Studies on Molybdena–Alumina Catalysts

XII. MoS₂ Surface Coverage from CO₂ Adsorption

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Adsorption of CO_2 on a number of sulfided Mo/Al_2O_3 catalysts of different Mo contents and Al_2O_3 supports was made by a pulse technique. Uptakes on the catalysts were lower than on their respective supports, from which the surface coverage of the Al_2O_3 by the MoS_2 phase was determined, since CO_2 did not adsorb on MoS_2. It was found that supports calcined up to 500°C and for Mo loadings up to 8%, the MoS_2 phase was present as a monomolecular layer. However, supports calcined at higher temperatures showed evidence of multilayers of MoS_2. The results are consistent with a model in which the MoS_2 clusters are oriented flatwise to the support. The lower coverage found in monolayer catalysts in the sulfide state compared to the oxide state is attributed to contraction of the coverage per Mo atom rather than to formation of multilayers. ESCA results on multilayer oxide catalysts showed qualitative correlation with calculated average numbers of multilayers present. © 1987 Academic Press, Inc.

INTRODUCTION

Molybdena supported on transition aluminas (γ and η) has been reported to be in a highly dispersed state up to at least 10% Mo loadings (*1*). ESCA results, showing a linearity of Mo/Al intensity ratios with Mo content, have often been taken to indicate monomolecular dispersion of the Mo phase (*2, 3*). However, this is not necessarily true as similar results would be expected if multilayer clusters of the same size were present, only their number increasing with Mo content. Recent theoretical calculations of monolayer coverage show reasonable correlation with experimental ESCA data, but there is some uncertainty in the escape depth values used in these calculations (*4, 5*).

Upon sulfiding, the Mo dispersion appears not to be appreciably changed (*3, 6*). The MoS_2 phase has been reported to be present as small monomolecular clusters of

about 10 Å, as determined by EXAFS (*7*). However, even here, one cannot be certain that several layers are not present, as the EXAFS data are more related to the lateral size than the depth of the cluster.

Hall and co-workers (*8, 9*) have recently shown by IR studies that CO_2 adsorbs exclusively on the alumina surface of a sulfided Mo/Al_2O_3 catalyst and not on the MoS_2 phase. We have applied this technique to assess the surface coverage of MoS_2 on a number of sulfided Mo/Al_2O_3 catalysts having different Mo loadings and on different alumina supports.

EXPERIMENTAL

The commercial supports used are given in Table 1. Catalysts containing various amounts of Mo were prepared by incipient wetness impregnation of the support (previously calcined at the indicated temperature for overnight) with an ammonium paramolybdate solution, adjusted to pH of 7.55 with ammonium hydroxide. The catalysts were oven dried and finally calcined at 500°C overnight.

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TABLE 1

CO$_2$ Adsorption on Alumina Supports

Support	Surf. area, A_{Al}^0 (m²/g)	CO$_2$ adsn., n_{Al} (μmol/g)
Ketjen (500)[a]	194	75.8
Ketjen (500)[b]	194	81.1
Ketjen (650)[a]	174	69.2
Ketjen (750)[a]	143	60.3
Ketjen (850)[a]	139	49.0
Ketjen (925)[a]	(100)[c]	30.6
Ketjen (1000)[a]	64	16.6
Amer. Cyan.[d]	180	63.8
Kaiser M[e]	196	96.8
Versal[f]	224	95.2
MoS$_2$	38	0

[a] Ketjen 000-1.5E, Batch I, calcined at °C indicated in ( ).

[b] Ketjen 000-1.5E, Batch II.

[c] Interpolated value.

[d] American Cyanamid 6094, precalcined at 600°C.

[e] Special laboratory preparation by Kaiser Aluminum.

[f] Kaiser Aluminum Versal 850, No. 2615-66-1A.

A pure MoS$_2$ sample was prepared by reacting MoO$_3$ with an aqueous solution of (NH$_4$)$_2$S at 70°C to precipitate ammonium tetrathiomolybdate (ATTM), which was filtered, washed with ethanol, and dried at 70°C. The dry ATTM was then heated in a flow of 10% H$_2$S/H$_2$ at a rate of 1.5°C/min to 400°C and maintained at this temperature for 4 h. The MoS$_2$ formed was subsequently flushed with helium and evacuated. After cooling to room temperature the MoS$_2$ was incrementally exposed to the atmosphere for passivation.

