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Physicochemical Investigations and Catalytic Activity Measurements on Crystallized Molybdenum Sulfide–Cobalt Sulfide Mixed Catalysts*

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Crystallized molybdenum sulfide–cobalt sulfide mixed powders were investigated for surface area, density, crystalline parameters, sulfur content and catalytic activity. They possess relatively high intrinsic activities in the hydrogenolysis of thiophene and the hydrogenation of cyclohexene in a sulfur-containing medium. The addition of a small amount of cobalt to pure MoS_2 simultaneously decreases the catalytic activity and the *c* parameter of MoS_2. A maximum of activity of the mixed catalysts is observed for a Co/(Co + Mo) ratio of 0.30–0.40 and is attributed to the synergetic action of the MoS_2 and Co_9S_8 phases. These phases are apparently in strong interaction. Much more sulfur is present in the powders than is required in the structure of MoS_2 and Co_9S_8. This sulfur is probably a component of the synergetic system.

INTRODUCTION

In previous publications (*1*, *2*), we reported our results concerning the catalytic activity of mixed molybdenum sulfide–cobalt sulfide prepared by a special technique. Although these catalysts contain no carrier, they exhibit high activities in the hydrogenolysis of thiophene and the hydrogenation of cyclohexene in a sulfur-containing medium. Their activity in the isomerization of cyclohexane was comparatively moderate. The activities per gram of sulfides in the first two reactions have values close to those calculated for industrial cobalt–molybdenum catalysts. A maximum activity for the three reactions is observed for a Co/(Co + Mo) ratio of 0.20. Unfortunately, these catalysts are very poorly crystallized, and our study, except for EPR measurements (*3*), could not progress much further.

Gently recrystallized samples retain relatively high catalytic activities in hydrogenolysis and hydrogenation. The present publication concerns surface area, density, crystalline parameters, sulfur content and activity measurements in recrystallized powders with Co/(Co + Mo) ratios varying from 0 to 0.6. It is known that hydrotreating catalysts attain a stable activity only after having worked for some time. In this work, special attention was paid to the modifications occurring during catalysis.

METHOD

The catalysts were prepared from the amorphous samples used in the previous studies (*1*, *2*). These amorphous catalysts had been prepared by co-digesting MoO_3 and Co_3O_4 in ammonium sulfide. The samples had been subsequently treated for 4 hr at 500°C in a mixture of 20% H_2S and 80% Ar, and subjected to vacuum for 2 hr (400°C, 10^{-2} mm Hg). The additional heat treatment for obtaining the recrystallized

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samples was conducted under argon and comprised the following cycle: heating from room temperature to 1000°C in 3 hr, holding at 1000°C for 4 hr, and cooling to room temperature in 15 hr.

The density of the samples was measured with a Beckman Model 930 air comparison pycnometer, or by xylene pycnometry. The samples were previously degassed under vacuum. Total porosity and pore diameters were measured by mercury porosimetry. The sulfur content was determined by dissolving the sample in aqua regia and using barium sulfate gravimetry.

The crystalline parameters were measured from Debye-Scherrer films (360 mm diameter camera), obtained with $CoK_{\alpha}1$ radiation, with α-alumina as the internal standard (*4*). They were calculated using a computer program similar to the one described by Burnham (*5*).

Catalytic activity measurements were made at 300°C, 30 atm, and with a total hourly space velocity of 4 hr^{-1}. The liquid feed contained 6% weight cyclohexene in *n*-heptane and 575 ppm thiophene. The H_2 (STP)/hydrocarbon (liquid) volume ratio was 600. Hydrogenolysis of thiophene is nearly complete under these conditions. The activities reported in this paper concern the hydrogenation of cyclohexene.

