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# Comments on the State of Dispersion of Molybdena on Sulfided Co–Mo–$Al_2O_3$ Catalysts

A current controversy exists on the sulfided state of Co–Mo–$Al_2O_3$ catalysts employed for hydrodesulfurization in the oil industry (*1*). There seems to be general agreement that, in the calcined oxidized form of the catalyst, the $MoO_3$ is highly dispersed on the $Al_2O_3$ support, most likely as a monolayer, at least for Mo levels below 10–15 wt%. The reason for this unusually high dispersion is attributed to a strong interaction between the molybdena and the $Al_2O_3$ support. The higher binding energy reported from photoelectron spectroscopy (ESCA) for the catalyst compared with bulk $MoO_3$ (*2–5*) has been cited as evidence for this interaction, although this effect has not been found by some workers (*6, 7*). Likewise, the development of a strong electron spin (ESR) signal due to $Mo^{5+}$ on partially reduced catalysts (not seen on partially reduced bulk $MoO_3$) (*8, 9*) can be attributed to this interaction.

In regard to the sulfided catalyst, ESCA results do not show the same binding energy shift (*3–5*), which has been taken as evidence for the presence of small crystals of $MoS_2$ on the catalyst. However, Walton (*10*) has pointed out that this interpretation may not be unequivocal, as molybdenum oxysulfide compounds show little shift from pure $MoS_2$, and some ESCA results show evidence of molybdenum oxides remaining in the sulfided catalysts (*5, 11*). Besides, ESCA (*5, 11*) and optical spectra (*12*) data indicated that reoxidation of the sulfided catalyst gave patterns identical to the original oxidized catalyst. This would not likely be expected if bulk $MoS_2$ existed on the sulfided catalyst, since oxidation should lead to bulk $MoO_3$ and not to redispersion into the monolayer. On balance, therefore, it does not seem that a separate $MoS_2$ phase has been proven. It should be mentioned that X-ray diffraction (XRD) analysis has failed to detect $MoS_2$ on these catalysts. To be sure, there are cases in which bulk $MoS_2$ has been observed on these catalysts (*3*). Such cases can occur when the catalyst has been sulfided under severe conditions or when the Mo–support interaction is weak. It is those cases in which neither of these conditions is present that is the subject of this communication.

DeBeer and co-workers (*13*), on the basis of elaborate activity tests with impregnated catalysts and mixed sulfide catalysts, have concluded that the monolayer oxide breaks up during sulfiding to form discrete $MoS_2$ crystals or intercalated $CoMoS_2$ crystals. Much of their argument relies on the intercalation model proposed for the Ni–$WS_2$ catalyst system (*14*). The special promotor role for Ni in this catalyst is attributed to intercalation of the $WS_2$ crystal with Ni in edge positions, resulting in formation of the $W^{3+}$ cation, which is regarded as the active catalytic site. For the sulfided Co–Mo–$Al_2O_3$ catalyst, the analogous $Mo^{3+}$ cation has not been detected by ESR or ESCA. Furthermore, a recent report declared that the Co is not observed by ESCA on the unsupported mixed sulfides of Co and Mo (*15*), contrary to what would be expected for the intercalation model. Delmon (*1*) has recently proposed an alternate model which requires

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a contact synergism between Mo and Co sulfide phases. Since this also involves phases separate from the $Al_2O_3$, it is included in the separate phase model discussed herein.

On the other hand, Massoth (*16*) has advocated the monolayer model for the sulfided Mo catalyst on the basis of stoichiometric sulfiding measurements. From optical reflectance studies, Mitchell and Trifiro (*12*) concluded that the Mo in the sulfided Mo and CoMo catalysts does not resemble $MoS_2$, but, rather, it resembles surface oxysulfide species. However, DeBeer *et al.* (*13*) claim $MoS_2$ to be present on their sulfided catalyst. Data for thiophene hydrogenolysis over a sulfided Mo–$Al_2O_3$ catalyst have recently been successfully correlated using the monolayer model (*17*).

Between these extremes, Ben-Yaacov (*18*) has presented data which led him to conclude that only when Co is present does a separate $MoS_2$ phase appear (as intercalated $CoMoS_2$), but the monolayer remains intact (as a sulfided monolayer) when only Mo is present. Furthermore, introduction of Co did not affect the Mo monolayer on the oxidized catalyst. These interpretations were based on butene adsorption, temperature-programmed thiophene desorption, and magnetic measurements.

