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The Influence of a New Preparation Method on the Catalytic Properties of CoMo and NiMo Sulfides

Catalysts based on molybdenum or tungsten sulfides, promoted by nickel or cobalt, have been used extensively for hydrotreating reactions. In spite of the great commercial significance of these catalysts, little is understood regarding the general fundamental basis for the origin of their catalytic activity. It is generally believed that an interaction between the active phase (Mo or W) and the promoter (Co or Ni) takes place. Different models have been suggested to explain the enhanced activity of the catalysts: the intercalation model (*1*), the synergy by contact model (*2*), the formation of a mixed promoter-active element-S phase (*3*), the electronic basis for the promotion effects suggested by Harris and Chianelli (*4*), etc. It has been stated that the behavior of unsupported catalysts as a function of the atomic composition is similar to that observed for supported catalysts (*5*). Nevertheless, it is important to note that the catalytic properties of the bulk sulfides are dependent on the catalyst preparation method. The comaceration method proposed by Hagenbach (*6*) seems to lead to less efficient catalysts than those prepared by the homogeneous sulfide precipitation (HSP) method developed by Candia *et al.* (*7*).

The aim of this work is to present a new preparation method of CoMo and NiMo bulk sulfides called "impregnated-thiosalt decomposition" (ITD) as well as the catalytic properties and morphological features of these catalysts.

Catalysts obtained by the HSP method were used as reference standards. The experimental conditions for sample preparation by the HSP technique were the same as those reported elsewhere (*5*). The impregnated-thiosalt decomposition method makes use of the classical concept of impregnation, practiced habitually in the preparation of supported metals. The "support" in the ITD method is an ammonium thiosalt, namely $(NH_4)_2MoS_4$, and the impregnating agent is a cationic hydrated salt of cobalt or nickel ($Ni(NO_3)_2$, $Co(NO_3)_2$). The ammonium tetrathiomolybdate was prepared by bubbling hydrogen sulfide through a solution of ammonium heptamolybdate and ammonium hydroxide in water, as reported elsewhere (*8*). The deep red $(NH_4)_2MoS_4$ crystals were separated by filtration, washed with acetone, and dried under vacuum at 298 K. The ammonium thiosalt is soluble in water, but slightly soluble in acetone, which becomes an advantage when using the thiosalt as support for impregnation with the promoter, since the promoter salt is soluble in acetone. An acetone solution containing Co or Ni (as promoters) is added dropwise to the $(NH_4)_2MoS_4$ crystals suspended in this solvent and stirred at room temperature until all the solvent has evaporated. In this manner a mixed-thiosalt precursor with the promoter placed primarily on the surface is obtained.

Two samples were prepared by each method, HSP and ITD, a cobalt–molybdenum catalyst with an atomic ratio Co/Co + Mo = 0.3, and a nickel–molybdenum catalyst with an atomic ratio Ni/Ni + Mo = 0.5. These atomic ratios were selected because the maximum synergic effect is observed around these compositions, for CoMo and

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TABLE 1

HDS of Thiophene at 523 K under Atmospheric Pressure

Catalyst Co/Co + Mo = 0.3	E_a (kcal/mol)	V_s(mol g^{-1} h^{-1}) $\times 10^4$	S_f(m^2 g^{-1})	V_i(mol m^{-2} h^{-1}) $\times 10^5$
HSP	21.5	6.87	38.50	1.78
ITD	20.0	9.33	11.20	8.33

NiMo catalysts. The precursors were heated in a flow of 15% H_2S–H_2 gas mixture (3.6 liters h^{-1}) and kept at 673 K for 4 h. After cooling to room temperature under the same gas flow, the samples were flushed and stored under nitrogen.

Surface areas were determined by the BET method using argon as adsorbate at 77 K. Samples were first outgassed at room temperature under vacuum (1.33×10^{-3} Pa) and then heated at 673 K until a steady weight was obtained. Scanning electron microscopy was used to characterize the morphological features of both preparations. A Jeol JSM-T200 microscope was used for this purpose.