It was verified that mass transfer processes could not be rate limiting. Concerning extragranular mass transfer, experiments were made in which the volume V of the catalytic bed and the flow rate R_F were changed simultaneously in such a way that R_F/V remained constant. Conversion remained unchanged. This demonstrated that the linear velocity of the reactant in the catalyst bed had no influence and, consequently, that no extragranular mass transfer limitations existed. Concerning intragranular limitations, the Thiele modulus was calculated for conditions corresponding to the maximum rates of reaction observed in our experiments and for the samples having the most unfavorable pore structure. The diffusion coefficient which was taken in these calculations, i.e., 0.0372 cm^2s^{-1}, has been evaluated by making use of the Satterfield equation (*6*). The maximum Thiele modulus, for our most unfavorable experimental conditions, was 0.35, corresponding to an effectiveness factor close to 1.

The conversion of cyclohexene was taken as a measurement of the activity of the catalysts. The analysis was made by gas chromatography. Results are expressed as raw conversions, calculated as the weight percentage of cyclohexene converted, in the first stages of the reaction (after 0.5 hr) and when the activity is stabilized (after 3.5 hr). The instrinsic activity is calculated by dividing the raw conversion by the surface area of the catalyst.

The various results concern either (i) *fresh catalyst*, i.e., unused catalysts or, for catalytic measurements, those taken at the end of the first 0.5 hr of the catalytic run, or (ii) *steady state catalysts*, i.e., catalysts having reached their stable activity (after 3.5 hr).

RESULTS

I. *Surface Area*

The specific surface areas of the various samples, when fresh and after having attained stable activity, are indicated in Fig. 1. The specific surface area of the fresh catalysts diminishes when the Co/(Co + Mo) ratio increase. Except for the sample containing only molybdenum,

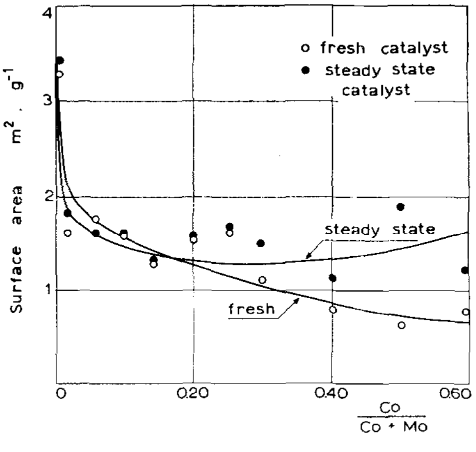

FIG. 1. Surface area of the mixed sulfides.

all steady state catalysts have approximately the same specific surface area. These effects are a consequence of a substantial increase of the surface area of catalysts with Co/(Co + Mo) ratios greater than 0.2 after operation.

II. *X-Ray Data*

The most significant X-ray diagrams are presented in Fig. 2, where the left part corresponds to fresh catalysts, and the right part to steady state ones. The results obtained with catalysts with Co/(Co + Mo) ratios of 0, 0.01, 0.15 and 0.50 are represented in this figure, where the principal Miller indices have been indicated (MoS_2: top; Co_9S_8: low middle, $CoS_{1.035}$: bottom).

The sample containing pure MoS_2 is poorly crystallized. Nevertheless, the hexagonal MoS_2 phase is easily identified on the X-ray diagram.

All samples with a Co/(Co + Mo) ratio greater than 0.005 are sufficiently crystallized to make possible the identification of the phases and the determination of the lattice parameter. For compositions characterized by a Co/(Co + Mo) ratio lower than 0.2, only two phases are apparent, namely hexagonal MoS_2 and Co_9S_8. Above this composition, the sulfide $CoS_{1.035}$ (7) is also present, but only in fresh catalysts. It is reduced to Co_9S_8 under the operating conditions. Except for this difference, no significant structural modification occurs between the fresh and the steady state catalysts (Fig. 2).

