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Catalytic Hydrodesulfurization

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I. INTRODUCTION

The present review is an attempt to up-date several previous reviews [1-13] devoted to hydrodesulfurization and related hydrotreating processes.

Hydrodesulfurization of sulfur-containing petroleum fractions has long been one of the major catalytic operations in the petroleum industry. The need to exploit the potential value of many fractions which were not treated previously, as well as the growing environmental constraints, have led in recent years to many additional developments. Many new types of hydrodesulfurization catalysts have been introduced on the market, and many new processes or modifications of processes have been developed. New data have thus become available and this justifies the present review.

The scientific approach to the study of hydrodesulfurization and hydrotreating catalysts has changed considerably in the last few years. It is known that these catalysts become extensively or completely sulfided during their life in the industrial reactor. Consequently, many people familiar with the corresponding industrial processes have long suspected that the active phases of these catalysts were also sulfided. However, most of the scientific information on this subject has been concerned almost exclusively with the oxide or with partially sulfided forms of the catalyst. There are many reasons for this. The catalyst which is charged to the catalytic reactor is in the oxidic form. Early in the development of hydrodesulfurization catalysts it was noticed that the preparation step was as critical here as in other fields of catalysis. It was thus not unnatural to focus many studies on the oxidic form. Furthermore, catalysts which had seen service for some time (and even for relatively long times) apparently or actually still contained substantial amounts of the oxidic phases of the active components. Possibly, some investigators have been misled by the fact that the oxidic forms (at least under certain conditions) have a higher desulfurization activity than the sulfides [14, 15] and did not (or experimentally could not) realize that this activity was only transient. This additional reason explains why so few investigations have been initially directed toward the phenomena involved in the genesis of the sulfided form of the catalyst and toward a thorough study of the nature of the active species. The first desulfurization catalysts were monometallic. The present review will concern the usual hydrodesulfurization catalysts, namely cobalt-molybdenum, nickel-molybdenum, and similar systems with tungsten, in their sulfide form. We shall examine in the first section the main arguments

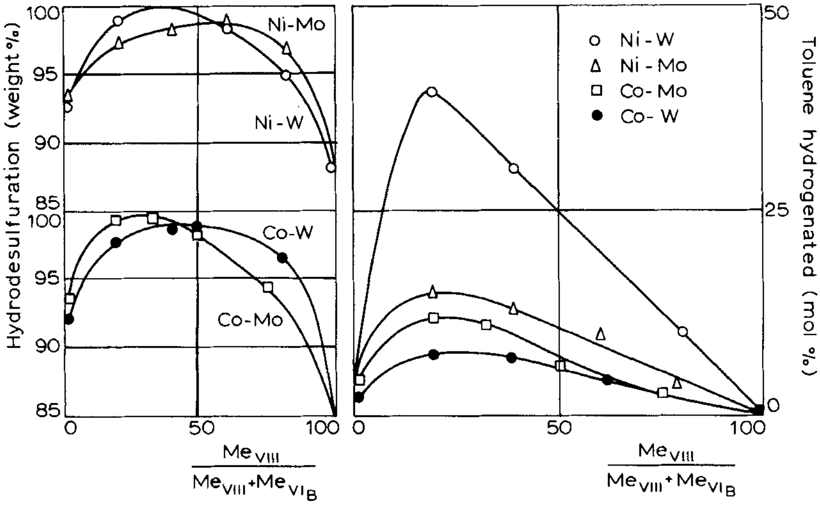


FIG. 1. Influence of nature and proportion of Groups VIII and VIB metals deposited on γ-alumina [16]. Left: hydrogenolysis of thiophene. Right: Hydrogenation of aromatics.

which have led us to focus our attention on sulfide phases. Then we shall study the various methods for preparing the active phase after briefly discussing the structure of compounds obtained by preparing the precursors by impregnation. We shall discuss the physicochemical investigation of the sulfide phases for both: unsupported fully sulfided active compounds and supported catalysts. We shall emphasize the relationships between the precursor in the oxide form and the active sulfide phase. The last part of this review will be devoted to a discussion of the models which have been proposed to explain such reactions.

The majority of data have been obtained on the Co-Mo system. The other systems (Ni-Mo, Co-W, Ni-W) have been studied less, but it is possible to generalize in most cases from the results obbained on Co-Mo catalysts. The comparison of these various systems has been summarized by Ahuja [16] as shown in Fig. 1. It is obvious that all the functions of the catalyst are not identical and that the ratio hydrogenolysis/hydrogenation is not the same for all catalysts, but the general behavior of all the catalysts is the same, and the synergetic effect occurs in all cases at almost the same ratio of MeVIII/MeVIII + MeVIB if (1) the methods and conditions of preparation of the catalysts are the same, (2) the same support is used and, (3) the nature and amount of promotors are identical.

II. GENERAL INFORMATION ON OPERATIVE CATALYSTS

In this section we shall outline the general information concerning the real composition of operative catalysts. The review will be centered on the role of the sulfides of Group VI and Group VIII elements in the chemical phenomena involved in hydrotreating. The present section summarizes the arguments proving the overwhelming importance of the sulfides in these processes.

A. Thermodynamic Data

A first set of arguments indicating that sulfides are the active phases comes from thermodynamic considerations. Indeed, the latter indicate that the only stable compounds are the sulfides [14]. McKinley [1] reviewed the main data concerning the phase diagrams of the sulfides of nickel, cobalt, iron, molybdenum, and tungsten. He noted that, in the hydrodesulfurization temperature range, only a small fraction of 1% of H_2S in H_2 is necessary to convert the metals to the lowest sulfide (Ni_3S_2, Co_9S_8, FeS, MoS_2, WS_2). Furthermore, he also mentioned that to maintain the maximum activity of WS_2 and similar catalysts, a definite partial pressure of hydrogen sulfide is required. Experimental evidence of this behavior is discussed later [17-19].

B. Direct Analysis of Used Catalysts

Information concerning the composition of used catalysts is rather disappointing. It suggests that the transformation to sulfides is not complete. It is not surprising that such findings are observed after relatively short runs (less than 300 hr, for example) or after a catalytic operation at low pressure because these conditions are not representative of industrial practice. But even for industrial conditions, some authors mention that the degree of sulfidation of metals deposited on the support (γ-Al_2O_3) is not complete [16], as shown in Fig. 2. The amount of sulfur on the catalyst is lower than the value which would correspond to stoichiometry (e.g., MoS_2 + Co_9S_8 in the case of CoMo catalysts).

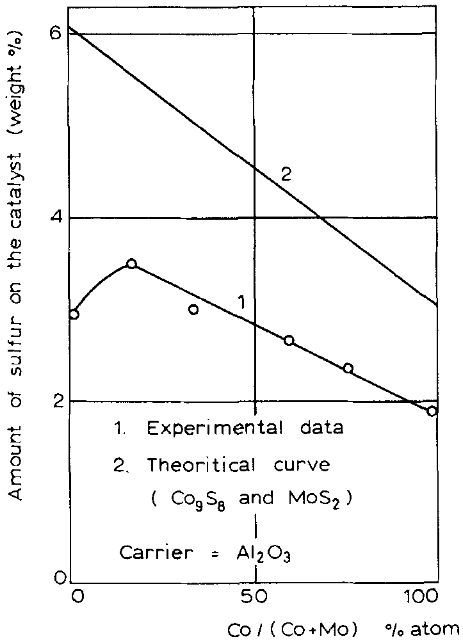


FIG. 2. Evolution of the sulfur content in a series of CoMo/ γ-Al_2O_3 catalysts [16].

One must consider the possibility that, in certain process conditions, the transformation to the sulfide is extremely slow or even possibly incomplete [20]. By gravimetric measurements, Kabe et al. [21] assumed that the average composition of the catalysts subjected to sulfidation is $CoSMoO_{1.5}S_{1.5}Al_2O_3$. Armour et al. [22] and Mitchell et al. [23] found no evidence for discrete Mo and Co sulfides, and they concluded that no more than one or two oxide ions, probably those bridging between Mo and Co, are replaced by sulfide. However, many observations may explain the apparent discrepancy between thermodynamic considerations and experimental results:

1. A number of the Group VIII and Group VI metals combine with the support and are withdrawn from possible sulfidation. On the other hand, it has been shown that bulk MoO_3 is partially sulfided by thiophene. More precisely, it seems that the sulfide is mainly distributed on the surface or near the surface [24].

The average thickness of the sulfide layer calculated from the values of the surface area of the solid and the density of bulk MoS_2 is 11.7 and 7.6 Å when the temperature of reaction of thiophene is, respectively 350 and 400°C [25].

2. If reduction-sulfidation is conducted under inappropriate conditions, MoO_2 may form. It is extremely difficult to reduce and to sulfide [26]. It is believed that the very careful start-up or activating procedures recommended by catalyst manufacturers or process licensors are designed, in part, to avoid such a phenomenon in normal situations.
3. Deposition of coke on the catalyst, if not accounted for in gravimetric measurements, may artificially minimize the sulfur content of the catalysts.
4. The sulfides of operative catalysts are extremely sensitive to oxygen [20, 27]. Any contamination by atmospheric oxygen leads to sulfur contents lower than the actual values.

Finally, it should be mentioned that x-ray diffraction, indicating the presence of compounds of Group VI and VIII elements, generally corresponds to sulfides and not oxides. Although the sensitivity of x-ray analysis is relatively low, this argument is in favor of the sulfides being the active phase.

C. Chemical Behavior of the Oxide and Sulfide Form of the Catalysts during Hydrotreatment

As it is not possible to get unambiguous data concerning the composition of industrial catalysts, more indirect arguments must be found. There are two kinds of arguments proving that the real, stable, active HDS species are the sulfided metals. These arguments are mutually complementary. The first kind stems from results indicating that the chemistry of hydrodesulfurization is abnormal when oxide phases are introduced and progressively changes as sulfidation proceeds. The second argument is that carefully unsupported sulfided catalysts behave very similarly to industrial catalysts while working normally.