Thiophene hydrodesulfurization and biphenyl hydrogenation were used as model reactions for CoMo catalysts. HDS of thiophene was carried out at 523 K in a conventional flow system under a hydrogen pressure of 1.013×10^5 Pa ($P_{TP} = 2.6 \times 10^3$ Pa). The products were analyzed by gas chromatography using a 3-m stainless-steel column filled with Carbowax 20M. The biphenyl hydrogenation reaction was performed in a dynamic high-pressure flow microreactor, SOTELEM RDP 830 (P_T = 23.5×10^5 Pa, $P_{BP} = 7.8 \times 10^2$ Pa, $P_{H_2S} = 4.3 \times 10^2$ Pa), at 530 K.

For the NiMo catalysts the cyclohexene hydrogenation reaction was used as a test reaction. Tests were performed in a Parr reactor at 573 K and at a hydrogen pressure of 5.5×10^6 Pa. The reaction was carried out without sulfur in the feed.

The hydrodesulfurizations of thiophene and biphenyl hydrogenation activities of CoMo catalysts prepared by the HSP method and the ITD method, as well as the surface area after reaction, are given in Tables 1 and 2. The specific activities reported in Table 1 show that the CoMo (ITD) catalyst is 1.4 times more active than the CoMo (HSP) sample in the HDS reaction at 523 K. Furthermore, the surface area of the ITD sample is lower compared to the surface area of the HSP catalyst, and hence the intrinsic activity of the ITD CoMo catalyst is 5 times higher than that of the HSP catalyst. The same trend is observed for biphenyl hydrogenation, Table 2. In this case, CoMo (ITD) is 3 times more active than the corresponding HSP catalyst. Concerning the NiMo samples, Table 3 shows the specific and intrinsic activities at 573 K

TABLE 2

Biphenyl Hydrogenation at 530 K Using a High-Pressure Flow Microreactor[a]

Catalyst Co/Co + Mo = 0.3	V_s(mol g^{-1} s^{-1}) $\times 10^8$	S_f(m^2 g^{-1})	V_i(mol m^{-2} s^{-1}) $\times 10^8$
HSP	8.5	38.5	0.22
ITD	7.7	11.2	0.68

[a] $P_T = 23.5 \times 10^5$ Pa, $P_{BP} = 7.8 \times 10^2$ Pa, $P_{H_2S} = 4.3 \times 10^2$ Pa.

TABLE 3

Cyclohexene Hydrogenation in a Parr Reactor at 573 K

Catalyst Ni/Ni + Mo = 0.5	T_R (K)	V_s(mol g^{-1} h^{-1}) $\times 10^4$	S_f(m^2 g^{-1})	V_i(mol m^{-2} h^{-1}) $\times 10^4$
HSP	573	9.9	31.9	0.31
ITD	573	51.2	18.4	2.77