The purpose of this note is to reanalyze some previously reported data and show that it is in agreement with a monolayer model for the sulfided catalyst, both with and without added Co.

Stoichiometry dictates that if the $MoO_3$ on the catalyst is converted to $MoS_2$, three oxygen atoms must be lost for each two sulfur atoms added, i.e., $O_L/S = 1.5$. Massoth (*16*) has shown that the major reaction which occurs during sulfiding of a Mo–$Al_2O_3$ catalyst is replacement of O by S. Although some additional O is lost in the process due to reduction, the net result is considerably less than the 1.5 ratio expected. Table 1 shows data on $O_L$ versus S for 8% Mo on $\gamma$- and $\eta$-$Al_2O_3$. (These data exclude reversibly adsorbed $H_2S$.) It can be seen that appreciable sulfiding occurred without commensurate loss of 1.5 oxygen atoms. Only at temperatures above 500°C (well above that normally employed in catalyst presulfiding) did the $O_L/S$ ratio approach stoichiometry for the $\gamma$-$Al_2O_3$ catalyst, and considerably higher temperatures would be required for the $\eta$-$Al_2O_3$ catalyst. If bulk $MoS_2$ is formed, then excess sulfur (over that stoichiometrically reacted with $O_L$ lost) must be present as other species. The last column in Table 1 shows that this is not insignificant. Other examples of incomplete sulfiding of molybdena catalysts can be found in the literature (*19, 20*).

Surface area measurements have been reported on occasion but few attempts have been made to analyze these data from the point of view of catalyst phase structure. For an impregnated Co–Mo–$Al_2O_3$ catalyst which has been calcined, the Co and Mo are located within the porous $Al_2O_3$ structure and, for simplicity, are assumed to be equivalent to $MoO_3$ and CoO. We will evaluate the two models, monolayer versus separate phase, for surface area predictions.

If the Co and Mo are deposited as a monolayer, the surface area of the $Al_2O_3$

TABLE 1

Stoichiometry of Sulfided 8% $Mo/Al_2O_3$ Catalysts[a]

| Support | Temperature (°C) | S/Mo | $O_L$/Mo | $O_L$/S | $S_x$/Mo[b] |
|---|---|---|---|---|---|
| $\gamma$-$Al_2O_3$ | 340 | 1.6 | 1.6 | 1.0 | 0.5 |
| | 400 | 1.8 | 2.1 | 1.2 | 0.4 |
| | 450 | 1.9 | 2.5 | 1.3 | 0.2 |
| | 500 | 1.9 | 2.7 | 1.4 | 0.1 |
| $\eta$-$Al_2O_3$ | 320 | 1.4 | 1.4 | 1.0 | 0.5 |
| | 400 | 1.6 | 1.8 | 1.1 | 0.4 |
| | 480 | 1.7 | 1.9 | 1.1 | 0.4 |
| | 560 | 1.8 | 2.3 | 1.3 | 0.3 |

[a] Data from Ref. (*16*); Temperature Series: 9% $H_2S/H_2$; 2 hr.

[b] Sulfur in species other than $MoS_2$ (see text).

TABLE 2

Surface Areas of Mo–$Al_2O_3$ Oxide Catalysts[a]

| $MoO_3$ (wt%) | $A_{cat}$ ($m^2/g$) | $A_{cat}/f$ ($m^2/g$ of $Al_2O_3$) | $V_{cat}$ ($cm^3/g$) | $V_{cat}/f$ ($cm^3/g$ of $Al_2O_3$) |
|---|---|---|---|---|
| 0 | 216 | — | 0.94 | — |
| 2 | 202 | 206 | 0.92 | 0.94 |
| 4 | 205 | 214 | 0.96 | 1.00 |
| 6 | 211 | 225 | 0.93 | 0.99 |
| 8 | 185 | 201 | 0.87 | 0.95 |
| 10 | 196 | 218 | 0.91 | 1.01 |
| 15 | 183 | 216 | 0.82 | 0.96 |
| Average | | 213 ± 9 | | 0.97 ± 0.03 |

[a] Data from Ref. (*21*).

would hardly change. Thus,

$$A_{Al} = A_{cat}/f, \qquad (1)$$

where $A_{cat}$ and $A_{Al}$ are surface areas, in square meters per gram, for catalyst and support $Al_2O_3$, respectively, and $f$ is the weight fraction of $Al_2O_3$ in the catalyst. Therefore, the value of $A_{cat}/f$ should be identical to the $Al_2O_3$ support value, if this model holds.