1. Evolution of Initially Oxidic Catalysts

The most detailed picture of the behavior of the oxidic catalyst during the first stage of the reaction was presented by Sotani et al. [25]. During the first period of reaction (which they called the aging phase) on MoO_3, they showed that the main product resulting from the conversion of thiophene is butene. They detected 1-butene, cis- and trans-2-butene, but not H_2S. This means that the sulfur removed from thiophene by the reaction was consumed by the sulfidation of the oxide. The catalyst may be sulfurized either by the thiophene or by the hydrogen sulfide produced by the hydrodesulfurization of the thiophene. Other authors have shown that during this stage, molybdenum oxide is transformed to a mixture of MoO_2 and MoS_2 [28]. These compounds are detected by x-ray diffraction. A compound like MoOS seems to be excluded [29]. Furthermore, MoO_2 cannot easily be transformed into MoS_2 even at high temperature (800°C) [26, 30].

Another illustration of the transformation of the oxide into sulfide and the enhancement of the activity when both cobalt and molybdenum oxide are present was given by Zabala et al. [15]. They showed that when a mechanical mixture of pure MoO_3 and Co_3O_4 reacted under a high H_2 pressure with a charge consisting of thiophene, cyclohexene, and cyclohexane, the catalytic hydrogenolysis of thiophene is greater than for the pure oxide. During the first stage of the reaction, the initial sulfidation of the oxide causes a higher transformation of the thiophene than the actual catalytic reaction of the sulfided solid. It is worthwhile to note that the state of sulfidation of the molybdenum oxide seems to have a considerable influence on the catalytic behavior of the catalyst.

2. Catalytic Behavior of Fully Sulfided Samples

The results mentioned in the previous subsection indicate that, under operating conditions, oxidic catalysts are similar to the stable active catalysts and contain progressively more sulfides.

Fully sulfided catalysts, unsupported [31-36] or supported [16, 37, 39], have been prepared. The general level of activity, the kind of reactions catalyzed, and the shape of the activity vs composition curve are so strikingly similar to those of industrial catalysts that there is a strong presumption that the superficial active species are identical [40]. In addition, one should mention the very careful XPS measurements of Declerck-Grimee [38] who demonstrated the presence of MoS_2 at the surface of sulfided industrial or laboratory made $CoMo/\gamma\text{-}Al_2O_3$ catalysts. These results do not agree with earlier results of Mitchell et al. [29], probably because the sample of Declerck-Grimee et al. was studied without any contact with the atmosphere between the sulfiding treatment and the XPS analysis. Indeed, it is well known that solid sulfides are immediately superficially oxided when contacted by air.

III. GENESIS OF HYDROTREATING CATALYSTS

A. General

A general scheme for the preparation of hydrotreating catalysts was reported by Lepage [12]. The usual preparation of hydrotreating catalysts comprises the mixing of a support or a support precursor with salts of Group VI and Group VIII metals, drying, and calcining of the salts to the oxides [12]. Final activation generally occurs in the industrial reactor, either by the normal charge to be desulfurized or by special pretreatment (e.g., H_2S, CS, with H_2).

The first stage (contacting the support with the active species) is usually done by impregnation, either simultaneously by salts of Group VI and VIII metals or successively. In the latter case the first impregnation is usually that of a Group VI metal, e.g., molybdenum in the form of ammonium paramolybdate. Some authors have impregnated salts on $Al(OH)_3$ instead of γ-Al_2O_3. In this way the formation of spinel is favored [41]. Another possibility is to grind the support with the salts.

Numerous other special methods have been proposed; for example, grafting [42]. Using this technique, it is possible to obtain a better dispersed molybdenum on the surface.

Several additives are sometimes used in the preparation of hydrodesulfurization catalysts, e.g., Si, Na, B, F, and P.

The present section describes the genesis of the catalysts. As mentioned previously, several reviews have already discussed the oxidic form of the catalysts, namely the product obtained after the first three forementioned steps. We shall therefore update results on the characterization of this phase and emphasize the last step (i.e., reduction-sulfidation).

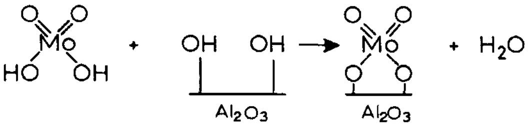
B. Physicochemical Characterization of the Oxide Precursors

There is a close relationship between the oxidic precursor structure and the sulfide active phase. Therefore it is important to consider first the oxide structure and outline the problems which can arise. What is the exact nature of the interaction between the oxide phase and the carrier? How do the nature of the support and the experimental conditions affect this interaction and the dispersion of the oxide phases on the support?

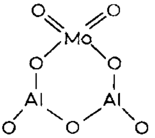
1. Interaction between MoO_3 or WO_3 and the Carrier

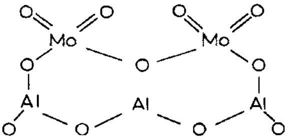
Al_2O_3

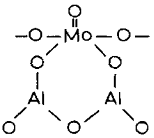
The interaction of molybdenum oxide with the alumina support has been discussed by many authors [4, 43-58]. The following interaction complex has been proposed:

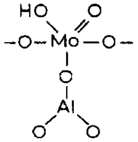


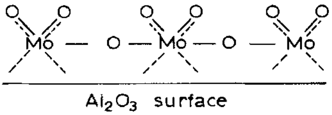
After the drying and calcination steps, the surface species obtained may be schematically represented by the following structures [47, 48, 51]:











Some authors suggest the epitaxial character of the monolayer, taking into account the structure of the alumina surface. Schuit et al. [4] describe the surface of the solid as follows: either $Al_{4/3}[Al_2O_4]$ + $2MoO_3$ (O_2 capping layer, $[Mo_2O_4]$ monolayer, $Al_{4/3}[Al_2O_4]$ outer alumina layer) or $[Al_2O_4]$ + $8/3MoO_3$ (O_4 capping layer, $Mo_{2/3}$ $[Mo_2O_4]$ monolayer, $[Al_2O_4]$ outer alumina layer), the monolayer being either in octahedral or tetrahedral coordination. On the other hand, Massoth developed another model of the molybdenum alumina system [59, 60] in the oxidic or partially reduced state. The model consists of a two-dimensional epitaxial monolayer of MoO_2 over a (110) γ-Al_2O_3 surface. The third O associated with the Mo^{6+} is located in the underlying oxide layer of the Al_2O_3.

Beside the formation of the monolayer, two other molybdenum compounds have to be considered: $Al_2(MoO_4)_3$ and bulk MoO_3. Molybdenum aluminate seems to be present only either for high molybdenum contents (detected by Raman spectroscopy [51]) or if the temperature of calcination of the solid is higher than 535°C [43-61]. However, Pott et al. [62, 63] consider that $Al_2(MoO_4)_3$ (detectable by luminescence spectroscopy by incorporation of C_2^{3+} tracer ions) cannot be formed if a wet method of impregnation is used during the catalyst preparation. On the other hand, bulk MoO_3 formation can be described as follows. First, it seems well established that the amount of free MoO_3 increases with the total load of the catalyst [61]. Furthermore, it decreases at constant load if the impregnation is made at pH 11 [64]. This may be the reason why impregnation is often done with ammonia or amines. It is reasonable to think that an optimization of the method of impregnation leading to a decrease or even an absence of free MoO_3 could result in a lowering of the useful molybdenum load of this type of catalyst. Furthermore, when bulk MoO_3 is formed it is associated with some impurities such as Ca [65]. It should be noted that the drying process has a strong influence on the formation of bulk MoO_3 species [66, 67].

Medena et al. [51] proposed a schematic representation of the various species of molybdenum formed on alumina by considering various loads of molybdenum on two supports of different specific surface area (Fig. 3a). The nature and amount of superficial species change with the amount of active phase and the surface of the support, all other conditions being equal.

SiO_2

In the case of molybdenum supported on silica, Castellan et al. [68], Gajardo et al. [69-71], and others [43, 62, 72, 73] have shown that, as in the case of alumina, a weaker interaction between silica and molybdenum exists. The proportion of the different Mo species present on the SiO_2 carrier depends on the molybdenum load and the preparation method (especially the calcination temperature [68-73]. In addition to combined molybdenum, free molybdenum is present. The amount of dispersed molybdenum bound to the surface of the carrier depends on the amount of molybdenum impregnated, as was shown by Delannay et al. [65].

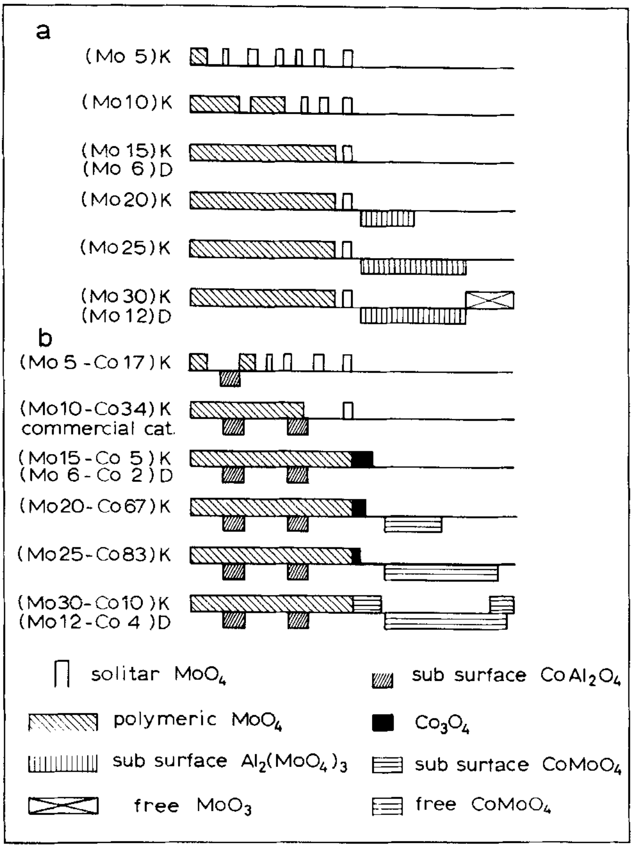


FIG. 3. Schematic repreaentation of the coverage of γ-Al_2O_3 with different molybdenum and cobalt species depending on the degree of surface coverage and nature of the support. (D: γ-Al_2O_3 = 80 m^2 g^{-1}; K: γ-Al_2O_3 = 240 m^2 g^{-1}) [51]. (a) Mo/γ-Al_2O_3. (b) CoMo/γ-Al_2O_3.