Certain X-ray lines of pure MoS_2 are relatively narrow, whereas others are broad. The lines corresponding to planes

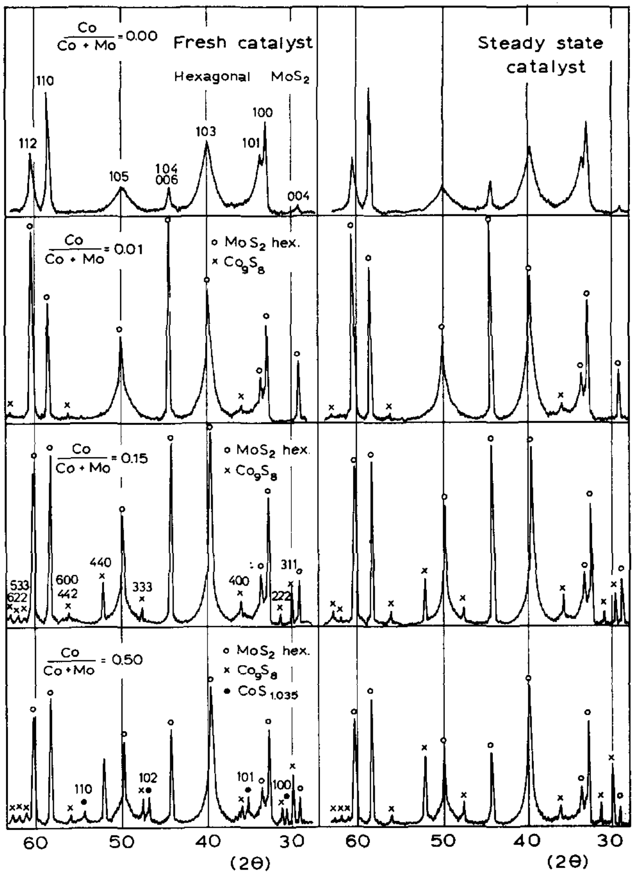

FIG. 2. X-Ray diffractograms.

parallel to the c axis, i.e., the (110) and (100) planes, are narrow. The maximum broadening occurs for the (105) plane. This plane is nearly parallel to the direction defined by a molybdenum atom and two immediately adjoining sulfur atoms (*8*). With increasing Co content, the lines corresponding to (101), (103) and (105) indices gain higher intensity, but remain relatively broad. Those with (004), (006) and (008) indices become considerably narrower.

The lattice parameters of Co_9S_8 and $CoS_{1.035}$ are those given in the literature (*7*). The parameter c of MoS_2 varies considerably with the composition of the mixed mass (Fig. 3), while a remains constant. The values of a and c for pure MoS_2 in Fig. 3 are those found in the literature (*8, 9*).

III. *Density*

The density of fresh and steady state catalysts vs composition is plotted in Fig. 4. In addition, the theoretical straight line giving the density of mixtures of MoS_2 and Co_9S_8 is presented. The experimental curves differ significantly from the theoretical line. Both are S-shaped, the one corresponding to the stable state of the catalysts being somewhat flattened.

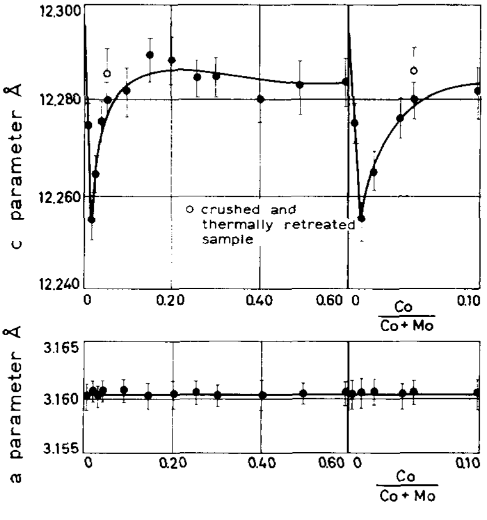

FIG. 3. Lattice parameters of the hexagonal MoS phase in the mixed catalysts.

