hr.

Catalyst[a] (wt % Mo)	Sulfur[b] (wt %[c])	ESR signal rel. inten.	%S/ %Mo[d]	ESR/ %Mo[e]	Mole fraction[f]		Sum Mo(IV) + (V)
					Mo(IV)	Mo(IV)	
2.0	0.73	3.8	0.37	1.90	0.55	0.54	1.09
4.3	1.32	10.7	0.31	2.49	0.46	0.71	1.17
9.0	3.39	15.2	0.38	1.69	0.56	0.48	1.04
12.7	5.15	21.3	0.41	1.68	0.61	0.48	1.09
15.6	5.76	12.2	0.37	0.78	0.55	0.22	0.77

[a] Analyzed by photospectrometry; est. rel. error, ± 8%.

[b] Analyzed by microcombustion; est. rel. error, ± 10%.

[c] Corrected for sulfur in support.

[d] %S/%Mo = 0.67 for MoS_2.

[e] ESR/%Mo = 3.53 for $MoO_{2.5}$.

[f] Mo(IV) = (%S/%Mo)/0.67; Mo(V) = (ESR/%Mo)/3.53.

is characteristic of Mo(V) (*2*). No hfs is evident due to the odd isotopes of Mo. However, the spectrum of the acid solution of the sample shows a sharp line on which is superimposed an isotropic hfs structure of six lines due to the odd isotopes of molybdenum.

Of the possible valence states of molybdenum, only the penta-, tetra-, and trivalent states are paramagnetic. At room temperature, the signal due to Mo(IV) is likely to be broad and not detectable. The signal due to Mo(III) has been observed at room temperature (*10*). Its absence, therefore, in our samples suggests that under the present conditions, reduction to the trivalent state is unlikely. So the samples analyzed here contained mainly Mo(IV) and Mo(V) and possibly Mo(VI) in small amounts. Oxides of pentavalent molybdenum are unstable but can be stabilized through coordination in a lattice or on the surface. This would explain the absence of Mo(V) signals on the unsupported samples.

The intensity of Mo(V) ESR line increases uniformly with total molybdenum content while at about 10 wt % it reaches a maximum and begins to drop. This behavior is characteristic of unsulfided systems reported earlier (*2*, *3*). The relatively lower Mo(V) content in the higher Mo-containing sample could be due to the presence of some bulk MoO_3, which on reduction would not form Mo(V), but rather MoO_2 (*11*). Alternatively, the inflection in the ESR signal intensity with molybdenum concentration may be due to dimer formation, which is favored with increasing molybdenum oxide content. Dimer formation would change the configuration from d^1 to d^2 and thereby inhibit the observation of the resonance at room tem-

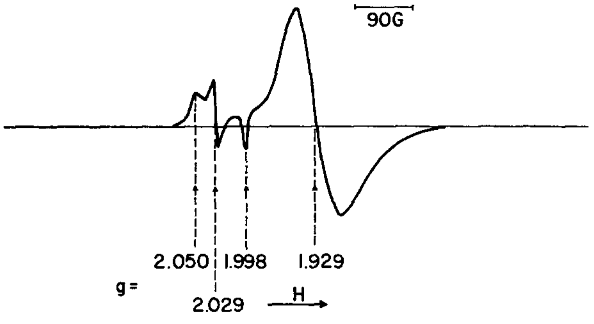

FIG. 2. ESR spectrum of sulfided molybdena–alumina catalyst (12.7 wt % in Mo; 5.15 wt % in S).

TABLE 2

RESULTS OF SULFIDED Mo/Al_2O_3 CATALYSTS—VARIATION IN SULFIDING TREATMENT

Catalyst: 9 wt. % Mo.