2. Interaction Between Group VIII Metals and the Carrier

The preparation and nature of the cobalt species present on alumina supports is quite clear and needs no elaboration. Bulk cobalt oxide Co_3O_4 may be present and $CoAl_2O_4$ may be formed. These two Co species are easily detected. Generally, the presence of free

Co_3O_4 is detected for solids containing more than about 1.5 atom% cobalt on alumina [49, 50, 74-77].

The trapping of cobalt by Al_2O_3 explains why so many efforts are made to decrease the reaction of Co with Al_2O_3 either by a precise order of impregnation, by promoting the reduction of cobalt [78], or by inhibiting the solid-state reaction between cobalt and Al_2O_3 [79].

The reactivity of Ni on a SiO_2 support has been reviewed by other authors [80].

3. Characterization of the Oxidic Form of the Cobalt Molybdenum System

Only the $CoMo/Al_2O_3$ system has been studied extensively by changing both the oxide content on the carrier and the atomic ratio Co/(Co + Mo) for the same amount of the oxide phase (15%). There are fewer results for the $CoMo/SiO_2$ system since the latter is less representative of industrial catalysts. However, by comparison with alumina, a better understanding of this system allows clarification of problems involving industrial catalysts.

The various species one can expect on $CoMo/\gamma\text{-}Al_2O_3$ oxidic catalysts are bulk MoO_3, MoO_3 monolayer, $Al(MoO_4)_3$, Co_3O_4, $CoAl_2O_4$, $CoMoO_4$, and "CoMo active complex."

The amount of these species depends largely on catalyst preparation. For catalysts containing the usual amounts of molybdenum, it seems that bulk MoO_3 formation only occurs with poor impregnation methods or with the presence of some impurities [65] in the impregnation solution.

If $Al_2(MoO_4)_3$ has been detected on Mo/Al_2O_3 catalysts, it seems that $CoMoO_4$ is formed at the expense of the $Al_2(MoO_4)_3$ species when cobalt is added to the Mo/Al_2O_3 catalyst [51]. The interesting points concerning the formation of $CoAl_2O_4$ are that:

1. $CoAl_2O_4$ concentration increases with increasing calcination temperature
2. Wet impregnation favors this species as compared to dry impregnation
3. A molybdenum monolayer on alumina enhances the dispersion of cobalt and the formation of $CoAl_2O_4$ [53].

This result is in contradiction with the interpretation of Gour et al. [81]. However, these authors observed that the samples prepared by impregnation of cobalt on $Mo/\gamma\text{-}Al_2O_3$ are blue compared to the greenish one prepared by impregnation on $Co/\gamma\text{-}Al_2O_3$

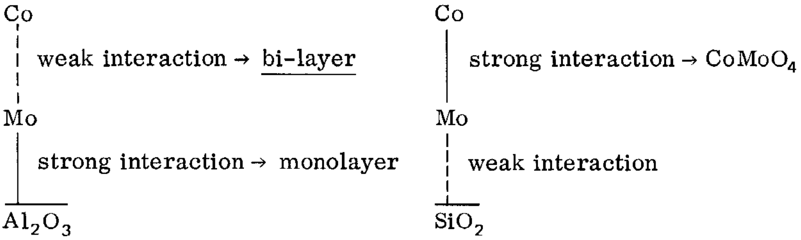
solid. The amount of free Co_3O_4 decreases for the same load when molybdenum is also present on alumina [77].

It is well established that a CoMo commercial HDS catalyst does not contain bulk cobalt molybdate. This was shown by Lipsch et al. [82] by IR and reflection spectroscopy, by Gajardo et al. [53] and Topsoe et al. [83] by Mossbauer measurements, and Villa et al. [84], Ashley et al. [49], and Ramaswamy et al. [78]. It does not exclude some interaction between cobalt and molybdenum. Richardson [85] was the first to propose an "active complex" of cobalt with molybdenum from magnetic measurements. Mone [86] has reported experimental evidence about the existence of a "cobalt molybdate" configuration. This author pointed out by IR and DRS the formation of a Lewis site band in the IR spectrum at 1612 cm^{-1} resulting from a cobalt-molybdenum monolayer interaction and, concomitantly, the formation of $CoAl_2O_4$. In this case the cobalt fraction remaining on the surface which forms a "cobalt molybdate" configuration depends on the calcination temperature. According to this author, Co occupies a "top" position in such a configuration. He observed the same phenomena in the NiMo/γ-Al_2O_3 catalyst. Interactions between cobalt and molybdenum were observed by Ishii et al. [87] using a MoO_3 extraction method. These authors detected the formation of some mixed cobalt molybdenum oxide on CoMo/γ-Al_2O_3 catalysts which seems to be different from the unsupported CoO-MoO_3 catalyst. Grimblot et al. [88, 89] reported the presence of Co_4Mo phases in the CoMo/γ-Al_2O_3 catalysts by reduction-gravimetric and XPS measurements. Recently Raman spectroscopy measurements corroborated their hypothesis [89]. Okamoto et al. observed by XPS a stabilization effect of cobalt on molybdenum [90]. The enhancing effect of cobalt on the dispersion of molybdenum observed by Martinez et al. [91] may account for a mutual action between both ions on the surface of carrier. The cobalt molybdenum interaction on the Al_2O_3 has been mentioned by Brown et al. [57]. These workers, using Raman spectroscopy, pointed out the presence of two bands at 941 and 952 cm^{-1} in CoMo/γ-Al_2O_3 catalysts which are also present in $CoMoO_4$. They indicate that cobalt may interact with molybdenum via terminal oxygen molybdenum bands (1006 cm^{-1}). Recently, Iannibello and Mitchell proposed the formation of Co-O-Mo bands due to the interaction between cobalt with the oxomolybdenum species [55]. Studying a series of catalysts with an atomic ratio Co/(Co + Mo) ranging from 0 to 1, Gajardo et al. [53] proposed a bi-layer structure of this oxidic compound in which Mo(VI) should be located in a tetrahedral oxygen environment, Co(III) being on this monolayer in an octahedral oxidic surrounding.

One can expect that the nature and amount of these species depend on the nature of the supports, the conditions of preparation, the temperature of calcination, the amount of the active phase, and the atomic ratio between cobalt and molybdenum.

Let us illustrate this with results obtained on CoMo/SiO_2 catalysts with a variable Co(Co + Mo) atomic ratio or the amount of oxide phase.

The formation of $CoMoO_4$ is ambiguous [9, 69, 70, 92]. This may be explained in the following way: the interaction between molybdenum and silica is weaker than with alumina as was previously reported. Thus one can expect a stronger interaction between cobalt and molybdenum. This fundamental difference of behavior between silica and alumina can be illustrated by the following scheme:



As shown later, it is reasonable to assume that the true active phase (after activation) proceeds from this bi-layer oxidic structure. Let us now summarize the structure of CoMo/γ-Al_2O_3 solids when the atomic ratio Co/(Co + Mo) ranges from 0 to 1 with an equal amount of oxidic phase (15 wt% oxidic) (Gajardo et al. [53]) (Fig. 4a).

This representation was deduced from XPS-DRS, electron microscopic and microprobe measurements, and a gravimetric study of the reduction by hydrogen. Another interesting parameter is the dispersion of both molybdenum and cobalt on the carrier as determined by the analysis of the intensities of the XPS lines and EPMA measurements and its comparison with the dispersion of the same species after sulfidation (Fig. 5).

The influence of amount of active phase and specific surface area of the carrier is illustrated in Fig. 3b (Medena et al. [51]).

Thus the structure of the oxidic phase depends on many parameters. Furthermore, we believe that by modifying the interaction between molybdenum and the carrier (by incorporation of doping agents), it is possible to change the nature of the bonds between Co and Mo and to modulate this interaction. In this context, let us recall the effect of some promotors:

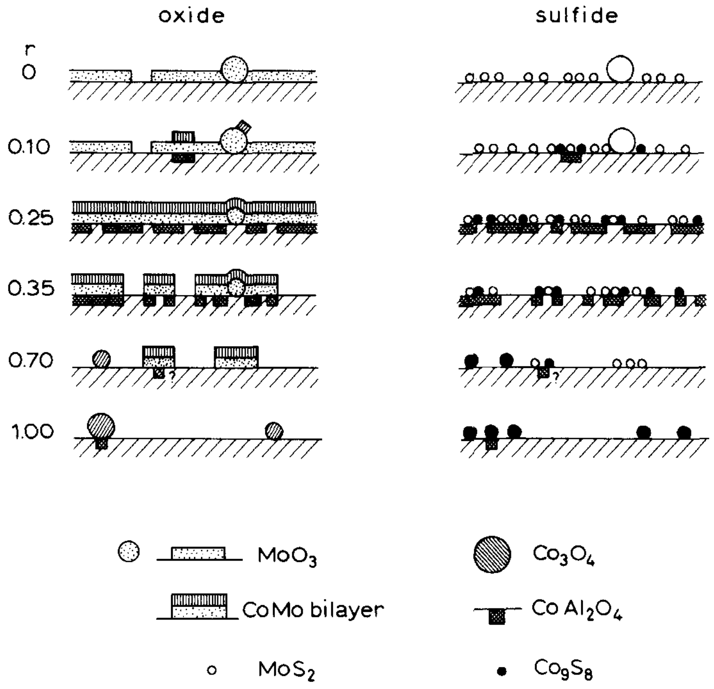


FIG. 4. Schematic representation of the various species on the surface of CoMo/γ-Al_2O_3 catalysts as a function of the atomic ratio r = Co/(Co + Mo) [123].

