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On the Catalytic Significance of a Co–Mo–S Phase in Co–Mo/Al_2O_3 Hydrodesulfurization Catalysts: Combined *in Situ* Mössbauer Emission Spectroscopy and Activity Studies

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A series of sulfided Co–Mo/Al_2O_3 catalysts with different Co/Mo ratios but with constant molybdenum content is investigated. The catalysts are characterized by *in situ* Mössbauer emission spectroscopy (MES) and investigated for their thiophene hydrodesulfurization activity. The catalytic activity shows a pronounced maximum at a Co/Mo ratio of about 1.0. The MES spectra reveal that cobalt may be present in three distinctly different phases: cobalt located in the alumina lattice (Co : Al_2O_3), cobalt in Co_9S_8, and cobalt located in the Co–Mo–S surface phase discussed in the preceding paper. It is found that the relative amounts of the three phases depend strongly on the Co/Mo ratio. The Co : Al_2O_3 phase and the Co–Mo–S phase are observed in all catalysts studied, whereas Co_9S_8 is observed only in catalysts with Co/Mo $\gtrsim$ 0.4. It is shown that the presence of Co_9S_8 cannot explain the promoting role of cobalt in the Co–Mo/Al_2O_3 catalysts. However, a linear relation between the catalytic activity and the amount of Co in the Co–Mo–S phase leads to the conclusion that the promoting effect of cobalt is associated with the presence of this phase.

1. INTRODUCTION

It is well established that elements such as Co, Ni, and Fe promote the hydrodesulfurization (HDS) and hydrogenation activities of Mo- and W-based sulfide catalysts. One of the observed characteristics which has attracted particular attention in this connection is the dependence of the catalytic activity on the loading of the promoter atoms. It is generally observed that upon increasing the concentration of the promoter atoms, the activity passes through a maximum. The origin of this behavior has been the subject of much attention, and possible connections between this property and the structure of the catalyst have been looked for in the light of the many different structural models which have been proposed for such catalysts (see, e.g., (*1*)). According to these models, the role of cobalt may be to stabilize the active surface layer (*2, 3*), to increase the dispersion of the layer (*4*), or to increase the number of anion vacancies in the active phase (*1, 5–8*). Other models have also been put forward in order to explain the promoting effect (*9, 10*).

In the preceding paper (*1*), we discussed the structure of a Co–Mo–S phase which was observed to be present in sulfided alumina-supported and unsupported Co–Mo catalysts. Several of the observed structural and chemical features of the Co–Mo–S phase suggested that the promoting role of cobalt is associated with the presence of the Co–Mo–S phase. This possibility is examined further in the present paper by studying a series of Co–Mo/Al_2O_3 catalysts with different Co/Mo ratios. In this series the molybdenum content is kept constant in order to avoid the complexities which arise when this parameter is changed (*11, 12*). Structural information about the different catalysts is obtained by use of *in situ* Mössbauer emission spectroscopy (MES) and the results are compared with thiophene conversion activities.

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II. EXPERIMENTAL

A. Sample Preparation

A batch of Mo/Al_2O_3 was prepared by impregnating 0.8-mm extrudates of η-Al_2O_3 ($250\ m^2g^{-1}$) with an ammoniacal solution of ammonium heptamolybdate. The sample was subsequently dried and calcined in air at 775 K for 2 h. Chemical analysis showed that it contained 8.6% Mo by weight which corresponds to less than a monolayer coverage. All Co–Mo/Al_2O_3 catalysts were then prepared by adding to the above Mo/Al_2O_3 catalyst appropriate amounts of Co in the form of an aqueous solution of Co nitrate, by the incipient wetness impregnation method. The samples were dried at room temperature in air and calcined at 775 K for 2 h. In addition one sample containing 6.5% Co and no Mo was prepared using the same alumina extrudates by impregnation twice (with a calcination step in between) with a solution of Co nitrate following the same procedure as above.

For Mössbauer experiments, five samples of 0.25 g each were prepared in parallel with those described above, but using a solution of Co nitrate which was doped with ^{57}Co. The amount of ^{57}Co was fixed at a constant level (ppm range) independent of total cobalt loading, giving a source strength (activity) of each sample of approximately 74 MBq (2 mCi).

The catalysts used for thiophene conversion and Mössbauer spectroscopy measurements are listed in Tables 1 and 2, respectively.