Some of the calcined catalysts were analyzed by ESCA using a Hewlett–Packard 5950B spectrometer having monochromatic Al$K\alpha$ radiation (1486 eV) and charge compensation. Spectra of Al2s and Mo3d ($\frac{3}{2} + \frac{5}{2}$) were integrated to obtain Mo/Al intensity ratios.

An atmospheric, flow pulse technique was used to measure CO$_2$ adsorption on the sulfided supports and catalysts. About 500 mg of sample was sulfided in a 10% H$_2$S/H$_2$ flow at 400°C for 2 h, purged in He for 2 h,

and the temperature lowered to 85°C. Pulses (~1 cm³) of CO$_2$ were introduced into the He stream every 4 min until no further adsorption was noted (about 10 pulses). The amount of CO$_2$ adsorbed was calculated from the total CO$_2$ introduced and the integrated area of the pulses. Average reproducibility in CO$_2$ uptakes from replicate analyses was ±2 μmol/g. Since MoS$_2$ did not adsorb CO$_2$, the surface coverage of MoS$_2$ in the catalyst, F_{expt}, was calculated by the formula

$$F_{expt} = 1 - n_{cat}/n_{Al}f_w \qquad (1)$$

$$f_w = 1 - 1.5 \times \%Mo/100, \qquad (2)$$

where n_{cat} is the CO$_2$ uptake per g cat and n_{Al} is the uptake per g Al$_2$O$_3$ support. In this calculation, the support adsorption is corrected for the weight fraction of support in the catalyst, f_w, based on an equivalent formula of MoO$_3$ in the calcined catalyst.

Calculations of monomolecular layer coverage of the MoS$_2$ on the Al$_2$O$_3$ support were made using an average MoS$_2$ area of 8.65 Å², derived from a unit hexagonal cell of 3.16 ± 0.001 Å (10) and assuming flatwise orientation, i.e., first layer of S on surface, followed by next layer of Mo above, and followed by last layer of S above that. The total area of MoS$_2$ for the amount of Mo present was divided by the support surface area, corrected for the amount of Al$_2$O$_3$ present. Thus, the predicted monolayer coverage, F_{mono}, is given by

$$F_{mono} = 5.41 \times \%Mo/A_{Al} \qquad (3)$$

$$A_{Al} = A_{Al}^0 f_w, \qquad (4)$$

where A_{Al} is the actual area of Al$_2$O$_3$ present in the catalyst and A_{Al}^0 is the surface area of the support.

RESULTS

CO$_2$ Adsorption

No adsorption of CO$_2$ was detected on a pure MoS$_2$ sample of 38 m²/g. The CO$_2$ uptakes for the various supports are given in Table 1. The results of CO$_2$ adsorption on

the supports as a function of surface area are shown in Fig. 1. A reasonably good linear correlation is obtained, which, however, does not go through the origin. The line passing through the origin applies to supports calcined up to 750°C, and gives an average uptake of 2.5×10^{13} CO_2/cm^2, which represents a coverage of about 2.5% of the alumina surface based on an O concentration of 1×10^{15} cm^{-2} (*11*). The uptakes on the supports calcined above 750°C are lower, indicating a partial loss of adsorption sites per unit area on heating to higher temperatures.