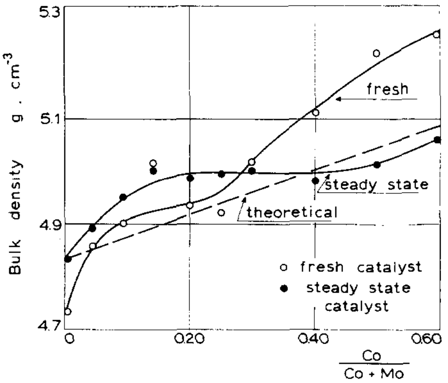

FIG. 4. Density of the mixed catalysts.

IV. *Sulfur Content*

The sulfur content in fresh and stable catalysts is plotted in Fig. 5. The theoretical content of a mixture of MoS_2 and Co_9S_8 is also indicated. All catalysts contain a considerable excess of sulfur. This excess changes significantly from fresh to stable catalysts. Changes are opposite for catalysts with Co/(Co + Mo) ratios lower and higher than 0.10–0.20.

V. *Catalytic Activity*

Figures 6 and 7 indicate the initial variations of activity of the various catalysts.

Initial and stable catalytic activities are plotted in Fig. 8. For compositions characterized by a Co/(Co + Mo) ratio lower than 0.20, the reaching of the stable state is accompanied by a loss of activity of the catalysts. The opposite is observed for ratios greater than this value.

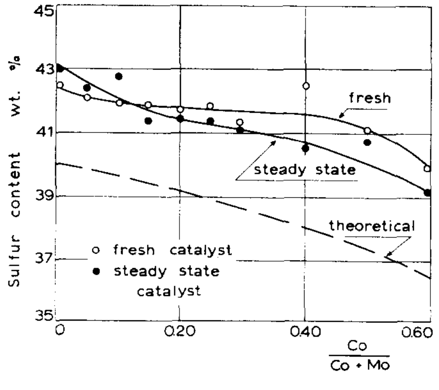

FIG. 5. Sulfur content of the catalysts.

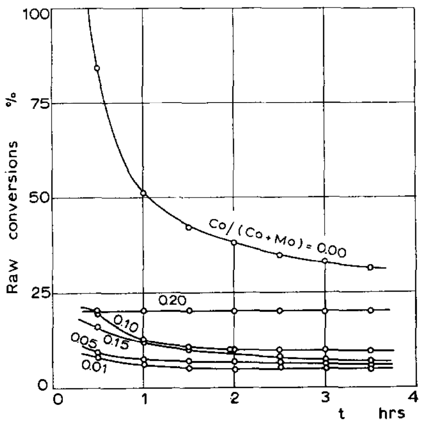

FIG. 6. Initial variations of the catalytic activity [Co/(Co + Mo) $\leqslant$ 0.20].

The intrinsic activities of the catalysts in their stable state were calculated. The intrinsic activity vs Co/(Co + Mo) ratio is plotted in Fig. 9. Maximum activity is reached for a ratio near 0.30–0.40. A very marked minimum is observed for very low Co/(Co + Mo) ratios.

DISCUSSION

I. *General Remarks*

A first remark concerns the variations in the properties the catalysts undergo after having been in operation. For practically all properties, three composition ranges, as characterized by the Co/(Co + Mo) ratio, must be distinguished, namely 0–0.10, 0.10–0.35; and greater than 0.35. The modifications of the catalyst during operation go in opposite directions in the first and the last ranges, i.e., surface area and conversion decrease and density and sulfur content increase for Co/(Co + Mo) ratios lower than 0.10, whereas surface area and conversion increase, and density and sulfur content decrease for Co/(Co + Mo) ratios higher than 0.35. In the middle range (0.10–0.35), there is practically no modification of the properties after the catalyst has been subjected to the operating conditions. The middle range thus appears to be one of marked stability for the solid mixture.