B. Mössbauer Emission Spectroscopy (MES)

The MES experiments were performed using a constant-acceleration spectrometer with a moving single-line absorber of $K_4Fe(CN)_6 \cdot 3H_2O$ enriched in ^{57}Fe (*13*). Zero velocity is defined as the centroid of a spectrum obtained at room temperature with a source of ^{57}Co in metallic iron. Positive velocity corresponds to the absorber moving away from the source. Room-temperature spectra were collected for at least 48 h, whereas spectra at 575 K were collected for at least 72 h.

The samples for the Mössbauer spectroscopy measurements were ground, pressed into thin, self-supporting wafers, and placed in a Pyrex *in situ* cell (*1*) connected to a gas handling system. The samples were activated at 625 K for not less than 15 h in a flow of 2% H_2S in H_2. Some samples were activated at 675 K. The spectra of these samples were identical to those obtained after 625 K sulfiding. All samples were

TABLE 1

Catalysts and Activity Data

Catalysts	$\frac{Co}{Co + Mo}$	Thiophene conversion[a] (%)	k_T ($cm^3\ min^{-1}\ g_{cat}^{-1}$)	β
Co/Mo = 0 (8.6 wt% Mo)	0	6.2 ± 3.0	3 ± 1	0.87 ± 0.09
Co/Mo = 0.09	0.08	32.9 ± 1.4	26 ± 3	0.80 ± 0.06
Co/Mo = 0.27	0.21	48.9 ± 1.1	83 ± 10	0.50 ± 0.13
Co/Mo = 0.44	0.31	56.8 ± 1.3	100 ± 20	0.57 ± 0.17
Co/Mo = 0.53	0.35	58.1 ± 2.1	115 ± 7	0.52 ± 0.09
Co/Mo = 0.75	0.43	62.3 ± 1.4	129 ± 17	0.53 ± 0.15
Co/Mo = 1.35	0.57	63.8 ± 0.8	131 ± 3	0.56 ± 0.03
		62.5 ± 0.8	129 ± 10	0.53 ± 0.12
Co/Mo = 2.09	0.68	50.8 ± 1.0	75 ± 10	0.62 ± 0.13
Co/Mo = ∞(6.5 wt% Co)	1	<0.2	<1	—

[a] At $SV = 200\ cm^3\ g^{-1}\ min^{-1}$. Uncertainties given at 95% confidence level.

TABLE 2

Relative Spectral Areas of Different Cobalt-Containing Phases

Catalysts	Relative spectral areas (%)[a]					
	300 K			575 K		
	Co : Al_2O_3	Co_9S_8	Co–Mo–S	Co : Al_2O_3	Co_9S_8	Co–Mo–S
Co/Mo = 0.09	11	0	89	20	0	80
Co/Mo = 0.27	15	0	85	27	0	73
Co/Mo = 0.53	18	10	72	19	32	49
Co/Mo = 0.75	17	30	53	12	70	18
Co/Mo = 1.19	8	73	20	4	85	11

[a] With respect to uncertainties, see the text and Fig. 5.

cooled in the gas mixture to 575 K, and Mössbauer spectra were collected at this temperature. Subsequently the samples were allowed to cool to room temperature in the gas mixture and spectra were obtained at this temperature. Hence, all measurements were carried out *in situ*.

C. *Catalyst Activity Measurements*

Activity measurements for thiophene HDS were carried out in a Pyrex-glass, fixed-bed reactor (inside diameter = 11.5 mm) at 625 K and at atmospheric pressure. Samples of 0.4–0.5 g catalyst were mixed with 3 g α-Al_2O_3. For both the catalyst and the α-Al_2O_3 the sieve fraction was 0.59 to 0.85 mm (mesh 30 to 20). On top of the catalyst layer, 10 cm of 2-mm glass balls was placed.

The catalysts were presulfided in the reactor at 675 K for 2 h using 6% H_2S in H_2. After presulfiding the reactor was purged with purified N_2, after which the temperature was lowered to 625 K.

Hydrogen was saturated with thiophene by flow through two gas bubblers, the first one kept at room temperature and the second one at 273 K. After 16 h on stream, a space velocity series was run by varying the H_2 flow rate. Measurements at the initial space velocity conditions were repeated at the end of the series in order to check for catalyst deactivation.

The reaction products were analysed by a gas chromatograph (Perkin–Elmer 452) attached to an integrator (HP 3385A Automation system). At each space velocity condition two determinations of the gas composition were carried out, each consisting of three consecutive samplings. The reactor charged alone with α-Al_2O_3 and glass balls (but without catalyst) showed no detectable thiophene conversion.