Adsorptions of CO_2 on the catalysts are given in Table 2. A plot of the data with the exception of the calcined series (see below) in terms of surface coverage vs predicted monolayer coverage is presented in Fig. 2. A good linear correlation with monolayer coverage is evident, with the exception of the 15% Mo catalyst ($R^2 = 0.982$ without last point). The latter catalyst showed evidence of a small amount of MoO_3 in the oxide form by XRD. This would be expected to form bulk MoS_2 on sulfiding, resulting in lower CO_2 uptake than for a monolayer. The value of 23% coverage on the standard 7.7% Mo catalyst (4th entry in Table 2) is in good agreement with a value
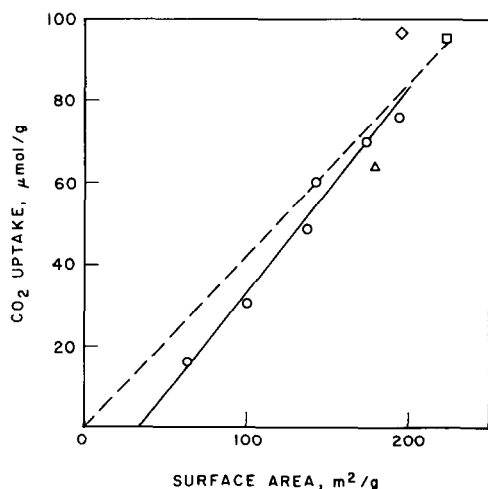
TABLE 2

CO_2 Adsorption on Mo/Al_2O_3 Catalysts

Catalyst		CO_2 adsn, n_{cat} (μmol/g)	MoS_2 coverage		
%Mo	Support		F_{expt}[a]	F_{mono}[b]	n_l[c]
1.98	Ketjen[d]	73.8	0.06	0.06	1.0
3.92	Ketjen[d]	68.7	0.10	0.12	1.2
5.83	Ketjen	58.6	0.15	0.18	1.2
7.69	Ketjen	51.6	0.23	0.24	1.0
11.32	Ketjen	40.0	0.36	0.38	1.1
14.82	Ketjen	31.8	0.46	0.53	1.1
7.69	Ketjen (650)	50.7	0.17	0.28	1.6
7.69	Ketjen (750)	43.0	0.19	0.33	1.7
7.69	Ketjen (850)	34.5	0.20	0.34	1.7
7.69	Ketjen (925)	23.3	0.14	0.47	3.3
7.69	Ketjen (1000)	13.4	0.09	0.74	8.5
3.92	Amer. Cyan.	63.8	0.12	0.12	1.0
7.69	Kaiser	64.7	0.24	0.24	1.0
3.92	Versal	78.7	0.12	0.10	0.8
7.69	Versal	66.7	0.21	0.21	1.0

[a] Experimental coverage from CO_2, Eq. (1).
[b] Calculated monolayer coverage, Eq. (3).
[c] Average number of layers $= F_{mono}/F_{expt}$.
[d] Batch II used to prepare these catalysts.

of 30% coverage for a similar catalyst containing 8% Mo reported by Millman *et al.* (*9*).

The good agreement between the CO_2 coverage and monolayer coverage implies that the MoS_2 phase in catalysts prepared by impregnation exists as a monolayer in the sulfided form. If multilayers were present, more alumina surface would be present, resulting in a larger CO_2 uptake
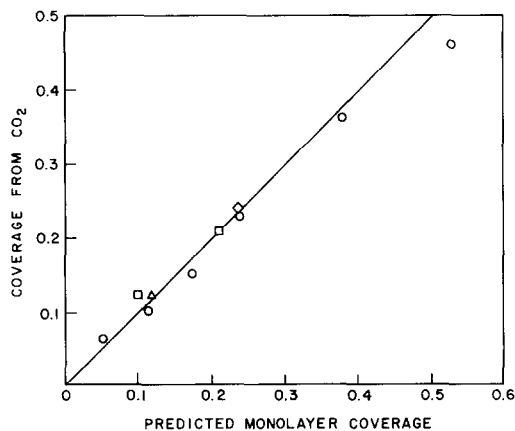

FIG. 1. CO_2 adsorption vs support surface area. Supports: (○) Ketjen, (△) Amer. Cyan., (◇) Kaiser, (□) Versal.

FIG. 2. MoS_2 coverage from CO_2 measurements vs predicted monolayer coverage for various catalysts. Catalyst supports as in Fig. 1.

and correspondingly lower surface coverage of the MoS_2 phase. Evidence of this was obtained for the catalysts prepared from the supports calcined at higher temperatures. Figure 3 shows these results, where it is seen that the surface coverage by CO_2 falls off from the monolayer line with increasing calcination temperature of the support. The lines in this figure represent coverages for MoS_2 phases having various average multilayers, viz, number of layers = F_{mono}/F_{expt}. Thus, the catalyst prepared from the 925°C support has an average of 3.3 layers of MoS_2 while the one from the 1000°C support has an average of 8.5 layers.