If discrete crystals of $MoO_3$ and CoO exist on the catalyst, they will contribute some additional surface area. Assuming a maximum average particle size of 40 Å (undetectable by X-ray diffraction), the bulk phase contribution will be given by,

$$A_B = 60{,}000/40\rho_B = 1500/\rho_B, \qquad (2)$$

where $A_B$ is the surface area in square meters per gram, $\rho_B$ is the density in grams per milliliter, and subscript B refers to the bulk phase under consideration. If these bulk particles do not block any pores in the $Al_2O_3$, then

$$A_{Al} = (A_{cat}/f) - \Delta A, \qquad (3)$$

where, for two separate bulk phases (besides $Al_2O_3$),

$$\Delta A = [(f_{B1}/f)A_{B1}] + [(f_{B2}/f)A_{B2}]. \qquad (4)$$

Here, $f_{B1}$ and $f_{B2}$ are the weight fractions of the two bulk phases. Therefore, if this model applies, $A_{cat}/f$ should be *larger* than $A_{Al}$ by the $\Delta A$ term. For example, for a catalyst consisting of 12% $MoO_3$ on $Al_2O_3$, $A_B = 320$ $m^2/g$ of $MoO_3$, and $\Delta A = 44$ $m^2/g$ of $Al_2O_3$. In other words, the calculated value of $A_{cat}/f$ should be larger than $A_{Al}$ by 44 $m^2/g$ of $Al_2O_3$.

In Table 2 are presented data for surface areas of impregnated catalysts having various Mo levels (*21*). The $A_{cat}/f$ values for all catalysts are in reasonable agreement with the $A_{Al}$ value. Certainly, no trend toward higher $A_{cat}/f$ values is evident with increasing Mo as would be expected if the separate phase model applied. The $A_{cat}/f$ values for the 10 and 15% $MoO_3$ catalysts are well outside the additional 44 $m^2/g$ predicted for the separate phase model. Smaller sized crystals should show even further divergence if this model applied.

It may be argued that the analysis presented above for the separate phase model should take into account possible blockage of $Al_2O_3$ pores by bulk $MoO_3$, thus reducing the available surface area for the catalyst. If appreciable pore mouth blockage exists, a substantial loss in pore volume should occur. This is not evident from the data of Table 2. Therefore, we need only consider blockage due to filled pores. Taking the 12% $MoO_3$ catalyst example, the condition that the loss in surface area by pore blockage compensates for the surface area gain due to bulk $MoO_3$

crystals (i.e., $A_{Al} = A_{cat}/f$ as shown in Table 2) requires that

$$A_p = (0.12 - y)A_{MoO_3} = 320(0.12 - y)\ m^2/g, \quad (5)$$

where $A_p$ is the surface area loss due to pore blockage and $y$ is the weight of $MoO_3$ in blocked pores. Now, the volume of $MoO_3$ in blocked pores is

$$v = y/4.7\ cm^3/g. \quad (6)$$

Assuming cylindrical pores, $A_p$ and $v$ are related by

$$A_p = 4v/d \times 10^4 = 8500y/d, \quad (7)$$

where $d$ is the pore diameter in angstroms. Equating Eqs. (5) and (7), the weight fraction of $MoO_3$ in pores is

$$f_p = y/0.12 = 1/(1 + 27/d). \quad (8)$$

The data in Table 2 give a mean pore diameter of about 180 Å, which corresponds to almost 90% of the $MoO_3$ in blocked pores according to Eq. (8). Even using a small pore diameter of 50 Å requires that two-thirds of the $MoO_3$ be in blocked pores. These results do not seem reasonable, and it must be concluded that pore blockage cannot adequately account for the experimental results using the separate phase model.

Thus far, we have shown that surface measurements for oxidized catalysts are consistent with the monolayer model. Equations (1)–(4) also apply to sulfided catalysts with appropriate substitution. For simplicity, we assume complete sulfiding to $MoS_2$ and CoS. Incomplete sulfiding will then give results somewhere between the complete sulfided and oxidized states.

Table 3 presents some surface area data reported for oxide and sulfide catalysts prepared in various ways (*22*). The original article (*22*) should be consulted for preparation details and catalyst compositions. The closeness of all $A_{cat}/f$ values to the $Al_2O_3$ value of 255 is remarkable and certainly well outside the values expected for the separate phase model. Of significance is the fact that the impregnated sulfided catalysts all fall within the expected monolayer range.

