The Origin of Catalytic Synergy in Unsupported Co–Mo HDS Catalysts

One aspect of Co–Mo hydrodesulfuriza-tion (HDS) catalysts which has intrigued re-searchers is that unsupported catalysts show an activity behavior ("catalytic syn-ergy") as a function of the Co/Mo ratio sim-ilar to that observed for supported cata-lysts. This suggests that the support is not essential for creating the active phase.

On the basis of their extensive work on unsupported Co–Mo catalysts, Delmon and co-workers (see, e.g., (1–4)) have sug-gested that the presence of bulk Co_9S_8 and MoS_2 in close contact with each other is responsible for the promoting effect. This proposal is often referred to as the contact synergy model. On the other hand, Furimsky and Amberg (5) found no evi-dence for Co_9S_8 in several unsupported Co–Mo catalysts with high activity.

Mössbauer emission spectroscopy (MES) has been shown to be a useful method for elucidating the state of the Co promoter atoms in Co–Mo catalysts (6–11). These studies have revealed the presence of a Co–Mo–S phase in such cata-lysts. Furthermore, for alumina-supported catalysts, it was shown that the catalytic activity correlates with the amount of co-balt present in the Co–Mo–S phase. For unsupported catalysts it was observed (8, 10) that, depending on the preparation method, Co_9S_8 or Co–Mo–S may domi-nate. In this Note we will present combined MES and activity results which show that the Co–Mo–S phase is also responsible for the promotion of the catalytic activity of unsupported catalysts.

The results have been obtained mainly on catalysts prepared by the homogeneous sul-fide precipitation (HSP) method described previously (8, 10). To illustrate the impor-tance of the preparation method, two sam-ples prepared by the co-maceration method (CM) employed by earlier investigators (see, e.g., (2)) will also be included. The procedures used for obtaining the MES spectra and measuring the conversion of thiophene have been given previously (8, 9).

In Fig. 1, the activities (expressed as the first-order rate constant) of HSP and CM catalysts are shown as functions of the Co/Mo ratio. A large promotional effect of Co is exhibited by the HSP catalysts. The most active catalyst has an activity which is 20 times greater than that of the unpromoted catalyst. For the CM catalysts a promo-tional effect is also observed but it is much
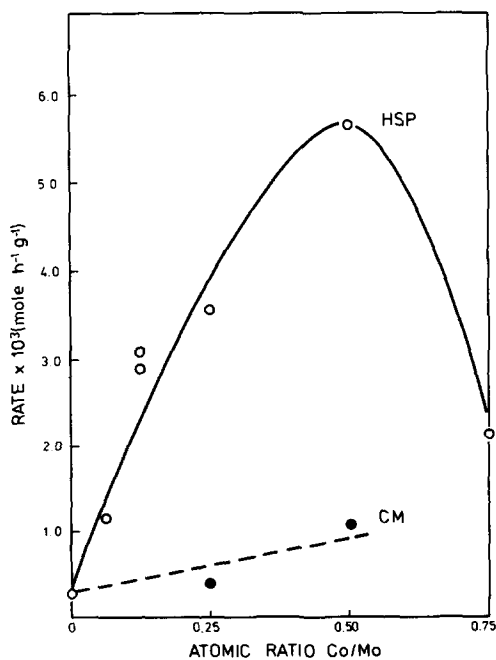

FIG. 1. Catalytic activity as a function of the Co/Mo atomic ratio for HSP and CM catalysts.
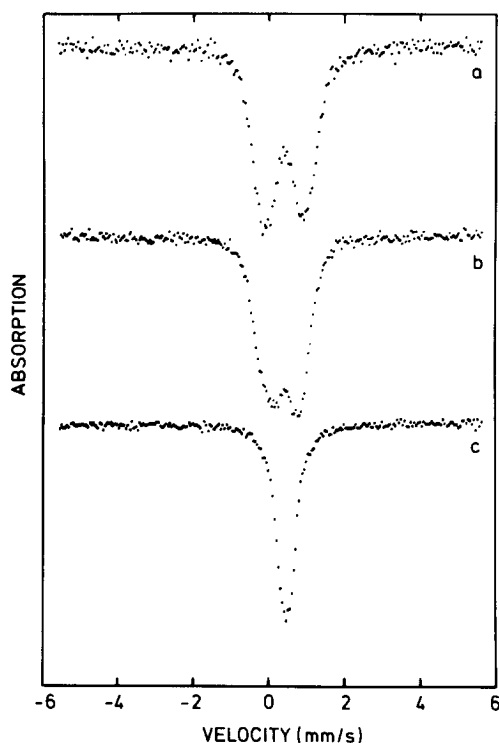
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FIG. 2. Room-temperature MES spectra of the HSP Co/Mo = 0.15 (a), HSP Co/Mo = 0.25 (b), and CM Co/Mo = 0.15 (c) catalysts.