ESCA Results

ESCA data on a number of catalysts in the oxide state are tabulated in Table 3. Figure 4 displays the experimental I_{Mo}/I_{Al} ratios vs the Mo to Al mole fractions present for the catalysts having different Mo loadings on the 500°C calcined Ketjen support. A good linear plot is observed up to about 8% Mo. Predicted monolayer values of I_{Mo}/I_{Al} were calculated following the method of Kerkhof and Moulijn (12). The appropriate equation is given by

$$\left(\frac{I_{Mo}}{I_{Al}}\right)_{mono} = \left(\frac{X_{Mo}}{X_{Al}}\right)\left(\frac{KE_{Al}}{KE_{Mo}}\right)\left(\frac{\sigma_{Mo}}{\sigma_{Al}}\right) Z, \quad (5)$$

TABLE 3

ESCA Mo/Al Intensity Ratios for Mo/Al_2O_3 Catalysts[a]

Catalyst		$(I_{Mo}/I_{Al})_{expt}$	$(I_{Mo}/I_{Al})_{mono}$[c]	%deviation[d]
%Mo	Temp. °C[b]			
1.98	500	0.19	0.19	—
3.92	500	0.38	0.38	—
5.83	500	0.59	0.59	—
7.69	500	0.81	0.81	—
11.32	500	1.16	1.26	8
14.82	500	1.53	1.76	13
7.69	650	0.78	0.83	6
7.69	750	0.80	0.93	7
7.69	850	0.84	0.94	11
7.69	925	0.95	1.18	19
7.69	1000	1.22	1.75	30

[a] On oxide catalysts with Ketjen support.
[b] Support calcination temperature.
[c] Calculated for monolayer coverage (see text).
[d] Percent lowering in I_{Mo}/I_{Al} from $(I_{Mo}/I_{Al})_{mono}$. Estimated error is ±5%.

where $(I_{Mo}/I_{Al})_{mono}$ is the predicted intensity (area) ratio for a monolayer of Mo on the support, X is the atomic fraction, KE is the kinetic energy of the electrons, σ is the photoelectron cross section, and Z is a correction term. The correction term is given by

$$Z = \frac{\beta(1 + e^{-\beta})}{2(1 - e^{-\beta})}, \quad (6)$$

where $\beta = t/\lambda$ and $t = 2/S\rho_{Al}$. Here, β is a dimensionless support thickness, t is the sheet thickness of the support, λ is the es-

FIG. 3. MoS_2 coverage from CO_2 measurements vs predicted monolayer coverage for support–temperature series catalysts.
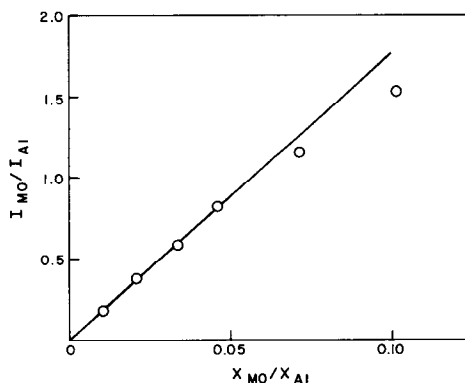

FIG. 4. Experimental ESCA intensity ratios vs Mo to Al mole ratio on oxide catalysts.

cape depth, ρ is the support density, and S is the support surface area.

Because the value of λ is not well known, it was calculated from the ESCA results for the four catalysts having the lowest Mo loading (Fig. 4) assuming the Mo in these to be in monolayer dispersion (see Discussion). Using the following values: $KE_{Al} = 1369$ eV, $KE_{Mo} = 1259$ eV, $\sigma_{Mo} = 9.50$, $\sigma_{Al} = 0.753$, $S = 194$ m^2/g, and $\rho_{Al} = 3.8$ g/cm^3, solution of Eqs. (1) and (2) for each experimental I_{Mo}/I_{Al} value gave an average value of $\lambda = 1.46 \pm 0.01$ nm. This value compares well with values of 1.3–1.8 quoted by Kirkhof and Moulijn (12). This value of λ was then used to calculate $(I_{Mo}/I_{Al})_{mono}$ from Eqs. (5) and (6) for the different catalysts, and the results are given in Table 3.