III. RESULTS

A. *Thiophene Activity Measurements*

The values of the conversion of thiophene at a fixed space velocity (SV = 200 cm^3 g^{-1} min^{-1}) are given in Table 1 for the different catalysts and the results are plotted in Fig. 1 as a function of the Co/(Co + Mo) ratio. These conversions were obtained by fitting the conversions obtained at different space velocities with a linear regression analysis program. In Fig. 1 the cobalt concentration is expressed as Co/(Co + Mo) in order to be able to depict the catalyst containing no molybdenum [Co/(Co + Mo) = 1]. In all the other figures as well as in the text, the atomic ratio Co/Mo is used.

The conversion of thiophene was observed not to be first order, but was shown to be inhibited by both reactants and products. In a recent study of different Co–Mo/Al_2O_3 catalysts, Massoth and Chung

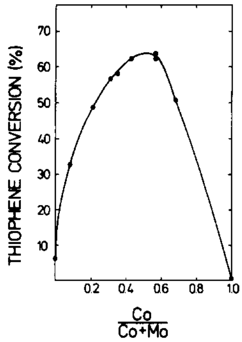

FIG. 1. Thiophene conversion at 625 K and atmospheric pressure. Space velocity: 200 cm^3 g^{-1} min^{-1}.

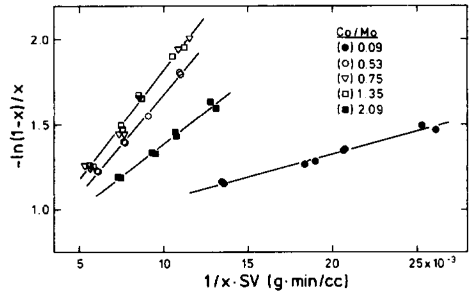

FIG. 2. Thiophene conversion data as a function of space velocity for catalysts with different Co/Mo ratios. The straight lines represent the best fit to the data according to Eq. (2).

(*14*) found that the following rate expression described their kinetic data rather well:

$$r_T = k_G p_T/(1 + K_T p_T + K_S p_S), \quad (1)$$

where r_T is rate of disappearance of thiophene, k_G is a global rate constant, p is the partial pressure, K is an adsorption equilibrium constant, and the subscripts T and S stand for thiophene and H_2S, respectively. Integration of Eq. (1) for fixed-bed reactor conditions and assuming constant partial pressure of hydrogen yield (*14*):

$$-\frac{\ln(1-x)}{x} = \frac{(K_S - K_T)p_T^\circ}{1 + K_S p_T^\circ} + \frac{k_G \cdot P}{1 + K_S \cdot p_T^\circ} \cdot \frac{1}{x \cdot SV} \equiv \beta + k_T \cdot \frac{1}{x \cdot SV}, \quad (2)$$

where x is the mole fraction of thiophene converted, p_T° is the partial pressure of thiophene at the reactor inlet, and P is the total pressure. In Fig. 2 we have plotted the kinetic data for catalysts with different Co/Mo ratios according to Eq. (2). It is seen that the rate equation (1) represents the data well within the measured range of conversions. The values for k_T and β are given in Table 1. Since k_T is proportional to k_G for given experimental conditions, k_T can be used as a measure of the catalytic activity.

The data given in Table 1 and Fig. 1 clearly show the promoting effect of cobalt also observed by many previous investigators. The unpromoted catalyst shows some thiophene HDS activity. However, this activity is substantially increased by addition of cobalt and increases until maximum activity is reached for Co/(Co + Mo) ~0.5. k_T for the most active catalysts is about a factor of 30 higher than that of the unpromoted catalyst. Increasing the ratio above 0.5 leads to a decrease in the activity. The pure cobalt catalyst is not completely inactive, but has an activity substantially below that of the pure molybdenum catalyst.

B. Mössbauer Spectroscopy

Mössbauer spectra obtained at room temperature and 575 K of the five ^{57}Co-doped samples are shown in Figs. 3 and 4, respectively. It is readily seen that the spectra gradually change upon increasing the cobalt loading (Co/Mo ratio), reflecting a change in the relative amounts of different cobalt-containing phases of the catalysts.

