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Synergy between "NiMoS" and Co_9S_8 in the Hydrogenation of Cyclohexene and Hydrodesulfurization of Thiophene

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A synergy in the hydrogenation of cyclohexene and hydrodesulfurization of thiophene is observed when the so-called "NiMoS" phase, prepared by the HSP method, is mixed with Co_9S_8. Compared to the properly weighted addition of the components, activities are increased by a factor of approximately 2 (for about 25 wt% of Co_9S_8 in the mixture) and 3.5 (for about 75 wt%), in hydrogenation and hydrodesulfurization, respectively. The results can be interpreted as due to the action of spill-over hydrogen on catalytic centers associated with "NiMoS" (remote control mechanism).

INTRODUCTION

This paper deals with the origin of synergy between sulfided Group VI and Group VIII metal elements in hydrotreating reactions.

There is little doubt that the so-called "CoMoS" and "NiMoS" (*1, 2*) phases may exhibit higher activities than the sulfides of the corresponding single elements. There are, however, strong indications that the formation of a special association between elements is not the only reason of synergy. We have shown that catalysts containing little or no "MeMoS" were quite active and sometimes had a more stable activity (*3–6*). On the other hand extensive physicochemical investigation of catalysts having worked shows that the "CoMoS" (*7–10*) or "NiMoS" (*11*) phases undergo some decay, to form single sulfides, while retaining most of, or all their activity.

Extensive studies with physical mixtures associating together pure or supported single sulfides (*12, 13*) gave substance to our hypothesis that the synergy, or at least part of the effect which is observed, could be explained by the remote control mechanism (*3, 4, 14–17*). Let us recall that, in the case of hydrodesulfurization catalysts, the remote control mechanism works in the following way: hydrogen is dissociated to spill-over hydrogen H_{SO} on Co_9S_8, NiS_x, or FeS_x; it migrates onto the surface of the other catalytic phase (MoS_2, "CoMoS") and reacts with it for activating or maintaining active the catalytic sites carried by this second phase.

The objective of the work is to show that higher catalytic activities are obtained when a sample exhibiting all the known characteristics of "NiMoS" is mixed with Co_9S_8. There were two reasons for investigating the "NiMoS"–Co_9S_8 system. The first was to compare the behaviour of "CoMoS" with that of "NiMoS" when mixed with Co_9S_8; a synergy was observed when "CoMoS" was mixed with Co_9S_8. The second reason was to produce another proof that an "MeMoS" phase did not exhibit the maximum possible catalytic activity and could be further activated by a separate phase.

We prepared unsupported "NiMoS" with 30% atom nickel by the homogeneous sulfide precipitation (HSP) method (*6–14*), which has been shown to maximize the amount of "MeMoS" produced. We verified that all characteristics of our sample, as

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determined by DTA, microelectrophoresis, and XPS measurements, were identical to those indicated in the literature for the so-called "NiMoS" phase. We used this well characterized mixed sulfide to prepare mechanical mixtures with Co_9S_8 and tested the catalytic activity of these mechanical mixtures in the simultaneous HDS of thiophene and HYD of cyclohexene at a pressure of 3 MPa. We also studied the temperature-programmed reduction (TPR) of our pure sulfides and mechanical mixtures in order to evidence that spill-over hydrogen created on the Co_9S_8 act as a powerful reducing agent of the "NiMoS" phase.

EXPERIMENTAL

The Co_9S_8 and "NiMoS" sulfides were obtained by treating 4 g of their precursors prepared by the HSP method (*6*, *14*) with a mixture of $H_2S(15\%)/H_2$ for 4 h at 673 K. Surface areas were: Co_9S_8, 14 m^2 g^{-1}; "NiMoS," 26 m^2 g^{-1}. These sulfides were used as such for the preparation of the mechanical mixtures.

Co_9S_8 and "NiMoS" mixtures of different compositions Rm = Co_9S_8/("NiMoS" + Co_9S_8) (by weight) were agitated in n-pentane which was then evaporated. The mixtures were resulfided *in situ*, under $15\%H_2S/H_2$ mixture (20 liter h^{-1}) at 573 K for 1 h before catalytic tests and TPR.

The catalytic activity measurements were performed in a stainless steel high pressure "Catatest" apparatus (Géomécanique), working in the continuous flow regime. The feed was a mixture of cyclohexene (29.5 wt%) and thiophene (0.5 wt%) in cyclohexane. The H_2(gas N.T.P.)/hydrocarbon (liquid) ratio was 600. The quantity of catalyst used in the reaction was 1 g. The reaction temperature and the liquid hourly space velocity (L.H.S.V.) were 623 K and 34 h^{-1}, respectively. The total pressure was 30 bars. Conversions were measured under the steady-state conditions after 12 h of reaction. The results are presented as conversion (%) per m^2 of catalyst.