The addition of boron decreases the amount of spinel formation ($NiAl_2O_4$) [79]

The addition of gallium favors a more normal spinel [93]

The introduction of sodium increases the bulk Co_3O_4 content

P and F, though less studied, increase the catalytic reactivity [79-94]

4. Conclusion

It seems that for industrial and equivalent catalysts, the active "CoMo" complex, well dispersed on the alumina support, may be described as a bi-layer in which Mo(VI) dispersed as a monolayer on the surface is covered by a layer of Co(III), the dispersion of the

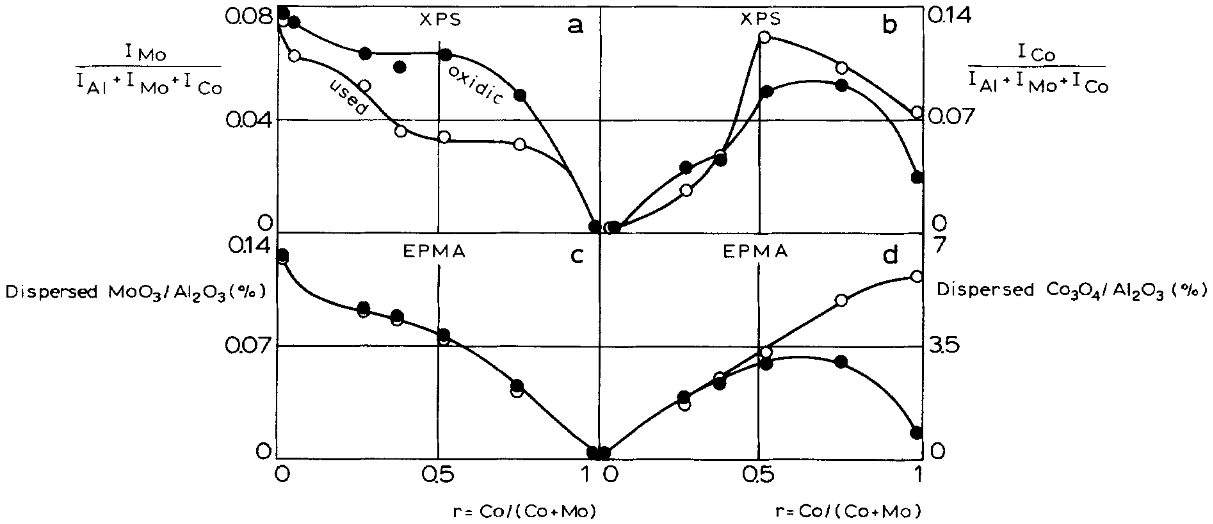


FIG. 5. Comparative dispersion of molybdenum and cobalt on the oxide precursor (open circle) and on the sulfided form (filled circle) measured by XPS and by EPMA [112].

cobalt species being improved by the molybdenum monolayer. However, the exact structure of this bi-layer is not yet well established.

For compositions which do not correspond to the usual loads [15% active phase for a Co/(Co + Mo) ratio equal to 0.3], the concentration of other species (bulk MoO_3 and Co_3O_4, $CoAl_2O_4$) increases.

C. Activation of the Oxidic Forms to the Sulfided Catalysts

The activation procedure is an important step in the preparation of the catalyst. For a better understanding we shall discuss reduction, sulfidation, and coupling of reduction with sulfidation for the cases of pure and supported oxides.

1. Reduction by Hydrogen

Unsupported Catalysts

The reduction of unsupported MoO_3 by hydrogen has been studied extensively during the last 10 years [95-98]. The amount of reduction depends on temperature and water vapor pressure. At 500°C, for example, using dry hydrogen, molybdenum trioxide is reduced to metallic molybdenum, while under H_2/H_2O mixtures at the same temperatures the reduction is stopped at MoO_2. The above results disagree with some previous ones but, in general, the water partial pressure is very difficult to control; especially in relatively deep beds intrinsic water vapor coming from the process itself may block the reactions at the MoO_2 stage. Although 400°C is too low a temperature to obtain the bulk reduction of MoO_3, surface reduction can nevertheless be observed by XPS [72]. When mixed or impregnated on MoO_3, cobalt oxide may accelerate the reduction of MoO_3 to MoO_2 or Mo but it has no influence on the reduction of MoO_2 to Mo [99].

Supported Catalysts

The behavior of the supported molybdenum oxide is completely different. Three main features characterize the phenomena: (1) the rate of reduction is higher on MoO_3 supported catalysts than on bulk MoO_3, (2) at the same temperature there is no induction period in the reduction, and (3) the amount of reduction is drastically smaller for supported catalysts [100]. The amount of the various reduced species of molybdenum has been investigated by many authors and especially by Hall et al. [45]. The high heterogeneity of the reduction is also corroborated by results of Kabe et al. [21], Massoth

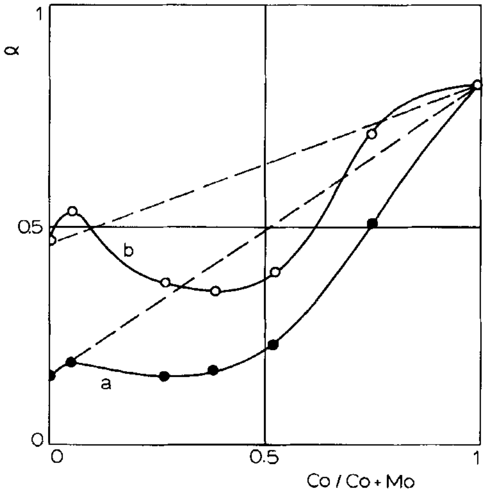


FIG. 6. Reducibilities of the catalysts after 10 hr of reaction at 400°C as a function of composition. (a) Assuming complete reduction of the metal oxide. (b) Assuming reduction of MoO_3 to MoO_2 [100].

[59], and Gajardo et al. [100]. By XPS measurements, Cimino [72] found that at 400°C the lowest oxidation state that can be obtained is Mo^{4+}. A fraction of Mo^{6+} is reduced to Mo^{4+} but part of it is in an oxidation state intermediate between 6+ and 4+. This Mo^{5+} intermediate was also proven by Masson et al. [101], Seshadri [102], Patterson [103], Hall [45], and Dufaux [104].

A greater degree of reduction of MoO_3/SiO_2 as compared to MoO_3/Al_2O_3 has been observed. This is due to the smaller degree of interaction between MoO_3 and SiO_2 than between MoO_3 and Al_2O_3, as already mentioned [69, 70].

An important feature is the behavior of CoMo supported catalysts under a reducing atmosphere in samples comtaining 15% of the active phase. Reduction inhibition was observed by Ratnasamy [105], Adamamska [106], and Gajardo et al. [100]. The latter showed that a minimum of reducibility was observed in the range which corresponds to the maximum of catalytic activity (Fig. 6). Two reasonable hypotheses can be proposed to explain this minimum:

1. Interaction between cobalt and molybdenum
2. Formation of some irreducible compound with Al_2O_3 such as $CoAl_2O_4$

In the first hypothesis, $CoMoO_4$ formation has to be excluded, as already mentioned. One has to consider either the Co_4Mo surface complex [89, 107] or the bilayer structure described earlier. The second hypothesis is consistent with the observed influence of Mo(VI) strongly bound to Al_2O_3 on the formation of a cobalt alumina surface compound. The molybdenum hinders the segregation of Co_3O_4 and favors the formation of $CoAl_2O_4$ [53, 65].

2. Sulfidation

Sulfidation is a most important process. It transforms the precursor oxide phase into the active sulfide phase.

Unsupported Systems

Let us examine what occurs on bulk molybdenum oxide. With a H_2/H_2S mixture, the transformation of MoO_3 into MoS_2 can be complete at high temperature [26, 108, 109] but at 500°C only MoO_2 can be detected by x-ray diffraction measurements and traces of MoS_2 by XPS analysis. The reduction occurs more rapidly in H_2-H_2S mixtures than in pure, dry hydrogen [26]. If the sulfidation is done on MoO_3 prereduced into MoO_2, the transformation into MoS_2 is never total even at high temperature, and the solid consists of a mixture of MoO_2 and MoS_2 [26]. Metallic molybdenum is quite easily transformed.

The same process occurs with a mixture of H_2 and thiophene [110], and the same observations concerning the extent and the rate of reaction can be made. The molybdenum oxide can be superficially sulfurized in two possible ways [30]:

$$MoO_3 + 2C_4H_4S + 3H_2 \rightarrow MoS_2 + 2C_4H_4 + 3H_2O \qquad (1)$$

or

$$C_4H_4S + H_2 \rightarrow H_2S + C_4H_4 \qquad (2)$$

$$MoO_3 + 2H_2S + H_2 \rightarrow MoS_2 + 3H_2O$$

The genesis of unsupported catalysts is summarized in Table 1.

Supported Catalysts

The reduction-sulfidation of supported catalysts is much more complicated than that of the unsupported ones, and there are many discrepancies between the observations and conclusions of various authors. However, much of the problem may be summarized by the following questions: Are well-defined molybdenum sulfide and cobalt

TABLE 1

Genesis of the Unsupported Catalysts

1. Reduction of the oxides	
$MoO_3 \rightarrow MoO_2$	Acceleration by Co, Co_9S_8, ... H_2S more active than H_2
$MoO_2 \rightarrow Mo$	No special remark
$Co_3O_4 \rightarrow Co$	No action of Mo or MoO_x
2. Sulfiding by H_2-H_2S	
$MoO_x \rightarrow MoS_2$	Co inactive
$Mo \rightarrow MoS_2$	Co inactive
$Co \rightarrow Co_9S_8$	Mo inactive
3. Sulfiding by sulfur containing hydrocarbons + H_2	
Pure $MoO_3 \rightarrow MoS_2$	The reaction is possible
Pure $Co_3O_4 \rightarrow Co$	Sulfidation of cobalt impossible in the absence of Mo or MoO_x
$Co_3O_4 \rightarrow Co_9S_8$ (in mixture)	Reaction possible if Mo or MoO_x is present
4. Coupling	
$MoO_3 + H_2S + (H_2) \rightarrow MoS_2$	Reaction possible starting from MoO_3
$MoO_2 + H_2S + H_2 \rightarrow MoS_2 + MoO_2$	Reaction slow and incomplete
$Mo + H_2S \rightarrow MoS_2$	Easy reaction

sulfide present on the surface of the activated catalyst? What are the true active species?