The room-temperature spectra of the Co/Mo = 0.09 and Co/Mo = 0.27 catalysts (Figs. 3a and b) are dominated by a quadrupole doublet, but the shoulder on the right wing shows that another quadrupole doublet is also present in these spectra. Thus in these samples cobalt is observed to be present in two different phases, each represented by a quadrupole doublet in the spectra. As the cobalt loading is increased (Figs. 3c–e), a third component, which appears as a single broadened line around 0.3 mm s^{-1}, gradually intensifies, and in the spectra of the Co/Mo = 1.19 catalyst (Fig. 3e) this component is the dominant one, even though the presence of the two former quadrupole doublets can still be detected. No other phases were found in the spectra of the catalysts, and it may thus be concluded that only three cobalt-containing phases are present in this series of catalysts. The cobalt phases that give rise to the three spectral components have been discussed in Ref. (*1*). It was found that the broad single line at the center of the spectra is due to Co_9S_8, the spectrum of which consists of three lines with positions indicated in the lower bar diagram in Fig. 3. These lines, however, overlap so strongly that they appear as a single broadened line in the spectra. The quadrupole doublet (isomer shift, $\delta = 1.0 \pm 0.2$ mm s^{-1} and quadrupole splitting, $\Delta E_Q = 1.9 \pm 0.2$ mm s^{-1}), which is shown in the upper bar diagram of Fig. 3, originates from cobalt located in the alumina. The phase giving rise to the third component (the middle bar diagram in Fig. 3) in the spectra is the Co–Mo–S phase, the nature of which was discussed in detail in Ref. (*1*).

In order to estimate the relative amounts of Co–Mo–S, Co : Al_2O_3, and Co_9S_8 the spectra have been computer analysed in terms of the three spectral components, i.e., the two quadrupole doublets and the Co_9S_8 pattern. The emission pattern of Co_9S_8 is, as mentioned above, well known, and the line positions, linewidths, and relative area ratios were constrained accordingly. For the Co–Mo–S doublet the two lines were constrained to equal areas. The same constraint was applied to the Co : Al_2O_3 doublet. The relative areas found from this analysis are given in Table 2.

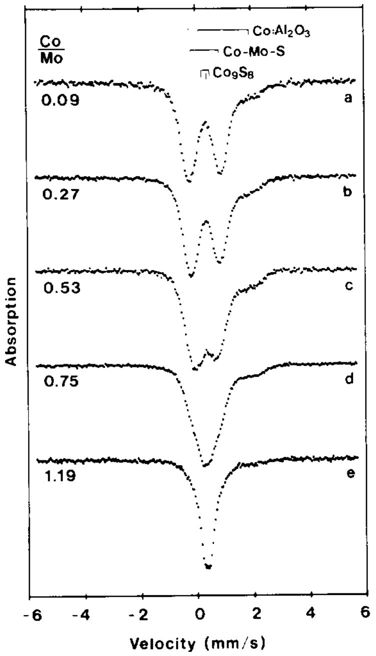

FIG. 3. *In situ* Mössbauer spectra obtained at 300 K of sulfided catalysts with different Co/Mo ratios. The bar diagrams indicate the line positions of the components of the three cobalt-containing phases.

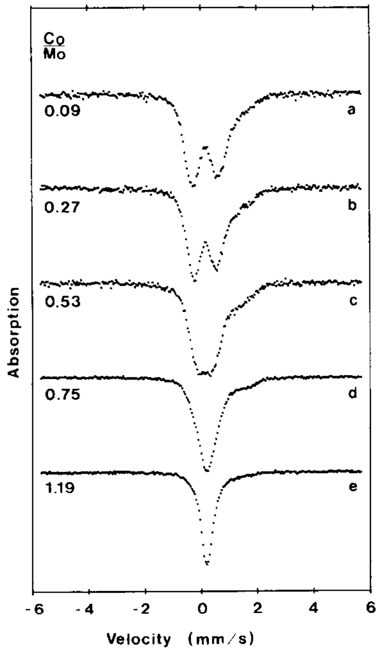

FIG. 4. *In situ* Mössbauer spectra obtained at 575 K of catalysts with different Co/Mo ratios.