A second remark is that all structure or composition properties show some irregularity. The sulfur content is always higher than that calculated from the

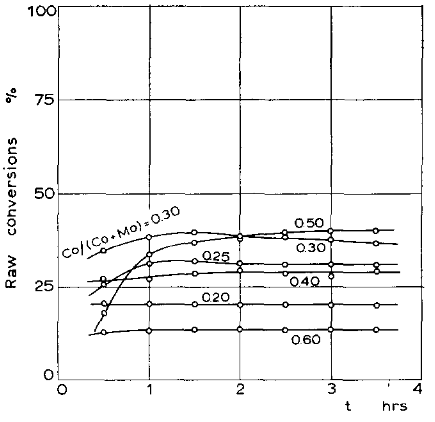

FIG. 7. Initial variations of the catalytic activity [Co/(Co + Mo) $\geqslant$ 0.20].

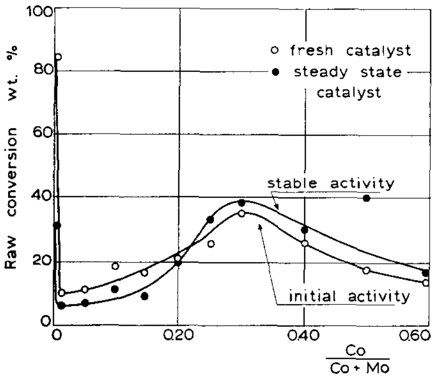

FIG. 8. Initial and stable catalytic activities in the hydrogenation of cyclohexene (raw conversions).

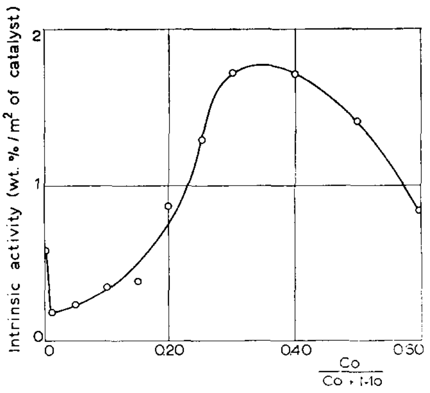

FIG. 9. Stable intrinsic activities in the hydrogenation of cyclohexene.

crystallographic composition. The density is practically never that of a mixture of MoS_2 and Co_9S_8 and varies in an intricate way. The parameter c of MoS_2 varies conspicuously. The opposite variation of the different properties in the Mo and Co rich ranges, together with these irregularities, points to an unusual complexity of the solid system.

We cannot presently interpret all the phenomena observed. We shall restrict our discussion to a few points where we believe our results allow tentative explanations.

II. *Very Low Cobalt Contents* ($Co/(Co + Mo) < 0.01$)

Let us first consider Fig. 3 illustrating the variation of the c parameter of MoS_2, and Fig. 9, relative to the intrinsic catalytic activity. The curves exhibit some similarity, i.e., the values of both the c parameter and the activity radiply decrease when a small amount of cobalt is present in the mixed catalyst, reach a minimum for $Co/(Co + Mo) = 0.01$, and then increase.

The variations observed for low cobalt contents do not relate to any previous observations for cobalt–molybdenum systems. They are discussed first.

Molybdenum sulfide, when pure, possesses notable catalytic activity, as indicated in Figs. 8 and 9. The addition of a small amount of cobalt ($Co/(Co + Mo) = 0.01$) considerably lowers this activity. Because of the extremely careful preparation method, cobalt is very intimately mixed with molybdenum. The results are therefore most easily interpreted assuming that cobalt is associated with the MoS_2 phase and negatively promotes it. The changes in the c parameter confirm an intimate interaction of cobalt with the MoS_2 lattice. The addition of small amounts of cobalt brings about a better crystallinity as well as a decrease in surface area. These modifications also indicate a very strong effect which is only possible if an intimate association is formed. The simplest hypothesis is that a certain amount of cobalt enters the MoS_2 lattice, either penetrating into vacancies of the MoS_2 lattice, or as a substitute for molybdenum atoms, or as an interstitial species between two MoS_2 layers.