Treatment conditions: Temp (°C)	Treatment conditions: H_2S (%)	Treatment conditions: Time (hr)	Sulfur[b] wt %[c]	ESR signal rel. inten.	%S/ %Mo[d]	ESR/ %Mo[e]	Mole fraction[f]: Mo(IV)	Mole fraction[f]: Mo(V)	Sum Mo(IV) + (V)
150	1	2	1.47	21.1	0.16	2.34	0.24	0.67	0.91
260	2	2	3.02	17.4	0.34	1.93	0.50	0.50	1.00
260	9	2	3.39	15.2	0.38	1.69	0.56	0.48	1.04
260	20	6	3.53	14.4	0.39	1.60	0.59	0.46	1.05
370	20	6	4.71	3.6	0.52	0.40	0.78	0.10	0.88
480	1	2	2.59	4.9	0.29	0.54	0.43	0.14	0.57
480	10	2	4.55	1.3	0.51	0.14	0.75	0.04	0.79
480	20	2	4.35	1.1	0.48	0.13	0.72	0.03	0.75
260[a]	9	2	2.99	9.1	0.33	1.01	0.50	0.27	0.77
150	100	2	3.73	8.0	0.42	0.89	0.62	0.20	0.82

[a] Prereduced in H_2 at 260°C for 6 hr.

[b–f] Same as Table 1.

perature. Analogous observations have been made by Hare *et al.* (*12*) in their work on $(NH_4)_2MoOCl_5$ in solution.

The results of chemical analysis combined with spin resonance signal intensity can provide some insight into changes taking place during sulfiding. A 9% by weight Mo sample reduced in H_2 at 500°F for 2 hr was examined by ESR along with the sulfided samples. The result was analyzed by the method suggested above, and a value of 0.70 was obtained for the mole fraction of Mo(V). This value is about 1.5 times greater than that obtained for the same catalyst sulfided under the same conditions (Table 1), suggesting that sulfiding favors the formation of tetravalent molybdenum. If it is assumed that all sulfur is associated only with tetravalent molybdenum as MoS_2, the corresponding levels of Mo(IV) and Mo(V) can be calculated. In the series of catalysts of varying Mo content, the total amount of molybdenum computed according to the above procedure accounts for the stoichiometric amount of molybdenum to within 15%, as shown in Table 1. Such agreement is gratifying in view of the fact that some of the sulfur appears as a free radical. These results support the assumption that sulfur exists mainly as MoS_2 in these catalysts.

In another series of samples studied, the level of sulfiding was varied but the initial concentration of Mo was constant. Table 2 shows the results obtained at increasing severity of sulfiding. Generally, increasing severity of sulfiding treatment results in lower Mo(V) and higher sulfide levels on the catalyst. The material balance for molybdenum is good at the lower temperature, but is consistently low at the higher temperature. The difference in results obtained at low versus high temperature sulfiding is visually depicted in Fig. 3, where the Mo(V) content of the sulfided

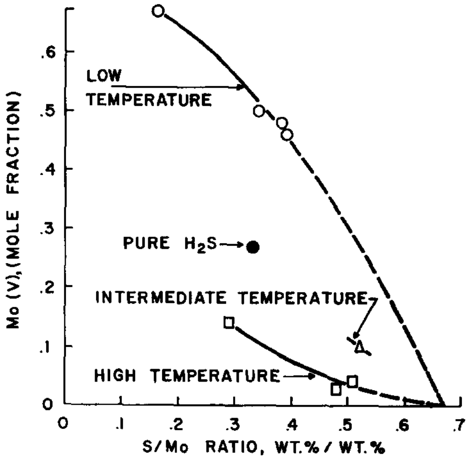

FIG. 3. Variation of Mo(V) concentration with degree of sulfiding.

catalysts is plotted against the degree of sulfiding achieved, expressed as the S/Mo ratio. Two extreme curves can be distinguished, depending on whether low or high temperature was employed in the sulfiding. Obviously, intermediate curves would be obtained for in-between temperatures as evidenced by the one point at 370°C.

