JOURNAL OF CATALYSIS **88**, 222–224 (1984)

NOTES

Electrophoretic Characterization of Unsupported Co–Mo Sulfided Catalysts Prepared by Different Methods

The hydrodesulfurization catalyst most commonly studied is that derived by sulfiding the oxides of cobalt and molybdenum supported on alumina (*1–3*). However, investigations have also been carried out with unsupported Co–Mo catalysts (*4–8*). In these studies it was suggested that structural and catalytic similarities can be found between unsupported and supported catalysts. Two of the models proposed for unsupported Co–Mo catalysts are (a) the contact synergism model and (b) the "Co–Mo–S" model. In the contact synergism model, proposed by Delmon and coworkers (*6–8*), the active system is regarded as two separate phases (MoS_2 and Co_9S_8). The promoting effect of cobalt is suggested to be the result of a contact synergism between these phases. In the "Co–Mo–S" model, proposed by Topsøe and co-workers (*4, 5*), it is considered that an active "Co–Mo–S" phase exists in both unsupported and alumina-supported catalysts.

It is well known that the method of preparation of hydrodesulfurization-supported catalysts is a critical factor in determining the catalytic structure and its activity (*9, 10*). Therefore, it is interesting to study whether the differences between these models can be attributed to differences in the procedure for obtaining the unsupported samples, as has been proposed by Candia *et al.* (*5*).

In our work we are studying unsupported Co–Mo catalysts (atomic ratio Co/Mo = 0.50) prepared by three different methods: (a) "co-maceration" (CM) as used by Hagenbach *et al.* (*7*), (b) homogeneous sulfide precipitation (HSP) as used by Candia *et al.* (*5*), and (c) a mixture of MoS_2 and Co_9S_8 reference samples obtained by the HSP method (*5*). These samples have been characterized by electrophoretic migration measurements, using ~20 mg of ~2 μm catalyst particles ultrasonically suspended in 200 ml of 10^{-3} *M* KCl solution, as was discussed before (*11*).

The ultrasonic treatment will only break up weak interactions; therefore if in any sample (CM or HSP) there are two phases (Co_9S_8 and MoS_2) two families or particles will be detected with isoelectric points (IEP) corresponding to pure phases. On the contrary, if there is only a single phase, one family of particles will be detected with a single zero point of charge (ZPC) that can be located between the IEP of each phase or not. The terms IEP and ZPC are used in accordance with the definitions given by Parks (*12*).

In this manner, the mixture of Co_9S_8 and MoS_2 shows clearly two families of particles as indicated in Figs. 1a and b, which can be assigned, obviously, to Co_9S_8 and MoS_2.

The zeta potential measurements of the HSP sample (see Fig. 1a) are different from those observed, either in the mixture or in separate reference samples. On the other hand, the HSP sample has a ZPC lower than Co_9S_8 and MoS_2, which suggests the formation of a new phase, different from Co_9S_8 or MoS_2. It is clear that this phase cannot be a mixture of Co_9S_8 and MoS_2 with a strong interaction, because the apparent ZPC of any mixture of phases must be between the IEP corresponding to each separate sample (*11*). (The ZPC of the HSP sample is ~1.5 while the IEP of the MoS_2 and the IEP of the Co_9S_8 are ~2.8 and ~2.0, respectively.) In our opinion, this

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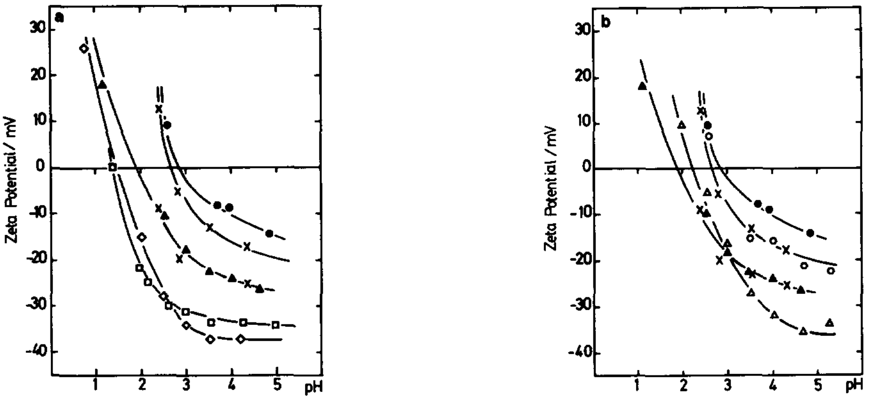

FIG. 1. Zeta potential at 22.5°C as a function of the suspension pH of (▲) Co_9S_8, (●) MoS_2, (×) mixture of MoS_2 and Co_9S_8 (Co/Mo = 0.50). (a) (◇) HSP sample (Co/Mo = 0.50), (□) HSP sample (Co/Mo = 0.15) (b) (○ and △) CM sample (Co/Mo = 0.50).

new phase corresponds to the "Co–Mo–S" phase described by Topsøe and co-workers. A HSP sample with Co/Mo = 0.15 shows similar behavior: a single phase is again detected.

The CM sample, however, shows an electrophoretic behavior similar to the Co_9S_8 and MoS_2 reference mixture (see Fig. 1b): two families of particles, which can be assigned to Co_9S_8 and MoS_2, respectively, are clearly observed. In this sample the interactions between the two phases were broken up by the ultrasonic treatment, and consequently both were observed by electrophoretic measurements. On the other hand, the behavior also suggests that these phases are not covered by the "Co–Mo–S" phase since (a) the IEP of the Co_9S_8–CM phase is greater than the IEP of the Co_9S_8-reference sample and (b) the IEP of the "Co–Mo–S" phase is lower than that of the Co_9S_8-reference sample. Therefore, if the Co_9S_8–CM phase is partially covered by the "Co–Mo–S" phase, its IEP must be lower than that of the Co_9S_8-reference sample.

The different IEP of the reference sample and that of the Co_9S_8–CM might be due to the fact that the Co_9S_8–CM phase would be partially covered by MoS_2, since the MoO_3 dissolves in the $(NH_4)_2S$ solution and would be converted into soluble ammonium thiomolybdate, whereas the Co_3O_4 is not soluble in a solution of excess sulfide ions (*5*). Moreover, the IEP of CM and that of the reference MoS_2 are more similar because the MoS_2–CM phase would not be partially covered by Co_9S_8 since the Co_3O_4 is not soluble in $(NH_4)_2S$ (*5*).

We can therefore conclude that electrophoretic measurements of unsupported Co–Mo catalysts show that, while in HSP samples there is only a single phase (Co–Mo–S), in CM samples there are two phases (Co_9S_8 and MoS_2). In addition, it is shown that the CM phases are not partially covered by the Co–Mo–S phase.

ACKNOWLEDGMENTS

We thank Professor B. Delmon for many valuable comments and suggestions. The authors are grateful to the Dirección de Investigaciones Científicas y Tecnológicas of the Universidad de Santiago de Chile.

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Received February 28, 1983