The X-ray diagrams of MoS_2 show that this substance usually has a very disordered structure. Mering and Levialdi (*10*) mentioned a molybdenum sulfide which contained a very large amount of metal vacancies. The high sulfur content and the low density observed for our fresh MoS_2 sample are consistent with these findings. Therefore, it seems possible for the MoS_2 structure to accommodate foreign atoms. The Mo–S bond length (2.42 Å) in the layers of the MoS_2 structure (*11*) and Co–S (2.39 Å) in Co_9S_8 (*12*) are not very different. A substitution of cobalt for molybdenum atoms would therefore leave the a parameter practically unchanged. The intensity of the ($00l$) lines of MoS_2 is considerably increased for samples containing a small amount of cobalt (Fig. 2). This suggests that the presence of cobalt induces a more regular stacking of the MoS_2 layers.

The preceding paragraphs give arguments in favor of the possibility of introducing some cobalt into the MoS_2 lattice, but do not allow any conclusion concerning the position of the cobalt atoms (as substitutes to Mo or as interstitials). Our results leave little doubt that some association of very small amounts of cobalt with MoS_2 actually occurs, but without giving many clues concerning the position of the cobalt atoms in the MoS_2 lattice. It could be remarked that in the case where the effect of the introduction of cobalt would be only to change the vacancy concentration, the number of vacancies in the MoS_2 lattice would very likely increase, rather than decrease, as the parameter c decreases. But it could also be argued that such an effect would be very important with regard to the small impurity atom concentration. Another hypothesis would be that the c distance between layers, which are held together only by van der Waals forces, responds, with a high sensitivity, to changes in the charge distribution inside the layers.

Whatever the nature of the mechanism of these changes, our results indicate that they induce, or are accompanied by, an important decrease of the catalytic activity.

Before concluding this part of the discussion, it should be noted that the present solid solution of cobalt in MoS_2 is probably not similar to the interstitial compounds of MoS_2 which have been described (*13*), because this insertion always brings about a degeneracy to monoclinic structures.

III. *Intermediate Low Cobalt Contents*
$(0.01 < Co/(Co + Mo) < 0.05)$

When the cobalt content is in excess of 1% (i.e., $Co/(Co + Mo) > 0.01$), the *c* parameter of MoS_2 progressively recovers its initial value. A hypothesis is that, with more cobalt being present, the nucleation of the Co_9S_8 phase is easier, and that the cobalt dissolved in MoS_2 is progressively segregated. This hypothesis is confirmed by an experiment in which a sample with 5% at. Co was thermally retreated under argon. The *c* parameter of MoS_2 in this sample significantly increased and practically reached the normal value (Fig. 3).

It should be noted that the catalytic activity does not recover as quickly as the *c* parameter when more cobalt is present. We have no explanation for this fact.

IV. *Higher Cobalt Contents*
$CO/(CO + Mo) > 0.05)$

We now come to a discussion of the effects observed for $Co/(Co + Mo)$ ratios higher than 0.05. The most important fact is the maximum catalytic activity for a $Co/(Co + Mo)$ ratio near 0.30–0.40. This maximum can no longer be attributed to a change in the MoS_2. The intrinsic activity of MoS_2, even pure, is actually much lower, and no further change in the lattice parameters is observed. There is clearly a synergy between MoS_2 and Co_9S_8. Although retaining their individuality, these phases act as a new and more active catalyst.

This result is important for the understanding of cobalt–molybdenum catalysts. A synergy is observed in supported industrial catalysts. Maximum activity occurs for $Co/(Co + Mo)$ ratios of 0.20–0.40 (*14, 15*). The same effect was observed with our amorphous masses for a ratio of 0.20. In neither instance is it possible to decide whether molybdenum and cobalt sulfides form a compound or are segregated. It is very likely that the catalytic activity of the crystallized powders is of the same nature as in the other catalysts. Our findings thus suggest that this activity is always of a synergetic nature and separate constituents are present in all catalysts.