The spectra of the catalysts at 575 K are shown in Fig. 4. Because of the temperature dependence of the quadrupole splittings, the lines overlap more in these spectra than in those obtained at room temperature, and therefore it is more difficult to resolve the spectral components. However, the phases present at this temperature are the same as those already identified in the room-temperature spectra. Thus, *in situ* room-temperature spectra, which are better suited for quantitative analysis, may be used to elucidate the structure of the catalysts under reaction conditions. The spectra at 575 K have been analysed following the principles given above, and the results are also shown in Table 2. It is observed that a change in sample temperature not only affects the line positions but also the relative and total areas of the various spectral components, due to the different *f* factors of the various cobalt phases (*1*). In order to calculate the relative and absolute amounts of cobalt of the different cobalt phases it is necessary to take into account their different *f* factors. These *f* factors can be estimated by use of the Debye model. The values of the Debye temperatures, θ_D, for the Co–Mo–S phase ($\theta_D = 200 \pm 5$ K) and for Co_9S_8 ($\theta_D = 305 \pm 30$ K) have been determined in Ref. (*1*), whereas the value of θ_D for the $Co:Al_2O_3$ phase has been taken as $\theta_D = 320$ K, a value which is observed for iron in spinels (*15*). By using these Debye temperatures and the fact that the spectral area is proportional to the number of atoms giving rise to the component multiplied by the *f* factor, the fractions of cobalt atoms present in the forms of Co_9S_8, $Co:Al_2O_3$, and Co–Mo–S were calculated. The results are shown in Fig. 5. These data and the known total amount of cobalt in each sample were used to calculate the absolute amounts of the three cobalt phases in the catalysts (expressed as mg Co per g Al_2O_3), shown in Fig. 6A.

The determination of the relative cobalt concentrations for the different cobalt phases can be carried out with an accuracy of about 5% of the total cobalt content. This accuracy is similar for all the catalysts although it depends on the Mössbauer counting statistics and the number of lines in the spectra. Thus, in calculating the total amount of cobalt in the different phases, the highest accuracy is obtained for catalysts with low Co/Mo ratios, whereas the accuracy is lower for catalysts with higher Co/Mo ratios. For example, the fact that no signal from Co_9S_8 could be detected in spectra of the Co/Mo = 0.09 and Co/Mo = 0.27 catalysts implies that the maximum possible amount of Co_9S_8 in these catalysts corresponds to 0.02 wt% Co and 0.07 wt% Co, respectively. Since the uncertainty in the amount of cobalt present in the form of Co–Mo–S in the Co/Mo = 1.19 catalyst is relatively high, the curve for this phase has been broken for Co/Mo ratios above 0.8 (see Fig. 6A).

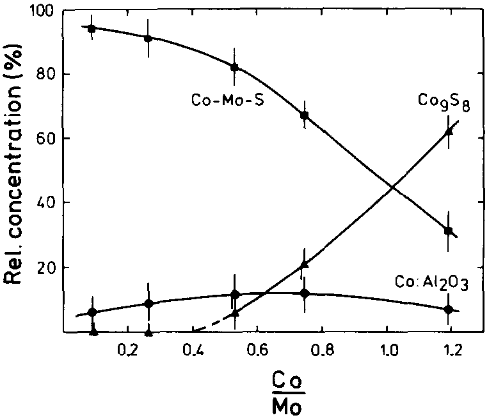

FIG. 5. Relative concentration of cobalt in the three cobalt-containing phases as a function of the Co/Mo ratio.

C. Comparison between Mössbauer and Activity Data

The values of the thiophene activity parameter, k_T, are shown in Fig. 6B for catalysts with $0 \leq$ Co/Mo ≤ 1.4 corresponding roughly to the range of compositions of the Mössbauer samples. In Fig. 7, the value of k_T is plotted as a function of the amount of

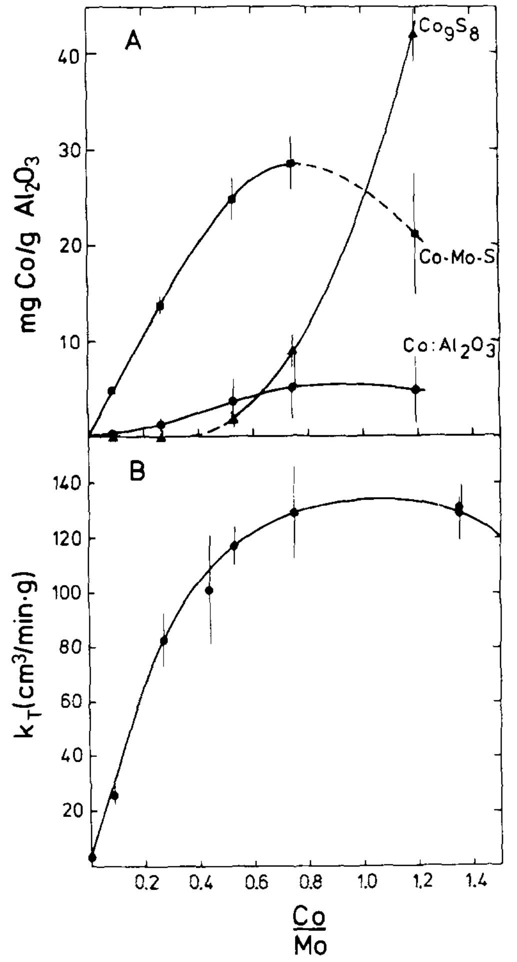

FIG. 6. (A) Absolute amount of cobalt in the three cobalt-containing phases as a function of the Co/Mo ratio. (B) The activity parameter k_T plotted as a function of the Co/Mo ratio.