Inspection of Table 3 shows that for the 15% Mo catalyst, the experimental I_{Mo}/I_{Al} is lower than predicted for a monolayer dispersion. Furthermore, the support-calcined catalysts show increasing deviation from monolayer dispersion with increased calcination temperature. Evidently, the Mo content in these catalysts exceeds the monolayer capacity of the available alumina surface area.

DISCUSSION

Orientation of MoS$_2$ on Surface

The assumption that the MoS$_2$ clusters lie parallel to the support surface (c-axis $\perp$ to surface) needs to be addressed. The MoS$_2$ layer consists of trigonal prisms connected at the corners, with Mo having six nearest neighbor S atoms, and with every other prism occupied by Mo (13). The natural form is approximately hexagonal in shape, as shown by electron microscopy (13, 14). From EXAFS (7) and LRS (15) studies on Mo/Al$_2$O$_3$ catalysts, the sulfide phase has been shown to be characteristic of MoS$_2$. Consequently, a unit prism side from X-ray crystallographic data on bulk MoS$_2$ was used to calculate coverages. For a monolayer slab (one S–Mo–S layer), the coverage can be calculated by a knowledge of the residual support area, the Mo content, and

the lateral area per Mo, resulting in Eqs. (3) and (4). On this basis, calculated MoS$_2$ coverages are compared to experimental values from CO$_2$ adsorption (Fig. 2). The straight line plot of slope unity for different Mo contents (up to 8% Mo) and different alumina supports indicates that the MoS$_2$ is present in monolayer form according to this model. One can then calculate the *average* number of layers present for catalysts giving less coverage than the monolayer, as shown in Fig. 3.

Carver and Goetsch (16) have suggested that the MoS$_2$ phase is oriented perpendicular to the surface. For a hexagon cluster of equal sides and n_1 slabs lying on the support via one side, the following calculations apply:

Let A_u be the area of one side unit consisting of four S positions. The area of a slab of L square units lying on one side is $A_u L$ and that for a cluster, $A_{s,c}$,

$$A_{s,c} = n_1 A_u L. \tag{7}$$

The number of Mo ions in a slab is given by

$$M_s = 3(L - 1) + 3L + 3(L - 1)^2, \tag{8}$$

where the first two terms account for the Mo ions at the edges and the third term for the Mo ions not at edges. Combination of Eqs. (7) and (8) leads to

$$A_{s,c} = n_1 A_u \sqrt{M_s/3}. \tag{9}$$

The total side area coverage, $A_{s,t}$, for N clusters is then

$$A_{s,t} = n_1 A_u N \sqrt{(M_s/3)}. \tag{10}$$

But, the number of clusters is

$$N = M_t/n_1 M_s, \tag{11}$$

where M_t is the total Mo atoms per gram of catalyst. Combination of Eqs. (10) and (11) and rearrangement yields

$$M_s = \tfrac{1}{3}(A_u M_t/A_{s,t})^2. \tag{12}$$

This equation shows that the number of Mo ions in a slab is a unique value depending on the total number of Mo atoms present and the surface coverage of MoS$_2$. For the

standard 7.7% Ketjen catalyst the following data apply:

$$A_u = (3.16)^2 = 10 \text{ Å}^2$$

$$M_t = 0.077 \times 6 \times 10^{23}/96$$
$$= 4.8 \times 10^{20} \text{ atom Mo/g}$$

$$A_{Al} = 194(1-1.5 \times 0.077) = 172 \text{ m}^2/\text{g}$$
$$= 172 \times 10^{20} \text{ Å}^2/\text{g}$$

$$A_{s,t} = 0.23 \times 172 = 39 \text{ m}^2/\text{g}$$
$$= 39 \times 10^{20} \text{ Å}^2/\text{g}.$$

Substitution in Eq. (12) then gives $M_s = 0.5$. This value for the number of Mo atoms in a slab is clearly impossible. Clausen et al. (7) have deduced a slab size of about 10 Å from EXAFS data and Burch and Collins (17) have invoked a model of 33 Mo/slab. Taking a value of 10 for M_s, Eq. (12) yields a value of $A_{s,t}$ of 8.8 m²/g, representing 5% coverage, much below the experimental value of 23%. Larger M_c's will give even lower coverages. The above argument and the excellent agreement between the coverages by CO_2 data and those calculated from flatwise orientation (Fig. 2) strongly suggest that orientation is flatwise on the support surface. Other geometries or MoS_2 unit coverages than used here could possibly be evoked. But, we believe the model adopted is entirely reasonable and consistent with known properties of MoS_2.