Our results give some clues concerning the interactions which could explain this synergy. MoS_2, when in the presence of Co_9S_8, is more perfectly crystallized than when pure, even when its crystalline parameters are normal. There must be strong interactions between both phases for promoting this better crystallization. Some degree of epitaxy between adjacent phases could explain the nucleating effects that our results suggest, namely those allowing Co_9S_8 to "pump" the cobalt out of the MoS_2 solid solution or to promote the crystallization of MoS_2. Very strong interacting forces probably are in action. It is striking, in this respect, that although the catalysts contain excess sulfur, the density of this element being only 2.07 g cm^{-3}, their bulk density is sometimes increased well beyond the theoretical densities of the mixture of pure MoS_2 and pure Co_9S_8, which range from 4.8 to 5.2 g cm^{-3} (Fig. 4). The interacting forces apparently vary considerably in intensity with the composition of the mixture, as indicated by the variations in density. The S-shape of the corresponding curves (Fig. 4) has no equivalent in the variations of the sulfur content. In the case of the stable catalyst, for example, the amount of excess sulfur varies only slightly with the $Co/(Co + Mo)$ ratio. The plateau observed in the density curve could indicate a progressive slackening of these forces. Maximum catalytic activity, as well as the relatively greater stability of the system mentioned earlier, are observed in a composition range where these forces seem to be partially relaxed.

Our results thus lead to conclusions

which are somewhat different from those formerly proposed in the literature. It has been suggested that the increased activity of MoS_2 (or WS_2) in the presence of cobalt (or nickel) results from a modification of the MoS_2 (or WS_2) structure which allows the creation of active sites. Beyond the optimum $Co/(Co + Mo)$ ratio, cobalt would start blocking the active sites. A detailed picture of such possible modifications, in terms of surface defects, has recently been proposed (*16*). Two distinct mechanisms have to be assumed, i.e., one leading to the formation of catalytically active defects, by incorporation of cobalt into the lattice (either in the bulk or near the surface) and another leading to a poisoning of these active sites by cobalt. Cobalt would thus be both activator and poison. An additional difficulty with this interpretation is that, with increasing overall quantities of cobalt ($0.01 < Co/(Co + Mo < 0.5$), less cobalt remains in the MoS_2 lattice. This indirect result, deduced from the variations of the c parameter, is supported by more direct magnetic susceptibility measurements in the case of Ni in WS_2 in a similar concentration range (*16*). Thus, the less activator incorporated in the lattice, the more effective would be the activation. For these reasons, all these interpretations should be questioned. The incorporation of cobalt into the bulk clearly reduces the catalytic activity. It should thus be assumed that incorporation of cobalt into the bulk is deleterious, whereas the incorporation into the superficial layers of the MoS_2 crystallites is beneficial. Such an interpretation is complicated and rather unsatisfactory. Furthermore, our results demonstrate that the segregation of cobalt, as a Co_9S_8 phase, which obviously reduces the cobalt-induced defects, far from being harmful to the catalytic activity, is very favorable. Moreover, it could also be reasoned that, when not dissolved in MoS_2, cobalt could more easily poison the active sites. Our results still give arguments against this interpretation.

We are thus led to a much simpler conclusion, namely that of a catalytic synergy between adjoining distinct phases. This synergy could be classically explained in terms of electron transfers between junctions (*17*). Various examples of such transfers have been reported in cases of mixtures of a metal with an oxide, and some in the case of two oxides (*17*). Such transfers are theoretically also possible between sulfides. If this is the mechanism involved, one would expect the optimum effect to occur for mixtures containing amounts of both components of the same order of magnitude, which is the case in molybdenum sulfide–cobalt sulfide systems. Doping effects brought about by dissolution of impurities in solids, on the contrary, usually appear for rather small quantities of the doping constituent.