It can be argued that sulfiding could lead to amorphous $MoS_2$ or other amorphous molybdenum species, not attached as a monolayer. This situation is more difficult to contend with. If the amorphous phase is of small particle sizes, then the same arguments as presented above apply. However, if the amorphous phase consists of rather large particle sizes, it is likely that they would have some considerable porosity

TABLE 3

Surface Areas of Various Co–Mo–$Al_2O_3$ Catalysts[a]

| Catalyst No. | Components | State | $A_{cat}$ ($m^2/g$) | $A_{cat}/f$ ($m^2/g$ of $Al_2O_3$) | $\Delta A$[b] ($m^2/g$ of $Al_2O_3$) |
|---|---|---|---|---|---|
| 0 | — | — | 255 | — | — |
| 1 | Mo–Al | Oxide | 227 | 258 | 44 |
| 2 | Mo–Al | Sulfide | 221 | 254 | 47 |
| 3 | Co–Mo–Al | Oxide | 217 | 259 | 57 |
| 4 | Co–Mo–Al | Sulfide | 213 | 260 | 66 |
| 5 | Co–Mo–Al | Sulfide | 209 | 255 | 66 |
| 6 | Zn–Mo–Al | Sulfide | 204 | 252 | 70 |
| 7 | Ni–Mo–Al | Sulfide | 210 | 256 | 66 |
| Average | | | | 256 ± 3 | |

[a] Data from Ref. (*22*).

[b] Based on Eq. (4) and catalyst composition data given in Ref. (*22*).

TABLE 4

Surface Areas of Ni–Silica Alumina Catalyst[a]

| | Catalyst | | |
|---|---|---|---|
| | 1 | 2 | $3^b$ |
| $A_{\text{support}}$ ($m^2/g$) | 447 | 475 | 475 |
| $A_{\text{cat}}$ ($m^2/g$) | 438 | 436 | 452 |
| $f_{\text{Ni}}$ | — | — | 0.193 |
| $f_{\text{NiO}}$ | 0.162 | 0.246 | — |
| $f$ | 0.838 | 0.754 | 0.807 |
| $A_{\text{cat}}/f$ ($m^2/g$ of support) | 523 | 578 | 560 |
| $\Delta A$ ($m^2/g$ of support) | 76 | 142 | 108 |
| $\bar{d}_B$ (Å) | 23 (NiO) | 28 (NiO) | 19 (Ni)<br>23 $(Ni)^c$ |

[a] Previously unpublished data.

[b] Catalyst 2 reduced in $H_2$ at 540°C.

[c] Calculated from results for Catalyst 2.

and, hence, should contribute to an increase in surface area. Also, larger amorphous particles should, in principle, be observed by electron microscopy. For sulfided catalysts having Mo levels below 10%, such particles were not observed (although the lower limit of detection was not determined); however, for high Mo levels, distinct particles were observed (*23*).

In order to demonstrate that the $\Delta A$ predicted by Eq. (4) can actually be observed experimentally for catalysts containing very small crystallites on a support, the author has resorted to some data he obtained while employed elsewhere, as no definitive data were found in the literature. Nickel catalysts on silica–alumina were prepared by a proprietary chemisorption technique. After calcination at 540°C, no evidence of nickel phases could be detected by XRD, whereas impregnated catalysts usually showed evidence of an NiO phase. Table 4 gives surface area data and various calculated values. The important point to observe is the rather large $\Delta A$ values calculated from the experimental data. Using Eqs. (2)–(4), values of average crystallite sizes, $\bar{d}_B$, were calculated [$\bar{d}_B$ replaces 40 in Eq. (2)]. These values are consistent with the failure to observe the nickel crystallites by XRD. Catalyst 3 was obtained by reduction of catalyst 2, and its $\bar{d}$ value is in reasonable agreement with that calculated from the data of catalyst 2, assuming NiO is converted to Ni without crystallite breakup or sintering. It can be concluded from these results that the sulfided Co–Mo catalyst should show similar effects if a separate phase of small crystallites existed.

In summary, the results presented here seem to be in accord with the monolayer model and at variance with the separate phase model for sulfided as well as oxidized catalysts. It is obvious that further research is needed before either model can be considered firmly established for the case of the mildly sulfided catalyst.

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