DISCUSSION

The disparity in the molybdenum balance at high temperature is evidently due to formation of MoO_2 (in addition to MoS_2) at the expense of Mo(V). [It should be remembered that the Mo(IV) listed in Table 2 is based on the sulfur level of the catalyst and represents only MoS_2 and does not account for any MoO_2 which may be present.] It has been shown that the degree of molybdenum reduction in hydrogen increases with temperature, but Mo(V) goes through a maximum; at high temperatures MoO_2 is favored (*11*). Our sulfiding results at high temperature can be explained on the same basis; namely, that MoO_2 is formed faster than it can be sulfided at the higher temperature. That MoO_2 sulfides slowly was demonstrated earlier with bulk molybdena. The effect was further demonstrated in a separate experiment in which the catalyst was reduced prior to sulfiding. Prereduction resulted in lower sulfide content and Mo(V) level compared to direct sulfiding (ninth versus third entry in Table 2). The low Mo balance obtained in the prereduction experiment, despite the low sulfiding temperature, is at the expense of Mo(V), indicating the presence of Mo(IV) as MoO_2. In this case, the MoO_2 was apparently formed in the prereduction step and was not appreciably sulfided during the sulfiding step. The significant products formed during sulfiding, then, are:

Low temperature: Mo(V), MoS_2,
High temperature: MoS_2, MoO_2, Mo(V).

These results are qualitatively in agreement with those reported by Masson and Nechtschein (*11*) for hydrogen reduction of molybdenum–alumina catalysts, and suggest that the main effect observed is due to reduction rather than sulfiding. Still, the detail is significantly different in that we are dealing with a sulfided phase in addition to the reduced phases that may be present. In order to ascertain whether the Mo(V) found in sulfided samples was due entirely to reduction by the hydrogen present in the sulfiding gas mixture, or could also arise from the sulfiding reaction itself, a sulfiding run was made using only hydrogen sulfide. In this case, the catalyst sulfide level was appreciably higher than a comparable run with H_2S/H_2 mixture, while the Mo(V) found by ESR measurement was lower than that expected at the temperature employed and the sulfur level obtained (see Fig. 3). It is significant, however, that Mo(V) was found, showing that the direct sulfiding also proceeds through a Mo(V) intermediate state.

A calcined, molybdena–alumina catalyst contains molybdenum only in the VI state (*7*). The Mo(V) signal arises from an interaction of the reduced molybdena with alumina, the latter stabilizing the Mo(V) state to further reduction under mild conditions. That an intimate contact between molybdenum and support is required is shown in another experiment in which a finely divided mixture of MoO_3 and Al_2O_3 (containing 8% Mo) was sulfided. No Mo(V) signal was observed even though a sulfur level of 2.2% was obtained. Apparently, a surface deposition of the molybdena on the alumina is required to achieve stabilization as proposed by Masson and Nechtschein (*11*). In addition, the chemical (or surface) nature of the support is important; α-alumina (*13*) and silica do not stabilize Mo(V) whereas magnesia (*3*) and activated aluminas do. The reason for the specific nature of the stabilization is not clear at present.

The variation of signal intensity with sulfur content in the several samples examined suggests that the triplet is due to paramagnetic sulfur. Paramagnetic sulfur has been detected in photolyzed carbonyl sulfide (*14*), amine solutions of elemental sulfur (*15*), and in liquid sulfur (*16*), but very little work has been done on paramagnetic sulfur adsorbed on surfaces (*17*). Since the signal has been observed around $g = 2.000$, it is not due to free sulfur atoms but most likely due to sulfur atom chains, which are sufficiently long to preclude the interaction of unpaired electrons at the extremities of the chain. The possibility that the triplet structure is due to different molecular sulfur species has been ruled out by saturation studies. The triplet structure, in all probability, is due to complete anisotropy of the g tensor, and the average of the observed three g values agrees well with that obtained from the spectrum of liquid sulfur (*16*) where, due to rapid rotation of the molecule, the g tensor is averaged out. Dudzik and Cvetanović (*17*) have observed a single line at 300°K and a triplet structure at 77°K in the spectrum of sulfur biradical trapped in molecular sieves. Perhaps sulfur molecules have greater freedom of motion in molecular sieves which have cage-like structure, while on surfaces of Al_2O_3 sulfur is probably held rigidly. This would account for the spectral differences observed at room temperature. The amount of sulfur in this form is not known, but it is evidently relatively small.

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