A detailed picture of the rates and stoichiometry of sulfidation of molybdenum-alumina catalysts has been published by Massoth [111]. He notes that, in the range of 350 to 420°C, the catalyst is not completely sulfided, the predominant reaction being an exchange between oxygen and sulfur. Mitchell et al. [23] from IR, electronic spectra, magnetic susceptibility measurements, and sulfur analysis concluded that cobalt and molybdenum are partly sulfided. For these authors the sulfur content is less than that corresponding to complete sulfiding. Spectroscopic changes on sulfiding indicate that the sulfide adds to MoO_4 tetrahedra and that not more than one or two oxygen ions, probably bridging between molybdenum and cobalt, are replaced by sulfur. The cobalt will be partially sulfided or not sulfided at all. [122]. These authors do not present evidence of discrete sulfides, i.e., MoS_2 or Co_9S_8.

The observations by XPS analysis of Hercules [103] are not in agreement with these results. If the catalyst is treated at 420°C, 89% of the molybdenum is in the MoS_2 form. Furthermore, the experimental Mo 3d $_{3/2}$ or 3d $_{5/2}$ ratio does not agree with the theoretical one. These authors have shown that sulfidation does not occur very quickly and that only 65% MoS_2 was formed after 35 min treatment. This means that there are no indications that after the treatment made by the authors the stable state is obtained, which one might expect after high-pressure reaction.

Additional data are supplied by Declerck-Grimee [74] who sulfided the catalyst in H_2/H_2S for 10 hr at 400°C. They found that practically all the molybdenum is in the MoS_2 state.

Delannay et al. [112] recently showed by high resolution microscopy the formation of well-dispersed MoS_2 crystallites on a CoMo catalyst which had been used at high pressure.

Another important fact must be considered. If the catalyst is reduced before sulfiding, the behavior of the solid is very different. After such treatment the catalyst is sulfided to a lesser extent than after direct sulfidation of the oxide [103-111]. This corresponds to similar observations on an unsupported compound [99].

On nickel tungsten alumina catalysts [113] it has been shown that sulfidation depends on the time and temperature of treatment and the nature of the sulfiding atmosphere. A very good parallelism can be made between the behavior of CoMo and NiW catalysts.

IV. CATALYTIC AND PHYSICOCHEMICAL PROPERTIES OF THE SULFIDED CATALYSTS

A. Unsupported Catalysts

Although unsupported catalysts have not found any industrial use up to now, their study may be important. Indeed, the supported system is so complicated that some simplification may be needed for understanding the various phenomena which occur. One type of simplification is to eliminate the support. We have summarized in Section II various arguments suggesting that unsupported catalysts like those prepared by Hagenbach et al. [31-33], Farragher et al. [114], Voorhoeve et al. [115-117], Delvaux et al. [34, 118, 119], Wise et al. [18, 19, 120, 121], Pirotte et al. [122], and Furimsky et al. [35, 36] exhibit some similarities with commercial hydrodesulfurization catalysts. For this reason we shall devote this first section to unsupported, fully sulfided catalysts.

The most extensive study on unsupported CoMo catalysts has been done by Delvaux [34, 118, 119]. Let us summarize the physicochemical properties of unsupported CoMo catalysts prepared by "co-maceration" [31-33] and compare their catalytic activity (Fig. 7). For a series of catalysts in which the Co/(Co + Mo) ratio ranges from 0 to 1, the evolution of all the parameters determined by different methods allows us to distinguish clearly two ranges of composition: low cobalt content, [less than Co(Co + Mo) = 0.05] and the synergistic range [$0.20 < Co/(Co + Mo) < 0.60$].

In the low concentration range, one can observe:

A decrease of the c parameter of the MoS_2 lattice [124] for samples treated at high temperature

An increase of the crystallinity of the very poorly crystallized MoS_2 [34]

A decrease of the specific surface area of the catalyst [34]

An increase of the EPR signal at low temperature [33]

An increase of the magnetic susceptibility signal [125]

An increase of the binding energy of the Mo and S levels, determined by XPS measurement after a catalytic run [34, 118]

A decrease of the total sulfur content measured by gravimetric analysis [34]

These anomalies can be correlated with those in the catalytic activity for thiophene hydrogenolysis, cyclohexene hydrogenation, and cyclohexane isomerization.

Two hypotheses have been put forward to try to explain the behavior of these catalysts in the low cobalt range:

1. The presence of Group VIII metals decreases the disorder normally observed in the MoS_2 structure. This could be explained by assuming that this small amount of promoter starts a nucleation process which facilitates the growth of MoS_2 crystallites. This view is supported by the fact that in $Mo_{(1-x)}S_2$ prepared by thermal decomposition of $(NH_4)\ MoS_4$, "x" decreases with increasing temperature of decomposition, and that the larger

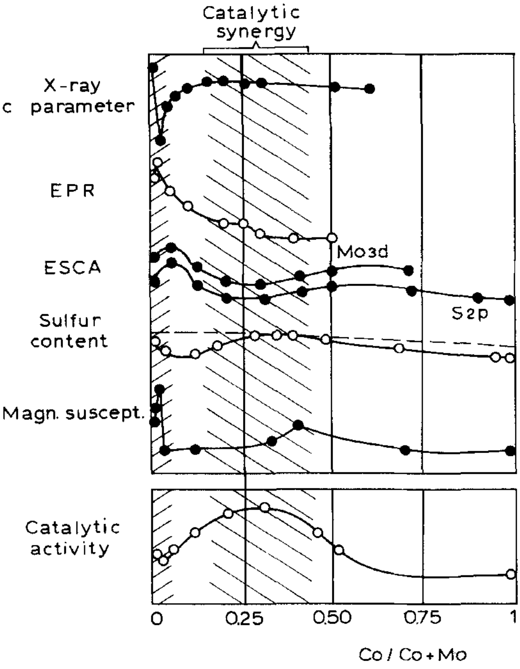


FIG. 7. Variation of the physicochemical and catalytic properties of unsupported fully sulfided CoMo catalyst.

the value of x, the stronger the observed disorder and the higher the value of the c parameter [126]. Furthermore, a correlation between the stoichiometry of WS_2 and the value of the c parameter has also been reported [127].

2. The second possible explanation of these anomalies of the physicochemical properties in the low cobalt range deals with an intercalation or pseudo-intercalation of the cobalt in the MoS_2 lattice. But in this concentration range, one never observe intrinsic activities approaching those observed in the higher concentration range, but rather a decrease of activity in most cases.

The same evolution was found in the low promoter range for NiMo, FeMo, CoW, and NiW catalysts [128].

Another interesting argument comes from Wise's work [122]. He impregnated a MoS_2 monocrystal with a cobalt nitrate solution of 0.1 mole%. He demonstrated by electrical conductivity measurements that qualitatively the electronic properties of n-type molybdenite are affected in an analogous way by the addition of S^{2-} anions or Co^{2+} cations to the lattice. The switch from n-type to p-type conductivity resulting from the addition of Co^{2+} to the n-type crystal catalyst can also be brought about by the introduction of S^{2-} anions during prolonged exposure to a H_2S/H_2 gas mixture. He also showed a correlation between HDS activity and electronic carrier density.

In the medium concentration range, which we call the synergistic range, we can summarize the physicochemical properties of the solids as follows:

The c parameter of the MoS_2 lattice recovers its normal value

There exists a small anomaly of the EPR signal

The binding energy of the Mo and S level retains its lower value

The sulfur content increases without recovering the theoretical value corresponding to the sum of MoS_2 and Co_9S_8

It is possible to note small variations of magnetic susceptibility value

Both hydrodesulfurization and isomerization intrinsic activity (per m^{-2}) increase. The hydrogenation activity does not present the same behavior.

These results agree very well with Furimsky's work concerning the sulfur content and reaction rate of thiophene hydrogenolysis of the series of unsupported CoMo catalysts prepared by impregnation of MoS_2 with $Co(NO_3)_2$ in liquid ammonia. Unfortunately, they do not check the low cobalt content region [$0.5 < Co/(Co + Mo)$] as described per Delvaux et al. However, they show a better correlation between the sulfur deficiency of the catalyst and the maximum activity than in previously reported papers.

The XPS results reported by Delvaux et al. illustrated in Fig. 7 [34, 118] require our attention. These results have been obtained by very careful measurements on a sample which has been used in catalysis at atmospheric pressure and then put (without any contact with air or moisture) into the XPS apparatus. It was found that in the synergetic range, the binding energies of both the Mo and S levels were lower than those corresponding to MoS_2 and the oxidation state could be represented as $Mo^{4+(-\epsilon)}$ and $S^{2-(-\epsilon)}$. In other words the total superficial oxidation state of molybdenum could be lower than 4^+ and a fraction of the sulfur could be present as $(S{-}S)^{2-}$ [129].

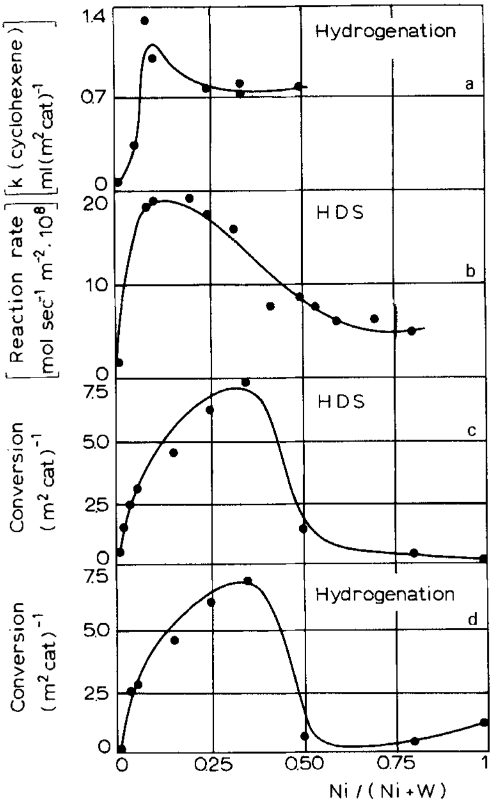


FIG. 8. Catalytic activity of unsupported fully sulfided NiW catalyst. (a) Ref. 117; (b) Ref. 36; (c) and (d) Ref. 130.