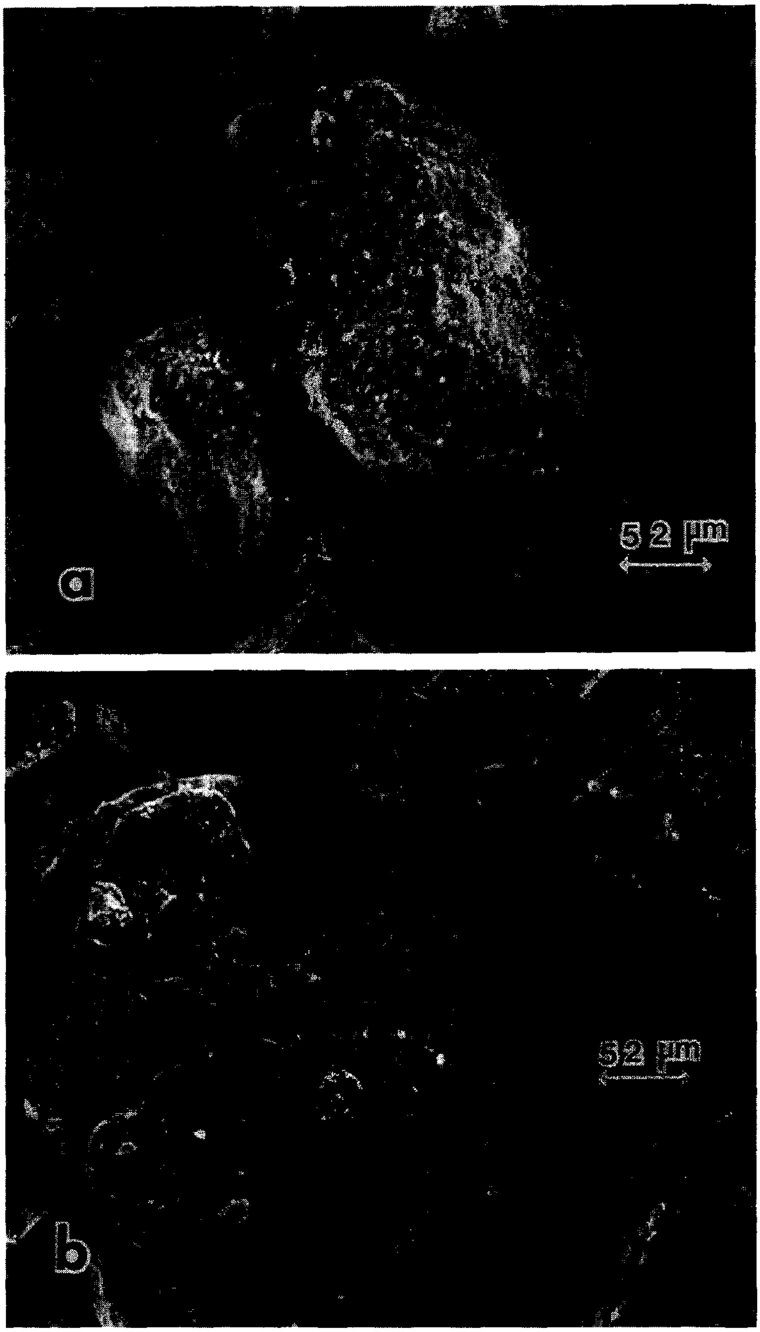

FIG. 1. SEM micrographs of CoMo catalysts, Co/Co + Mo = 0.3. (a) Prepared by HSP; (b) prepared by ITD.

for the cyclohexene hydrogenation reaction. The NiMo (ITD) catalyst is 9 times more active than the NiMo (HSP) catalyst. These activity results strongly suggest that the ITD preparation method leads in a general way to improved catalysts independently of the promoter metal (Co or Ni), the reaction (HDS or hydrogenation), and the