cobalt in the Co–Mo–S phase. Both quantities are normalized to unit molybdenum content in order to take into account the small decrease in the concentration of molybdenum (per g catalyst) with increasing Co/Mo ratio.

IV. DISCUSSION

A. Effect of Co/Mo Ratio on Catalyst Activity

The results shown in Fig. 1 and Table 1 show that cobalt is a very efficient promoter for the activity of Mo/Al_2O_3 catalysts. For the most active catalysts, the conversion is more than a factor of 10 higher than the conversion of the unpromoted catalyst. This promoting effect of cobalt is qualitatively in agreement with several previous studies (e.g., (*3*, *4*, *16–19*)).

The kinetic equation (Eq. (1)) was applied in order to calculate kinetic parameters for all the catalysts. It is observed that this rate equation neatly represents the data at all the measured conversions (Fig. 2). In Table 1 values of β are also listed. At given experimental conditions, β is determined by the values of the adsorption equilibrium constants for thiophene and hydrogen sulfide (Eq. (2)). The results show that β is constant (~0.55) within the experimental error for all catalysts with Co/Mo $\gtrsim$ 0.1, whereas for catalysts with Co/Mo ratios below this value, the value of β is higher (~0.85). For catalysts with Co/Mo $\gtrsim$ 0.1,

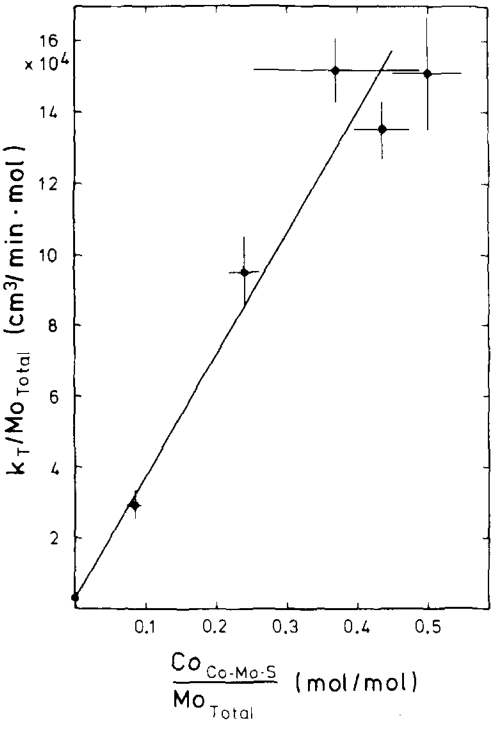

FIG. 7. Activity parameter plotted as a function of the amount of cobalt in the Co–Mo–S phase. Both quantities are normalized to unit molybdenum content.

where β is constant, k_T is observed to vary, suggesting that for these catalysts the reaction mechanism and the type of active sites remain unchanged, whereas the number of active sites is changed. The relatively high value of β for the Co/Mo = 0 catalyst (and the Co/Mo = 0.09 catalyst) suggests that the nature of the active sites in the nonpromoted Mo/Al_2O_3 catalyst is different from that of the active sites present in promoted catalysts with Co/Mo $\gtrsim$ 0.1. It should be noted that k_T may also contain parameters describing the adsorption of hydrogen. It cannot therefore be ruled out that cobalt promotion may also affect the hydrogen adsorption.

B. Effect of Co/Mo Ratio on Catalyst Structure

As discussed in Section III.B cobalt may be present in three distinctly different phases, viz., cobalt located in the alumina lattice ($Co:Al_2O_3$), cobalt in Co_9S_8, and cobalt located in a Co–Mo–S surface phase. Furthermore, the results show that the relative amounts of the three phases strongly depend on the Co/Mo ratio (or the cobalt loading, since the molybdenum content is not varied).

$Co:Al_2O_3$. In all catalysts studied, a signal from cobalt in alumina is observed. Such a component was also observed in a different type of alumina-supported catalyst (*1*), but the relative amount of cobalt in the alumina phase was observed to be lower in the present study, indicating that the amount of this phase may be sensitive to the preparation conditions.