Another unsupported fully sulfided system, namely Ni-W, has also been extensively studied by Voorhoeve et al. [115-117], Farragher et al. [114], Furimsky et al. [136], and Thakur et al. [130].

The catalytic behavior of such systems prepared in two different ways (heating sulfur in quartz tubes at high temperature [115-117] and by the "co-maceration" method [130]) can be compared. Benzene hydrogenation in the presence of CS_2 at 48 atm, hydrogenolysis of thiophene at atmospheric pressure and at 30 bar, and hydrogenation of cyclohexene at 30 bar are presented in Fig. 8. However, the anomaly which has been reported for the CoMo system having a low promoter concentration is not present for "co-macerated" samples. From magnetic and EPR studies, the first group of authors concluded the presence of W^{3+} as active sites. These active sites are created by the incorporation of the promoters in the edges of the WS_2 structure, inducing a random faceting of the surface as shown by electron microscopy. According to Farragher et al. [114], metals which prefer to be intercalated in octahedral holes increase the catalytic activity for benzene hydrogenation by an amount which is proportional to their "goodness of fit" in the holes of the imperturbed WS_2 lattice (Table 2).

TABLE 2

Intercalated ion in WS_2	Radius, Å	Activity
Hole	0.76	1.0
Mn^{2+}	0.80	5.0
Cr^{2+}	0.89	18
Co^{2+}	0.72	90
Ni^{2+}	0.69	48
Al^{3+}	0.51	3
Ga^{3+}	0.62	0.4

Other systems associating Mo with Ni or Fe, i.e., unsupported NiMo and FeMo, exhibit the same behavior as the Co-Mo systems shown in Fig. 9 [128].

For a low promoter content: a decrease in HDS activity, specific surface area, and value of the c parameter of the MoS_2 lattice for the catalyst calcined at high temperature.

In the medium promoter range: an increase of the HDS activity, specific surface area, and value of the c parameter of the MoS_2 lattice.

The behavior of the Co-W system is comparable to the Ni-W one [36, 128]. Complementary information is given by Stevens et al. [131] who prepared two MoS_2 catalysts having different basal-plane edge ratios. From selective adsorption of thiophene and hydrogen, they suggested that the basal plane of MoS_2 catalyses hydrogenolysis

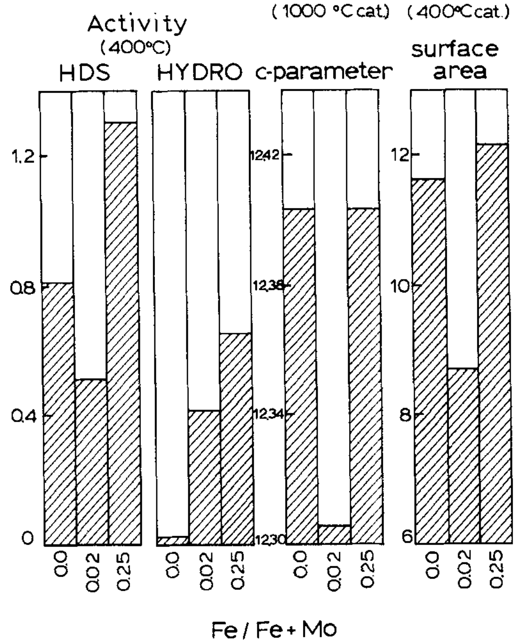


FIG. 9. Evolution of the c parameter, surface area, and catalytic activity for hydrogenolysis of thiophene and hydrogenation cyclohexene on unsupported fully sulfided FeMo catalyst (D. S. Thakur, unpublished results).

where the edge plane promotes a variety of other hydrogenation reactions.

Considering the influence of the sulfidation temperature on the physicochemical and catalytic activities of unsupported CoMo catalysts, one can mention two facts [119]:

A catalyst sulfided at 600°C presents the highest activity in hydrogenolysis

The oxidation state of Mo in this solid, after catalytic runs, is higher than that at 400°C but less than 4^+

So it seems that the oxidation state of the more active catalytic catalyst should be intermediate between 3^+ and 4^+.

B. Supported Catalysts

1. General Pattern of Catalytic Activity. Position of the Maximum

In these investigations, two kinds of catalysts have been used: commercial or laboratory made supported catalysts. For the latter, many studies have been devoted to the CoMo/γ-Al_2O_3 catalyst. To a lesser extent, silica was also used as a support as well as amorphous silica-aluminas [16] and zeolites [39].

An important feature has to be taken into account considering the general catalytic behavior of supported catalysts over the whole range of composition when the catalyst is put into the reactor either in the oxidic phase or after presulfiding by H_2/H_2S mixtures. It has been shown that, if the general shape of the catalytic activity (hydrogenolysis and hydrogenation) is the same, the range and the intensity of the synergetic effects are different [37] (Fig. 10). The reduction sulfiding treatment in a H_2/H_2S atmosphere at 400°C increases both the intensity of the synergetic effect and the domain in which this effect is observed.

2. Alumina Supported Catalysts

Cobalt Molybdenum System

The first point to be examined is the nature of the phases present in the sulfided catalyst. X-ray diffraction gives no valuable information because these phases are generally amorphous. The following phases may be present: MoS_2, Co_9S_8, reduced cobalt species, $CoMo_2S_4$, remaining MoO_3, molybdenum oxysulfide, $CoAl_2O_4$, and mixed CoMo compounds. Although there is general agreement concerning the presence of MoS_2, the presence of Co_9S_8 is not admitted by all authors. For example, Brinen et al. [132] recently suggested that the cobalt in the active phase is not sulfided.

The Nature of the Sulfide Phase. Before considering physicochemical characterizations, one important feature is the determination of the sulfur content of the active phase. Indeed, the sulfur content is often subject to discussion. It depends on (1) the calcination temperature of the oxide. If this temperature is too high, $CoAl_2O_4$ formation increases and consequently the sulfidation of the oxide phase will be lower than expected [20, 132, 133]. (2) The treatment of the catalyst: whether the sulfur content was measured after sulfidation by H_2/H_2S at atmospheric pressure or after catalytic use

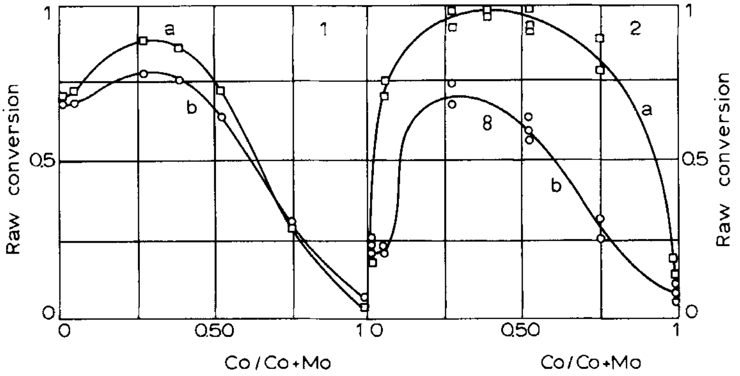


FIG. 10. Steady-state activity in the hydrogenation of thiophene and hydrogenation of cyclohexene vs composition [33]. (a) Oxide catalysts. (b) Same series of catalysts sulfided at 600°C for 6 hr with H_2-H_2S mixture.

at high pressure. Taking into account these facts, it is reasonable to assume that in stable condition the active phase is deficient in sulfur even when considering the H_2S adsorbed on Al_2O_3 [134, 135] or the formation of surface sulfide on Al_2O_3. A fraction of molybdenum is not completely sulfided and part of the cobalt is trapped in the form of $CoAl_2O_4$.

Gates et al. [4] assumed that MoO_3 is partially sulfided to such an extent that the maximum possible S/Mo ratio is 1. The Co-species was thought to be inaccessible to sulfur. De Beer et al. [20] showed that for commercial CoMo/γ-Al_2O_3 catalysts sulfided at 400°C by H_2/H_2S, the degree of sulfiding was 0.95 (S/Mo ratio = 2.44, S/Co = 0.63). By comparison with Mo/Al_2O_3 treated at the same conditions, he concluded that besides MoS_2, 70% of the Co was converted into Co_9S_8. Furthermore, he also showed that the presence of molybdenum facilitates the sulfurizability of the cobalt species. This last result was confirmed by Delannay [112], and is due to the enhancement of the dispersion of the cobalt by molybdenum. Ripperger et al. [94] state that the Co-Mo catalyst incorporates only 70 to 80% of the theoretically possible sulfur content which would correspond to the complete transformation of cobalt and molybdenum into Co_9S_8 and MoS_2, respectively, and argue in favor of oxysulfides. Pollack et al. [137] identified the MoS_2 structure on Mo/Al_2O_3 and

$CoMo/Al_2O_3$. But in the case of used catalysts, other Co and Mo species are present, especially unsulfided Mo, reduced cobalt species, and $CoAl_2O_4$.

To conclude, in addition to the various forms of sulfur already mentioned, some authors have observed the presence of S polymers [129, 134].

Arguments from Physicochemical Measurements. ESR spectra have been used to try to elucidate the nature of sulfide species. In a sulfided catalyst, many signals are detected. Let us examine the main ones.

Signal I (g value = 1.933). This signal, present in molybdenum-based catalysts supported on alumina, has been extensively studied [101, 134, 140-142]. It has been assigned to the Mo^{5+} species. These species exist provided they are stabilized by an active carrier [101, 134] like Al_2O_3. The signal intensity is lower with SiO_2 [9, 47, 92, 142, 144, 145] but it does not appear in unsupported MoS_2 or MoO_3 [134, 140, 141]. It decreases with increasing time of sulfidation [142]. Such oxidic species are thought to be responsible for part of the hydrogenation activity of Al_2O_3 supported CoMo catalysts [92].

Signal II (g value = 2.0028) can be attributed to paramagnetic species present in polyatomic sulfur radicals. A very similar signal has been reported by Dudzik et al. [146] on an imprenated zeolite. The stability of these biradicals was thought to depend on the pore structure of the support. So, depending on the support and the recording temperature, the single signal becomes a triple one. A similar triple band has been found by Seshadri et al. [134] who attributed it to a paramagnetic sulfur atom chain. However, there is some confusion concerning the origin of this triple band. Lo Jacono et al. [139] observed it only if O_2 is present in the system. In contrast, Dudzik et al. [146] indicated that this triple signal disappears if the catalyst is exposed to air.