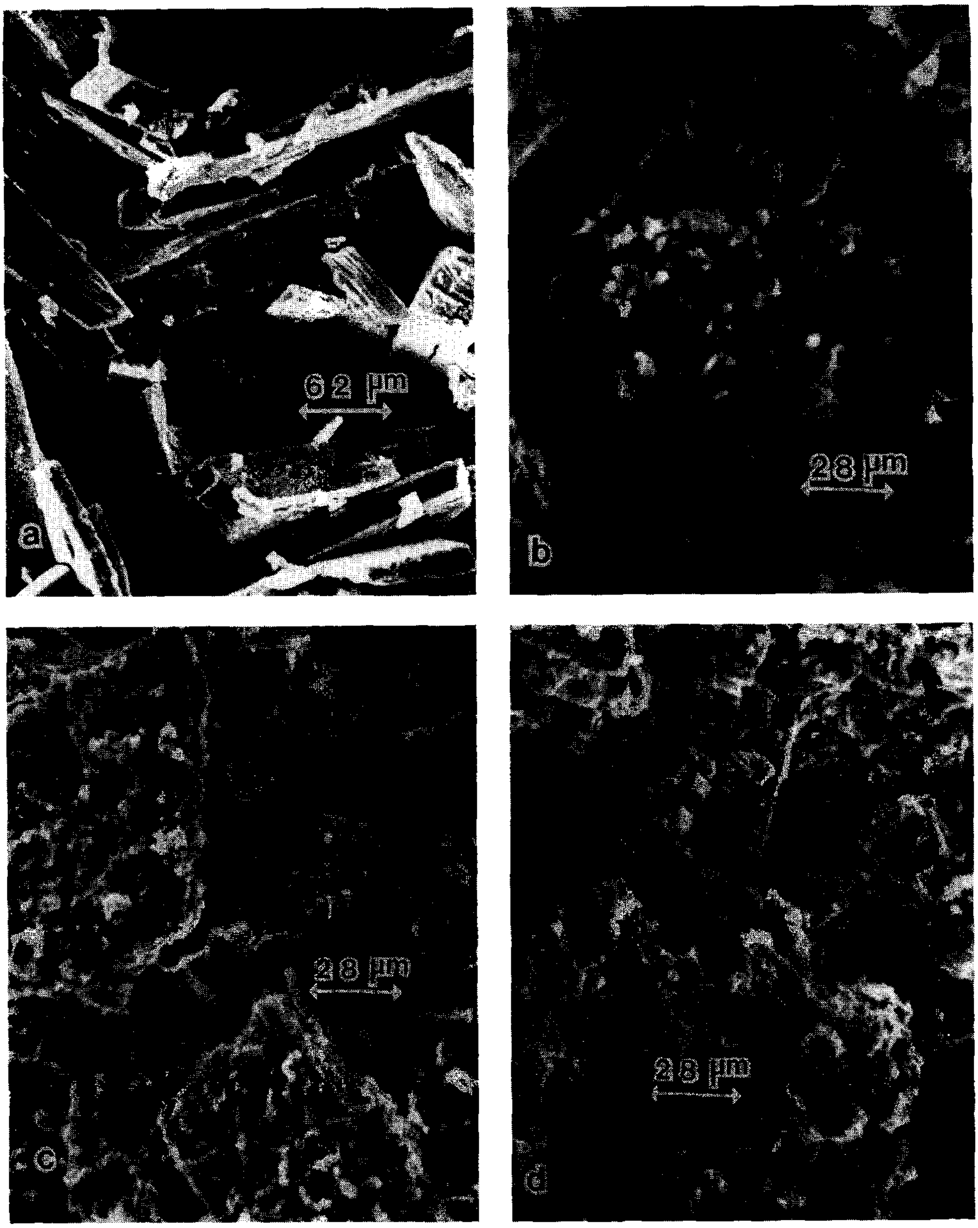

FIG. 2. SEM micrographs of NiMo catalysts prepared by ITD. (a) MoS_2, (b) Ni/Ni + Mo = 0.4, (c) Ni/Ni + Mo = 0.5, (d) Ni/Ni + Mo = 0.6.

experimental conditions (atmospheric or high pressure, static or dynamic).

Scanning electron microscope (SEM) micrographs of CoMo-0.3 catalysts prepared by ITD and HSP methods are shown in Fig. 1. Morphological differences between these samples are evident. The HSP sample shows an irregular shape and significant porosity, Fig. 1a. On the other hand the ITD sample shows particles of MoS_2 of well-defined morphologies. These particles are pseudomorphous with the $(NH_4)_2MoS_4$ precursor. The surface of the MoS_2 appears decorated by clusters, Fig. 1b. This fact is more evident from the micrographs shown in Figs. 2a–2d for a series of NiMo catalysts with varying nickel concentrations (MoS_2, Ni/Ni + Mo = 0.4, 0.5, 0.6). In these micrographs a progressive surface decoration was observed as a function of the promoter concentration. This phenomenon seems similar to that observed in supported metal catalysts in which metal crystallites covering the support grow and sinter after an increase in metal loading.

Improved catalytic properties were obtained by using the ITD method of preparation. The goal of the impregnation method (very useful in the case of supported noble metals) is to disperse an active phase onto a substrate in order to increase the number of active surface site. This concept seems to be well adapted to mixed bulk sulfides. Thus, the ITD method leads to mixed catalysts which are composed of MoS_2 crystals with the promoter sulfide decorating their surfaces as shown from the SEM experiments. The number of active surface sites in this preparation seems to be enhanced. This is supported by the comparison between the intrinsic activities values of ITD and HSP catalysts.

It has been recognized that the active sites in MoS_2 probably lie on the edge planes of the crystals and that the basal planes (002) are quite inert (*9*). On the other hand, studies on single crystals have shown the preference of promoter atoms to lie on the MoS_2 crystal edges (*10*). In the case of catalysts obtained by ITD we observed that both basal planes and the edges of MoS_2 crystals appear decorated by clusters, presumably of the promoter sulfide. The role of the different species obtained from the "impregnation" of the $(NH_4)_2MoS_4$ with the promoter is a subject of further research already in progress.

In conclusion, it has been shown that the ITD method leads to more efficient CoMo and NiMo bulk sulfides. This efficiency enhancement might be related to an increase in the number of active surface sites.

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