MoS_2 Coverage

It is surprising that multilayer clusters of MoS_2 start to form at coverages much below the total monolayer capacity of the alumina. For example, for the Ketjen support, multilayer growth starts above 8% Mo, and for the support temperature series, substantial multilayer growth occurs between the 850° and 925° support treated catalysts. Thus, total monolayer coverage in the sulfided state is not achieved in any of our samples prior to multilayer formation. In the literature, the fall off in HDS activity observed to occur at about 10–12% Mo has often been ascribed to completion of a monolayer. Our calculations show that not enough Mo is present for a complete monolayer at this level and our results indicate that the fall off is probably due to formation of larger, multilayer clusters.

Coverages on Oxide Catalysts

Millman et al. (9), from CO_2 measurements on a series of oxide Mo/Al_2O_3 catalysts of increasing Mo content, reported no residual CO_2 adsorption for a catalyst containing 8% Mo with an alumina of 186 m²/g. Assuming complete monolayer coverage of the Mo oxide phase, the average coverage per Mo, σ_{ox}, is

$$\sigma_{ox} = \frac{A_{ox}}{M_t} = \frac{186(1-1.5 \times 0.08) \times 10^{20}}{5.0 \times 10^{20}}$$
$$= 33 \text{ Å}^2.$$

We have also found no CO_2 adsorption on our standard 7.7% Mo catalyst in the oxide state, corresponding to $\sigma_{ox} = 35$ Å². These values are in excellent agreement with a theoretical value of 33.6 Å² for octahedrally coordinated Mo (18). Since at high Mo coverages, octahedral Mo is present (19), we conclude that the Mo-oxide phase is present essentially as a two-dimensional monolayer.

According to this analysis, catalysts having lower surface areas (see support calcination series in Table 2) or higher Mo levels have an excess of Mo above the complete monolayer and should result in multilayers. The average number of layers, $n_{l,ox}$, can be calculated from

$$n_{l,ox} = M_t \sigma_{ox}/A_{Al} \qquad (13)$$

Using a value of σ_{ox}34 Å² from above, the plot of Fig. 5 was constructed, in which the average number of layers is plotted vs the ESCA percent deviation from monolayer (Table 3). A reasonably good correlation is observed for the support–temperature series, but the higher Mo content catalysts deviate from this correlation. Lack of a better overall fit may be due to the simplification of an average number of layers present. Obviously, a fractional number of
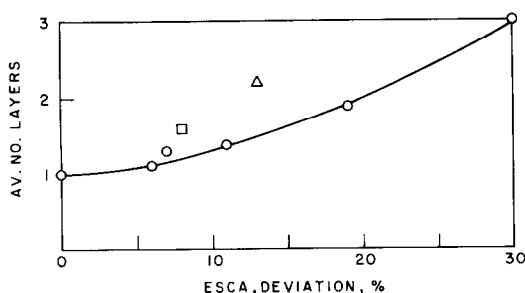
FIG. 5. Average number of layers in oxide catalysts calculated from Eq. (13) vs % deviation of ESCA ratios from monolayer. Symbols: (○) Support–temperature series, (□) 11.3% Mo, (△) 14.8% Mo.

layers cannot be present; there must be some integer number of layers less than and some more than the average value. Depending upon the specific distribution of layer sizes, two catalysts having the same average number of layers could give different I_{Mo}/I_{Al} ratios. It is therefore concluded that ESCA can only give qualitative information on the presence of multilayers in these catalysts.