Signal III ($g = 1.995$, $\Delta H = 68$ G). This signal was found by Konings et al. on evacuated sulfide samples. They attributed it to trivalent paramagnetic surface ions (M_S^{3+}).

Signal IV ($g = 2014$, $\Delta H = 208$ G). The signal appears for catalysts containing high cobalt loads and disappears for catalysts containing the usual CoMo ratios supported on alumina. (It is still present in silica supported catalysts.) Lo Jacono et al. [139] pointed out that this signal disappears when the catalysts are exposed to thiophene or H_2S. It is likely that this signal is due to a cobalt species resulting from the interaction of Co_9S_8 with hydrogen, namely a sulfided cobalt species more reduced than bulk Co_9S_8. XPS results seems to confirm the presence of such a species in addition to Co_9S_8.

XPS measurements are also a valuable method to detect surface species of such a catalyst, and recent work has been devoted to this.

For our present discussion the most significant XPS analysis concerns samples having actually been used as catalysts at high pressure and then introduced without contamination into the XPS apparatus. Let us compare the results of such experiments with other XPS measurements made on sulfided catalysts or catalysts having been employed at atmospheric pressure.

The questions which arise are: (1) What is the nature of the surface species present (especially cobalt)? (2) How much is actually present on the surface and how is it dispersed on the surface of the support?

Gajardo [153] has described a series of catalysts, containing Co/(Co + Mo) ratios ranging from 0 to 1 which had been sulfided at atmospheric pressure with H_2/H_2S and then operated at 30 kg H_2 for 8 hr with a mixture of thiophene, cyclohexene, and cyclohexane. The samples were then introduced into the XPS machine by a special device [147].

We shall first emphasize the identification of the surface species and then comment on the quantitative XPS results.

The sulfur level S_{2p} presents 3 peaks. Taking into account previous studies on the adsorption of H_2S on Al_2O_3 [135, 138], adsorption of thiophene on oxidic $CoMo/Al_2O_3$ in a He atmosphere [103] and XPS results on alumina treated at the same temperature with H_2S/H_2 at 10 atm, Gajardo [137] attributes the first peak (160.4 eV) to the sulfur of MoS_2 and/or Co_9S_8 and the two other peaks (164.1 and 168.4 eV) to coke containing sulfur due to the cracking of thiophene.

Determination of the binding energies of the S_{2p} level allows the determination of the binding energies of the S_{2s} level and then the decomposition of the Mo_{3d} spectrum. So it is possible to detect the presence of molybdenum sulfide and unreacted molybdenum oxide. Other authors have reported the same conclusions in different conditions. Okamoto et al. [148] reported the presence of such species after thiophene hydrodesulfurization over oxidic catalyst in runs of 100 min duration. Patterson et al. [103] found that sulfidation was not complete after 10 hr of exposure to a H_2S/H_2 mixture at 400°C, and that there is strong evidence that much of the molybdenum surface is attached to only one sulfur atom. For Brinen et al. [132], less than 10% Mo^{6+} remains. Declerck-Grimee et al. [74, 149] show the presence of MoS_2 but do not agree with the presence of a remaining oxidic phase. So it seems that in the steady state the active phase contains both MoS_2 crystallites and unreacted molybdenum oxide. EPR provides additional proof for the presence of molybdenum oxide. Electron microprobe analysis demonstrates the presence of MoS_2 crystallites.

The identification of the surface cobalt species is difficult. It is based on the fact that paramagnetic Co^{2+} species are characterized by a spin orbit splitting of 16 eV for the Co_{2p} level and are generally accompanied by a satellite structure. A diamagnetic Co^{3+} compound and metallic Co^0 present a spin orbit splitting of 15 eV without satellite [74, 132, 148-152].

The $Co_{2p}{}^{3/2}$ level of a catalyst that performed at high pressure presents three bands (one peak without satellite and one with a satellite).

Gajardo ascribes one peak to a Co_9S_8 species. The other signal would correspond to $CoAl_2O_4$ in the composition range corresponding to an atomic ratio Co/(Co + Mo) $\simeq 0.3$ and to a sulfur-deficient Co_9S_8 probably in a high spin state for high cobalt concentration catalysts.

On the other hand, Brinen et al. [132] compared both oxidic and activated catalysts supported on γ-Al_2O_3 and carbon, and they postulated that the cobalt in the activated phase is reduced but not sulfided. Patterson's results [103] show some evidence that cobalt is sulfided but that further treatment either by pure hydrogen or with thiophene at 500°C does not strongly affect this species. Furthermore, he postulated that there is a better possibility of the formation of discrete sulfur species like CoS, CoS_2, or Co_9S_8. However, it is worthwhile to note that the presence of Co_9S_8 on Co/Al_2O_3 catalysts can be detected by x-ray diffraction and that CTEM measurements suggest the presence of some sulfided species similar to Co_9S_8 [153].

It is useful to note a relation found by Declerck-Grimee [149] between activity measurement and sulfide Co/Mo ratio determined by ESCA. This indicates that only the sulfided cobalt species has a promotor effect on the active phase in HDS catalyst (Fig. 11).

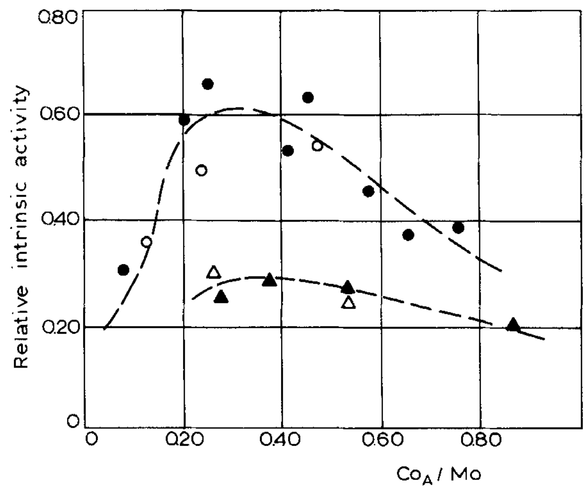


FIG. 11. Intrinsic activity vs active Co(CoA)/Mo ratio of catalysts prepared by impregnation with either Mo or Co first and then calcined at 500 or 700°C [38].

Calcination T	500°C	700°C
Mo first	●	○
Co first	▲	△

Another interesting result concerns the analysis of the intensities of the XPS bands. This gives some idea of the "spreading" of the Mo and Co species on the catalysts. In Fig. 5, XPS and EPMA analyzed results concerning a series of catalysts both in the oxidic and the activated form are compared [153]. The main conclusions can be summarized as follows:

A general pattern concerning the degree of dispersion of both Mo and Co is maintained in the active state compared to the oxidic one. However, the formation of microcrystallites of pure MoS_2 coming from the destruction of the monolayer brings about a decrease in the dispersion of Mo. In the case of cobalt, only the high cobalt content catalysts or pure cobalt solids present a cobalt sulfide phase more dispersed than the oxidic one.

It is obvious that there is a strong enhancement of cobalt dispersion by the presence of molybdenum.

Analytical electron microscopy (AEM) brings strong arguments in favor of the presence of individual MoS_2 and Co_9S_8 phases. Delannay et al. [112] showed the presence of small crystallites of MoS_2. However, unambiguous formation of Co_9S_8 crystallites is detected only for $Co/\gamma\text{-}Al_2O_3$ sulfide catalysts.

A survey of the literature concerning physicochemical measurements shows some recent Mossbauer results obtained for the sulfide phases. Topsøe et al. [83] state that a separate Co_9S_8 phase in catalysts corresponding to a composition typical of that used industrially is not present. But then they claim that the structure resembles that proposed in the "pseudo-intercalation" model [114]. For higher cobalt concentrations, they detect a separate Co_9S_8 phase. To summarize this data on the sulfided CoMo catalyst, the following species have been identified:

MoS_2. This is present in the form of small crystallites.

Oxidic Mo^{4+} and Mo^{5+}. These species are strongly attached to the Al_2O_3 surface and may be considered as remaining parts of the oxidic Mo^{6+} monolayer.

$CoAl_2O_4$. This compound, present in the oxidic precursor form of the catalyst, remains after activation.

Cobalt sulfide. The presence of this phase is not accepted by all authors. However, we believe that Co_9S_8 and sulfur-deficient Co_9S_8 are likely present in the catalysts.

Other Systems

The NiW/Al_2O_3 system has also been studied but to a lesser extent. One of the most detailed XPS studies of sulfide phases was presented by Ng et al. [113]. They summarize their conclusions as follows:

The oxidic phase sulfided by 7 vol% thiophene in H_2 gives Ni_3S_2 and WS_2.

The oxide phase sulfided by 9 vol% H_2S in H_2 gives Ni_3S_2 and WS_2.

A tungsten surface complex intermediate was formed during sulfiding. The intermediate has both a terminal oxygen and a terminal sulfur.

Ni^{2+} ions are found to diffuse to the surface during sulfiding. No W^{3+} ions or other anion vacancies are observed.

3. Other Carriers

Some studies have been carried out on silica supports and compared with the corresponding alumina carrier.

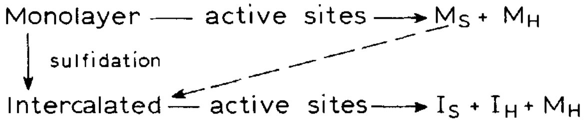
Since the nature and the dispersion of the oxide species on a silica supports is different from the alumina one, it is logical to have a different distribution of the sulfide species on the silica support. The separate sulfides come from the bilayer structure in the case of alumina systems, and $CoMoO_4$ is the main oxide produced in the case of a silica support. Furthermore, the oxide species remaining from the monolayer form will no longer be present when silica is used as a support. Consequently, the catalytic behavior of SiO_2 supported catalysts will be more comparable with unsupported catalysts.

Carbon has also been proposed as a support for CoMo catalysts by Stevens et al. [154]. In this system both MoS_2 and cobalt sulfide species are the only phases present on the surface of the carbon after catalytic reaction. In this instance the selectivity of the catalyst is very high. These authors postulate that this is mainly due to the cobalt promotion of the MoS_2 basal plane. However, no remaining oxide phase is present.