The absolute amount of Co in Al_2O_3 is observed to increase slightly with increasing Co/Mo ratio (Fig. 6A), but in all the catalysts studied, the total amount of this phase is quite small.

The observation of the $Co:Al_2O_3$ phase is in several respects in accordance with previous investigations, since it has been proposed that, upon sulfiding, cobalt may remain completely (*2, 20*) or partly (*4, 16, 21, 22*) inside the alumina. However, the former possibility can be excluded for the present catalysts. It has been proposed (*16, 23, 24*) that cobalt and alumina form stoichiometric $CoAl_2O_4$, but in all the spectra of the catalysts the lines are found to be broad, which indicates that no well-defined phase such as $CoAl_2O_4$ is formed in any of the catalysts. This is supported by direct comparison with spectra of $CoAl_2O_4$ (*25*).

Co_9S_8. The presence of Co_9S_8 in sulfided $Co–Mo/Al_2O_3$ catalysts has been suggested by several investigators (*16, 21, 24, 26*). However, the present results show that Co_9S_8 is not found in the catalysts with Co/Mo $\lesssim$ 0.4. Above this value, Co_9S_8 is formed and the content increases rapidly with increasing cobalt loading. For catalysts with Co/Mo ratios higher than ~1.0, Co_9S_8 is observed to be the dominant phase.

Co–Mo–S. Previously (*1, 13, 27*), the Co–Mo–S phase was observed in coimpregnated $Co–Mo/Al_2O_3$ catalysts and it has been suggested by Mitchell (*28*) that the presence of the Co–Mo–S phase might be specific to the coimpregnation method employed. However, the fact that the Co–Mo–S phase is detected in the present catalysts, prepared by sequential impregnation as well as in unsupported catalysts (*1*), leads us to conclude that the presence of the Co–Mo–S phase is a general feature of sulfided Co–Mo catalysts.

For catalysts with Co/Mo $\lesssim$ 1.0 the Co–Mo–S phase is the most abundant phase (see Fig. 6A). Adding cobalt to the Mo/Al_2O_3 catalyst gives rise to an almost linear increase in the total amount of the Co–Mo–S phase for Co/Mo ratios in the region $0 <$ Co/Mo $\lesssim 0.4$. Above this region the curve levels off and for Co/Mo ~ 0.8 it reaches its maximum value. At higher Co/Mo ratios the amount of Co–Mo–S seems to decrease but as discussed above the exact shape of the curve is somewhat uncertain in this region.

The quadrupole splitting, ΔE_Q, of the doublet due to the Co–Mo–S phase is not constant for all the catalysts, but decreases from a value of $\Delta E_Q = 1.17 \pm 0.03$ mm s^{-1} for the Co/Mo = 0.09 catalyst to a value of $\Delta E_Q = 0.97 \pm 0.08$ mm s^{-1} for the Co/Mo = 0.53 catalyst. Since the quadrupole splitting is a measure of the local symmetry, the results show that the surroundings of the cobalt atoms in the Co–Mo–S phase vary because of changes in the cobalt concentration or because of possible changes in the size of the Co–Mo–S domains. A similar variation in quadrupole splitting as a function of the cobalt concentration has been observed for unsupported catalysts (*1*).

It is of interest to estimate the amount of cobalt that can be incorporated in the Co–Mo–S phase. Figure 6A shows that the Co/Mo = 0.75 catalyst seems to contain the highest amount of the Co–Mo–S phase. It is possible to estimate a lower limit for the Co/Mo ratio in the Co–Mo–S phase assuming that all the molybdenum atoms participate in the phase. The result of this calculation gives a value of about 0.5 for the Co/Mo = 0.75 catalyst. The observation of such large amounts of cobalt in the Co–Mo–S phase is in accordance with the description of the structure given in Ref. (*1*) where it was proposed that the Co–Mo–S phase in alumina-supported catalysts consists of patches of single S–Mo–S slabs with cobalt atoms most probably located at molybdenum sites.

Chung and Massoth (*22*) have recently investigated a series of Co–Mo/Al_2O_3 catalysts by a gravimetric technique. They postulated the presence of three different cobalt species, viz., cobalt in the alumina (Co_A), a bulk cobalt sulfide (Co_B) presumably Co_9S_8, and a sulfidable surface species (Co_S). These results are in qualitative agreement with the present study, which shows the presence of three distinctly different cobalt-containing phases. Furthermore, the present structural investigation shows that the Co_S species can be identified as Co–Mo–S. This is further substantiated by the fact that these authors reported (*14*) a correlation between k_T and Co_S quite similar to that reported below for the Co–Mo–S phase.