The two interacting phases would be Co_9S_8 and MoS_2. Our results show, in conformity with results from various authors, that MoS_2 in the mixture has a quite different texture than when pure. Cobalt obviously allows MoS_2 to crystallize better. This might be interpreted in terms of the presence of cobalt near the growth defects of the MoS_2 crystallites (*16*). This is the MoS_2 modification which is active and sensitive to electronic transfer promoting. But our point is that at least part of the promoting effect is caused by some electron transfer from or to Co_9S_8. We additionally suspect that the right MoS_2 modification has actually a *depressed* activity (Fig. 9, low cobalt contents), compared to pure MoS_2, so that the electronic promotion has to increase the activity from this low value, through the restored activity of pure MoS_2, up to quite substantially increased activities [by a factor of about 3 (Fig. 9)].

V. *Sulfur Content*

The sulfur content in supported catalysts is always found to be lower than the theoretical value (*15*). The reason certainly is that the transformation of the starting oxides to sulfides is not complete. Our study shows that a substantial amount of sulfur in excess of the stoichiometric content of the sulfides is actually present. This excess could be a necessary part of the synergetic association.

VI. *Possible Influence of Undetected Amorphous Phases*

Our observations do not preclude the presence of amorphous phases in our samples, although the recrystallizing treatment is carried out at a very high temperature (1000°C). The very good crystallinity of WS_2 samples prepared at a lower temperature (900°C), as well as the spectra obtained after a treatment of pure MoS_2 at 1000°C (*18*), or after a treatment of other molybdenum sulfides in hydrogen at 800°C (*19*), suggests that very little, if any, amorphous phase should be present in our samples. But even this possibility could not modify our conclusions, because the catalytic activity of the amorphous molybdenum sulfide–cobalt sulfide phases is well known from our previous studies (*1*, *2*). In particular, the curve giving the hydrogenation activity vs cobalt content presents an overall concavity towards the bottom of the figure in the range of Co/(Co + Mo) ratios 0–0.3, whereas the concavity is towards the top with the recrystallized samples (Figs. 8 and 9). Consequently, by subtracting the possible effect of amorphous phases we would just *increase* the effects already apparent on Figs. 8 and 9.

CONCLUSION

The catalytic system in cobalt–molybdenum sulfides results from a delicate balance of many factors, some of which certainly lie in the chemical surface interactions between MoS_2 and Co_9S_8. Three major conclusions emerge from our discussion.

The first conclusion concerns the effects observed at very low cobalt contents. The incorporation of cobalt into the MoS_2 lattice, which apparently leads to a metastable compound with a very low miscibility domain and a strong tendency to segregation, is harmful to the catalytic activity. This incorporation of cobalt brings a marked decrease of the *c* parameter of MoS_2.

The second conclusion concerns composition ranges comparable to those where synergy effects between molybdenum and cobalt are observed in conventional catalysts. A mixture of distinct MoS_2 and Co_9S_8 phases shows catalytic synergy effects, which are best explained by interfacial interactions between phases. These effects are probably similar to those responsible for the catalytic synergy observed in the usual supported hydrotreating catalysts.

An additional observation is that the domain of maximum activity of the mixed system seems to correspond to a greater stability with respect to the influence of the external atmosphere on surface area, density and sulfur content modifications. This could suggest that the interfacial interaction between MoS_2 and Co_9S_8 somehow buffers the action of the external medium on the solids. This buffering capacity might be linked to the increased catalytic activity.

The MoS_2–Co_9S_8 system seems to constitute an example of what was once called the adlineation theory of catalysis (*20*, *21*) and can now be explained in terms of electron transfers between adjacent phases (*17*). This is probably the first example concerning mixtures of sulfides. Presumably, electron transfers between adjoining phases, together with extra transfers caused by excess sulfur, adjust the catalytic activity of MoS_2 (and/or, possibly, of Co_9S_8) to a more favorable value.

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