HSP and CM catalysts. The HSP catalyst with Co/Mo = 0.15 shows only the typical quadrupole split pattern of the Co–Mo–S phase (spectrum a). Upon increasing the Co/Mo ratio to 0.25 in the HSP catalyst (spectrum b) the presence of Co_9S_8 is also detected. The spectrum of the CM catalyst (spectrum c) shows that even at a Co/Mo ratio of 0.15, Co_9S_8 is by far the most abundant phase. An increase in the Co/Mo ratio to 0.33 in the CM catalysts gives rise to a very similar spectrum. From MES spectra one can quantitatively determine the distribution of cobalt in different phases following the principles described elsewhere (8). Table 1 gives the relative amount of Co
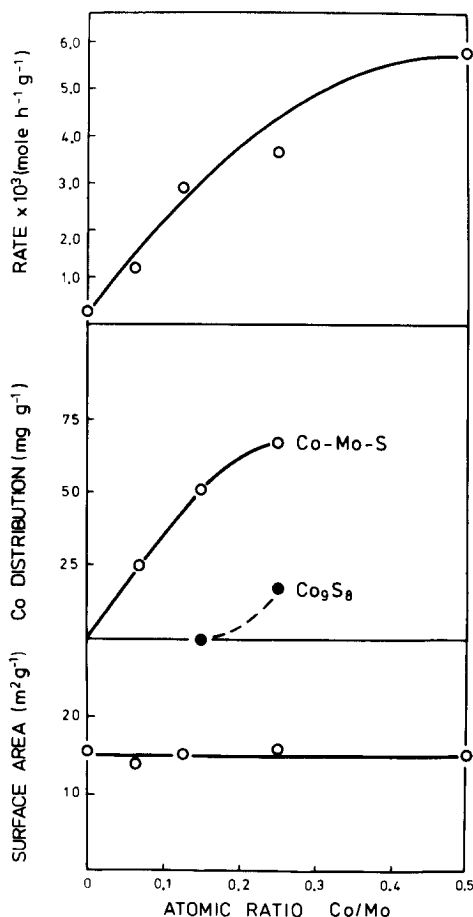
smaller than that found for the HSP catalysts. The different catalytic activities of the CM and HSP catalysts are not related to differences in the surface area of the samples (the CM catalysts have about 30% lower surface areas) but rather reflect differences in the cobalt phase distribution.

The type of cobalt phases present were determined by means of *in situ* MES. Figure 2 shows examples of MES spectra of

TABLE 1

Distribution of Co in Different Phases Determined by MES

Catalyst	Co/Mo	Co as Co–Mo–S (%)	Co as Co_9S_8 (%)
HSP	0.15	100	0
HSP	0.25	80	20
CM	0.15	≤7	≥93
CM	0.33	≤7	≥93

FIG. 3. Dependence of the catalytic activity, the amount of Co in Co–Mo–S and as Co_9S_8, and the BET surface area on the Co/Mo atomic ratio for HSP catalysts.

present as Co–Mo–S and Co₉S₈ for HSP and CM catalysts.

For the HSP catalysts Fig. 3 shows the dependence of the catalyst activity, phase distribution, and BET surface area on the Co/Mo atomic ratio. It is seen from this figure that the Co promoter concentration does not influence the total surface area for the HSP catalysts to any appreciable extent. Therefore, the dramatic activity increase observed is not related to changes in the surface area. On the other hand, it is apparent that the increase in the catalytic activity observed when the amount of promoter atoms is increased is directly related to the amount of Co present in the Co–Mo–S phase and not to the amount of Co in the form of Co₉S₈.

Figure 4 shows a plot of the catalytic activity versus the amount of Co in the Co–Mo–S phase for both HSP and CM catalysts. It is observed that for both catalyst systems the activity correlates with the amount of cobalt present in the Co–Mo–S phase. Thus, although Co₉S₈ itself has some HDS activity, its contribution to the promoting effect appears to be minor in comparison to that caused by the Co atoms present as Co–Mo–S. The very low promotional effect of cobalt in the CM catalysts is therefore related to the small fraction of co-

balt present in the Co–Mo–S phase. The reason for the different abundances of Co–Mo–S in the CM and HSP catalysts (for a given Co/Mo ratio) is attributed to differences in the preparation procedures, as discussed by Candia et al. (10). From a comparison of the present results with those for alumina-supported catalysts (9, 11) it can be concluded that the often observed similarity in catalytic activities of supported and unsupported catalysts is related to the presence of the Co–Mo–S phase in both catalyst systems.

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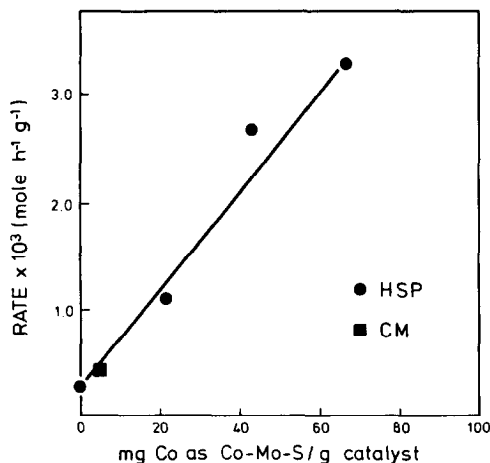Haldor Topsøe Research Laboratories,
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FIG. 4. Relationship between the catalytic activity and the amount of Co present as Co–Mo–S.