V. HYPOTHESIS ON THE NATURE OF THE ACTIVE SYSTEM

Various attempts have been made to elaborate models explaining the nature and the role of the active phases in hydrotreating catalysts.

A first important hypothesis, the "monolayer model," has been discussed in detail by Schuit et al. [4]. It will not be reexamined here. Furthermore, it applies only to the oxide precursor form. After sulfidation, i.e., in operating industrial conditions, the oxide monolayer is partially sulfided. This transformation has to be accompanied by diffusion of the promotor cations from the surface layers of the alumina support to the surface. But according to de Beer [9], if the greater part of the monolayer is converted into MoS_2 crystals, there remains a fraction of the molybdenum species strongly bonded to the support (in the case of alumina). In the case of silica, a greater amount of molybdenum would be converted into molybdenum sulfide because of the weaker interaction between the support and molybdenum. These two types of molybdenum would therefore act as two different functions as shown in the scheme below [9].



I_S = desulfurization
I_H M_H = hydrogenation

The active sites for hydrogenolysis would be synthetized during the sulfidation of the catalyst, i.e., the support would not play any role for this step. In this hypothesis the cobalt would activate the molybdenum in the same way as in the "intercalated model" [114]. On the other hand, the hydrogenation sites would depend almost exclusively on the interaction between the oxide phase (molybdenum) and the support. This could therefore explain the low hydrogenation activity of SiO_2 supported catalysts as well as the low ratio of butane/total C_4 products found for $CoO(MoS_2 + \gamma\text{-}Al_2O_3)$ and $CoO(WS_2 + \gamma\text{-}AlO_3)$ catalysts [155]. It is obvious that in this model the carrier only affects the selectivity of the catalyst but that activity is better defined by an intercalation of unsupported sulfides.

The second model, the "intercalation model," was first described by Voorhoeve et al. [115-117] on unsupported NiW phases. It was further developed and discussed by Farragher et al. [114] who mainly studied hydrogenation. The intercalation of Ni (Co) may occur at the layer edges between the WS_2 (MoS_2) layers in octahedral holes situated adjacent to W (Mo) ions. Bulk interaction is not possible. Thus intercalation would lead to the formation of single or dual sites of exposed W^{3+} (Mo^{3+}) ions scattered above a square planar array of sulfur ions at the edges of each WS_2 or MoS_2 layer. It also causes a faceting of the surface. It is useful to correlate this hypothesis with the observations of Stevens [131] who demonstrated the different activities and adsorptivities between basal planes and edges. The plane edges were shown to be strong sites for thiophene adsorption and also for activated hydrogenation centers. On the other hand, the basal plane of MoS_2, although active for thiophene conversion, is much more selective, thus giving high levels for thiophene and hydrogen absorption and low levels of products of hydrogenation. In conjunction with this observation we note the finding of Tanaka [156] which demonstrates evidence of two kinds of sites on MoS_2

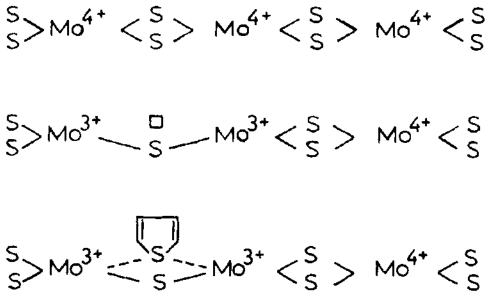
which may have different degrees in coordinate unsaturation. Although the hypothesis of Voorhoeve [115-117] and Farragher et al. [114] is very interesting, many questions are raised. First of all, it is very surprising that it is necessary to have such a high Co/(Co + Mo) ratio to obtain the synergetic effect (0.25 to 0.50). In fact, in this case, a small amount of Ni or Co should be sufficient to produce the intercalation of this species in the edges of the molybdenum or tungsten sulfide. Furthermore, these authors had demonstrated that only 1 or 2% of Ni is incorporated into the tungsten sulfide. It has also been demonstrated that the introduction of a small amount of cobalt or nickel into MoS_2 and WS_2 brings about the incorporation of the Group VIII metal into the sulfide. This incorporation of Co in Mo or Ni in W strongly enhances the hydrogenation activity but does not affect hydrogenolysis strongly. For a higher Co(Ni) content added to the molybdenum sulfide there exists a sort of segregation of the Co outside of the sulfide, and the catalytical activity is enhanced.

A third model has recently been proposed by Jacquin [12]. He suggested that a mixed sulfide $(Co_xMo_{1-x})S_{2\pm x}$ can be formed. At a higher cobalt content this mixed phase will disappear and two phases MoS_{2-x} and Co_9S_8 will be present. However, no mixed sulfide has been detected even when unsupported sulfide catalysts have been treated at high temperature.

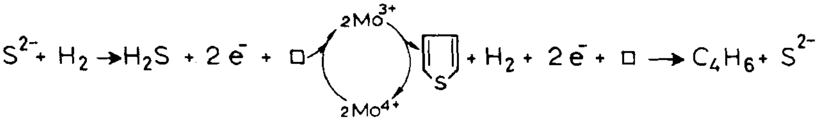
The fourth hypothesis, the "contact synergism" or "junction model," has been postulated by Delmon et al. [31-34, 37, 40, 128, 157-159]. In this hypothesis the system is essentially bi-phasic, and synergism would be a consequence of the mere contact or vicinity of Group VIII sulfide particles with Group VI sulfide crystallites. The essential difference from the other models is that synergism is not explained as a consequence of some influence of the carrier nor as a consequence of the higher activity of a doped MoS_2 or WS_2 phase, but rather by interaction between MoS_2 or WS_2 and Co_9S_8 or NiS. This hypothesis is strongly supported by the fact that a synergetic effect is also observed in mechanical mixtures of unsupported oxide or sulfide mixtures [28]. Furthermore the catalytic behavior presented by the doped compounds at low Co or Ni content proves that such an effect cannot explain the increase of activity at high Co or Ni content. The presence of the two sulfide phases, i.e., Group VIb and Group VIII, is observed quite easily in many catalytic systems in the range of composition corresponding to the maximum of the synergetic effect.

In the "junction model" the active phase is supposed to be formed at the interface between the two separate sulfides, the active sites probably being a more reduced valence state of molybdenum like Mo^{3+}.

The cobalt sulfide increases the possibility of vacancy formation by the activation of hydrogen. One can illustrate the formation on these sites and the adsorption of thiophene in the following way:



the global scheme being described as



Two adjacent Mo^{3+} sites are involved in this kind of reaction. XPS measurements on unsupported fully sulfided catalysts after use in catalytic reactions seem to corroborate the idea of getting reduced molybdenum ions. Furthermore, the fact that Mo^{3+} sites are the supposed active centers involved in HDS is demonstrated by the theoretical considerations of Duben [159] and Delmon [161, 162].

Kilanowski et al. [160] suggested the presence of two kinds of sites: an adjacent pairs of anion vacancies and a single anion vacancy.

The special oxidation state of the molybdenum has to be controlled. The hydrogen/H_2S ratio and the cobalt content are the two essential factors determining the optimal level of the catalyst.

It is obvious that, for the moment, there is no definite proof which supports the latter hypothesis nor justifies the intercalation model.

Phillips et al. [161] developed a new class of models to explain the behavior of promoted molybdenum catalysts. The "surface complex" model or "boundary" model, which may be roughly illustrated by the intercalation model and by the junction model, respectively, appear equally plausible. However, the authors explain (1) why the synergy is at a maximum for a certain promotor concentration, (2) why this maximum differs for different metals, and (3) why the catalytic activity falls below the catalytic activity of the pure sulfide at high promoter concentration.

Concerning hydrogenation properties, we emphasize the comparison between the catalytic behavior of unsupported sulfides and Al_2O_3, SiO_2, or C-supported sulfide catalysts. The hydrogenation activity is highest:

1. For unsupported CoMo, NiMo, or NiW catalysts whose compositions correspond, in our opinion, to a doped or intercalated structure, namely a low $Co(Ni)/\{Co(Ni) + Mo(W)\}$ ratio
2. For CoMo/γ-Al_2O_3 supported catalyst as compared to a CoMo/SiO_2 or CoMo/C catalyst. In the first instance it has been shown that the superficial oxidation state of molybdenum seems to be higher than Mo^{4+}, some Mo^{5+} being possibly present. In the second instance it is striking that catalysts which present the highest hydrogenation activity contain some remaining oxidic molybdenum. Mo^{5+} or some vacancies are probably formed.

In these conditions one can easily imagine that hydrogenation sites, different from HDS sites, are related either to the Mo^{5+} species or to vacancies due to the incorporation of the VIIIb elements in the MoS_2 lattice or resulting from the stabilization of the molybdenum by the carrier.

If the role of molybdenum seems to be clear, that of cobalt is not yet resolved and subject to many controversies. However, in our hypothesis in the stable active phase, we are led to consider that active cobalt must be present as a Co_9S_8 phase, this species possessing a possible hydrogen activation. However, if under certain conditions part of this cobalt is in a more reduced state, it is likely that catalytic activity will decrease.

VI. CONCLUSIONS

The main features of HDS catalysts can be summarized as follows:

In the oxidic phase, the dispersion of the cobalt oxide phase increases when molybdenum is first impregnated, followed by cobalt impregnation—in other words, the amount of $CoAl_2O_4$ increases with the degree of Co dispersion.

MoS_2 and Co_9S_8 phases are the active components present on the catalysts. Co_9S_8 probably activates hydrogen. Reduced Co_9S_8, when present, is less active.

The dispersion of the sulfide phase is closely related to the dispersion of the oxide precursor.

Hydrogenolysis and hydrogenation are related to two different active sites.

For hydrogenolysis, some arguments seem to indicate that Mo^{3+} (formed by sulfur vacancies) are the real active sites.

Results demonstrate that the remaining oxide monolayer also contributes to the hydrogenation processes.

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Note Added in Proof. A new mechanistic model describing the "contact synergism hypothesis" has been published [162, 163]. This recent work takes into account almost all of the experimental data.