Genesis of MoS₂ Formation

Now, the question arises as to why a catalyst having a complete monolayer in the oxide state ends up having only a partial (23%) coverage in the sulfided state. We believe the answer lies in the contraction of the oxide phase to the sulfide phase during sulfiding. In the monolayer oxide catalyst, LRS studies (20) have shown the presence of a surface "interaction" species and no evidence of MoO₃-like species. During sulfiding, the attachment to alumina is broken resulting in characteristic MoS₂ monolayer species (7). Also, LRS studies (15) have identified MoS₂ and no evidence of surface "interaction" species. Thus, the MoS₂ on the sulfided catalyst should exhibit its characteristic MoS₂ geometric shape. Hence, we envision during sulfiding a breakup of the complete oxide monolayer into small patches (slabs) of MoS₂ as a result of contraction from an oxide coverage of ~33–35 Å² per Mo to a sulfide coverage of 8–9 Å² per Mo.

The next question to address is why do catalysts having lower surface areas (support–temperature series) exhibit multilayers in the sulfided state (Fig. 3) while coverage remains relatively low (Table 2); i.e., why do these catalysts not give higher monolayer coverages? We believe the answer is related to the multilayers present in the oxide state as discussed above. Figure 6 presents the average number of layers in the oxide catalysts together with the data from the corresponding sulfide catalysts versus the area of alumina in these catalysts. It can be seen that increasing multilayers in the sulfide catalysts parallel increasing multilayers in the oxide catalysts. However, larger multilayers develop in the sulfide catalysts as compared to the oxide catalysts. This may be rationalized as follows: after monolayer coverage in the oxide state, additional Mo will result in three-dimension growth of MoO₃ crystallites since further attachment to the alumina surface is no longer possible. Thus, the *average* number of layers in the oxide catalysts probably consists of a monolayer coverage with isolated patches of larger three-dimensional MoO₃-like domains on top. The latter would be expected to give large bulk (three-dimensional) MoS₂ on sulfiding, on top of
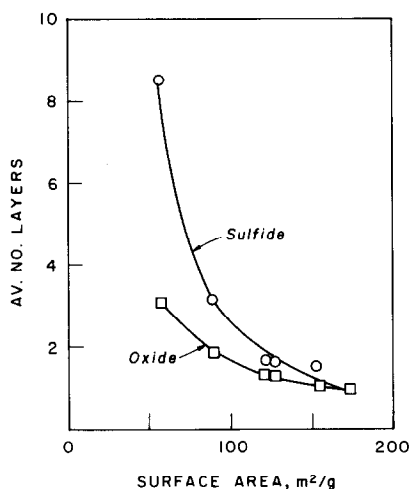

FIG. 6. Average number of layers in support–temperature series oxide and sulfide catalysts vs support alumina area.

the monolayer MoS_2, resulting in a greater average number of layers. Consequently, during sulfiding, we envision that monolayer oxide catalysts form monolayer MoS_2 slabs whereas multilayer oxide catalysts form multilayer MoS_2 clusters.

CONCLUSIONS

In summary, it has been found that CO_2 adsorption is a good technique for assaying the surface coverage of the MoS_2 phase in alumina catalysts as it adsorbs on the alumina but not on the MoS_2 phase. Arguments are advanced for a model consisting of MoS_2 monolayers oriented flatwise on the support surface. Together with calculated monolayer coverage, a value of the *average* number of MoS_2 layers can be estimated. The results indicate that in sulfided catalysts up to about 8% Mo on alumina, the MoS_2 is dispersed as a monolayer. However, higher Mo to support surface area ratios can result in multilayer MoS_2 phases.

These results are interpreted as due to breakup of the monolayer Mo–oxide–alumina surface species into smaller domains of essentially unattached monolayer MoS_2 slabs, the latter having considerably smaller surface coverage per Mo atom than for the oxide species. Thus, a catalyst having a complete monolayer coverage in the oxide state results in only 23% coverage in the sulfide state after sulfiding.

ESCA analysis was also found to be a useful technique to assay coverage in the oxide catalyst when combined with theoretical predictions of monolayer coverage.

Finally, it should be appreciated that these techniques do not give any information on the lateral size of the MoS_2 clusters in these catalysts.

ACKNOWLEDGMENTS

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