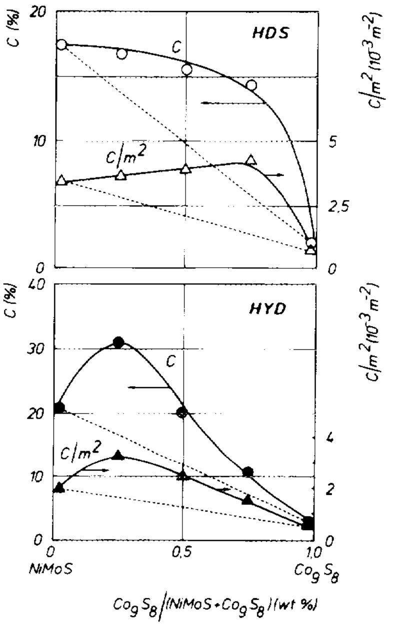

FIG. 1. Activity of the "NiMoS" + Co_9S_8 mechanical mixtures in the HDS and HYD reactions.

TPR were performed on 200 mg sample with ultra pure hydrogen (99.9999%). During the TPR reaction, the temperature was raised (10 K min^{-1}).

RESULTS

The results of the catalytic activity measurements for both HDS of thiophene and HYD of cyclohexene are presented in Fig. 1. Dotted lines represent the activity (conversion) due to the arithmetic addition of the activities of the separate catalysts forming the mixture (assuming zero-order kinetics). The synergy, i.e., the additional conversion due to the *simultaneous* presence of both powders, is the difference between the ordinate of the corresponding experimental point and the dotted straight line. In the case of HDS, for Rm = 0.75 (Fig. 1), the *additional* conversion is 2.5 times higher than the conversion which would result from the added action of the individual components if these were not in contact.

The TPR diagrams of the Co_9S_8 and "NiMoS" sulfides and of the "NiMoS" +

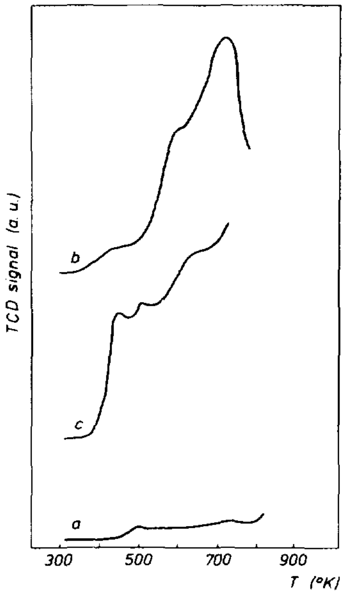

FIG. 2. TPR diagrams of (a) Co_9S_8, (b) "NiMoS," and (c) "NiMoS" + Co_9S_8 (Rm = 0.4).

Co_9S_8 mechanical mixture are presented in Fig. 2.

In agreement with literature, Co_9S_8 (Fig. 2a) presents only a low-intensity peak around 450 K, assigned to weakly bound sulfur species (*9*, *18*, *19*). The increase of the signal observed at about 730 K corresponds to the release of H_2S due to the start of Co_9S_8 decomposition (*19*). The TPR diagram of "NiMoS" (Fig. 2b) consists of a weak peak around 450 K, assigned to weakly bound sulfur species, and an intense double peak in the range 500–770 K. The production of H_2S in this region must be attributed to the partial reduction of MoS_2 crystallites and to some labile sulfur. The TPR diagram of the "NiMoS" + Co_9S_8 mechanical mixture (Fig. 2c), as compared to that of the "NiMoS" sulfide (Fig. 2b), and taking into account that only 60 wt% of "NiMoS" is present in this mechanical mixture, exhibits a higher release of H_2S in the low temperature region (more than 100 K lower than for pure "NiMoS").

DISCUSSION

As no textural effect could explain the observed increase of activity, two ready explanations exist for the observed synergy: remote control or further contamination of the "NiMoS phase" by cobalt. The second explanation would suppose that, in contradiction with literature, the decoration positions were not saturated with 30 atom% nickel. In addition, decoration corresponds to a non stable situation. X-ray diffraction measurements of the used catalysts show that "NiMoS" segregate to Ni_3S_2 during reaction (*20*). Our interpretation was that the observed synergy was due to the remote control mechanism, caused by the production of spill-over hydrogen by Co_9S_8.

The TPR results show that Co_9S_8 promotes the reduction of "NiMoS": an extensive reduction takes place at a temperature more than 100 K lower in the presence of Co_9S_8.

CONCLUSIONS

1. Co_9S_8, mechanically mixed with the "NiMoS" species, brings about an important increase in activity.

2. The results are consistent with the remote control theory: spill-over hydrogen emitted by Co_9S_8, creates catalytic centers on "NiMoS."

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