C. Relationship between Catalyst Structure and Catalyst Activity; Origin of the Promoting Role of Cobalt

In this section we will discuss the possible catalytic significance of the three cobalt phases, Co : Al_2O_3, Co_9S_8, and Co–Mo–S, which have been observed in the catalysts.

It is likely that the cobalt located in the alumina lattice, Co : Al_2O_3, does not make any direct contribution to the catalytic activity, because this phase is present in Co/Al_2O_3 catalysts (*1, 13, 21, 27, 29*) which are quite inactive (Fig. 1).

The contact synergy model (see, e.g., (*24*)) proposes that the cobalt promotion of the catalytic activity of Co–Mo catalysts is associated with the contact between bulk phases of Co_9S_8 and MoS_2. It is, however, difficult to bring the present results into accordance with the proposal that Co_9S_8 is the origin of the promoting effect of cobalt. First of all, for catalysts with Co/Mo ratios less than ~0.4, the presence of even minor amounts of Co_9S_8 can be excluded (see Section III), but in the same region the catalytic activity increases by a factor of about 30 and reaches a value close to its maximum (Fig. 6B). Secondly, it is observed that in the region where Co_9S_8 becomes the dominant phase (i.e., Co/Mo $\gtrsim$ 1.0) the catalytic activity actually decreases. It must therefore be concluded that although Co_9S_8 is present in catalysts with Co/Mo $\gtrsim$ 0.4 (Fig. 6A) the present results show that this phase is not responsible for the positive promotion of the catalytic activity in Co–Mo/Al_2O_3 catalysts.

It has been suggested (*1*) that the promoting effect of cobalt is associated with the Co–Mo–S phase. This hypothesis was based on the structural and chemical characteristics of this phase. The present results provide data which directly support the above proposal. When Figs. 6A and B are compared, it is observed that there is a relationship between the amount of the Co–Mo–S phase and the catalytic activity. This is corroborated in Fig. 7 which shows that within the experimental uncertainty a linear relation exists between the concentration of cobalt in the Co–Mo–S phase and the rate parameter. The fact that the correlation seems to be linear is in accordance with the high dispersion (i.e., single-slab structure) of the Co–Mo–S phase.

For all the cobalt-containing catalysts with Co/Mo $\gtrsim 0.1$, β was observed to be essentially constant (Table 1) and, as previously mentioned, this suggests that only the number of active sites, and not the reaction mechanism, changes in this region. The active sites are generally believed to involve anion vacancies, and the presence of such sites in the Co–Mo–S structure was shown to be consistent with its proposed structure (*1*). It is therefore likely that one of the promoting roles of cobalt in the Co–Mo–S phase is to create more anion vacancies.

Although the present study only includes MES data on catalysts with Co/Mo ≤ 1.19, the results seem to indicate that the decrease in activity observed for catalysts with Co/Mo $\gtrsim 1.0$ is caused by a decrease in the amount of cobalt in the Co–Mo–S phase. However, taking into account the relatively high uncertainty in the determination of this amount for the Co/Mo = 1.19 catalyst, the amount of Co–Mo–S may in fact be constant for catalysts with Co/Mo $\gtrsim 0.8$. The loss of activity could then be explained by a covering of the active Co–Mo–S phase by excess cobalt in the form of Co_9S_8. These possibilities are now under investigation.

The precise value of the Co/Mo ratio at which maximum activity has been reported to occur differs somewhat from study to study. This can be understood in view of the present results since the catalytic activity is shown to be directly related, not to the overall cobalt concentration, but to the presence of cobalt in the Co–Mo–S phase and the amount of cobalt in this phase will undoubtedly depend on the details of the preparation method.

V. CONCLUSION

The present results on alumina-supported catalysts show that the catalytic activity is correlated to the amount of cobalt in the Co–Mo–S phase. This finding is consistent with the observed maximum in activity *versus* Co/Mo ratio. The Co–Mo–S phase has also previously been observed in carbon- and silica-supported catalysts (*27*), in unsupported catalysts (*1*), and (as Fe–Mo–S) in Fe–Mo/Al_2O_3 catalysts (*13, 30*). It is therefore concluded that the role of promoters such as Co, Ni, and Fe in Mo- or W-based catalysts is related to the presence of Co–Mo–S-type phases or their tungsten analogues.

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