Preparation and Activity of Solid-State
Hydrodesulfurization Catalysts

There has been much work done in the field of MoS_2-based hydrodesulfurization catalysis trying to establish what phase is responsible for catalytic activity. Much of this research has focused on the effect of the Co promoter and whether its predominant contribution is of the electronic or structural nature. Schuit et al. (1) proposed that the promoter ions stabilize a molybdenum oxide monolayer which is responsible for the observed catalytic activity. Farragher and Cossee (2) postulated that the promoter was "pseudo-intercalated" between successive layers of MoS_2 and that this structural change was accompanied by a surface reconstruction triggering HDS activity. Delmon et al. (3) argued in favor of Co_9S_8 and MoS_2 coexisting as the active species. In this "remote-control model" H_2 is dissociatively adsorbed on the cobalt sulfide and transferred to the MoS_2 surface where it then reacts with an adsorbed sulfur-containing compound. As another possible explanation for the promoter effect of Co or Ni, Pratt and Sanders (4) and Vrinat and co-workers (5) proposed that the promoter stabilizes very small particles of MoS_2. This notion was also supported by more recent NMR experiments performed by Ledoux et al. (6). Topsøe and co-workers (7, 8) were able to correlate HDS activity with a unique but structurally difficult to define "Co–Mo–S" phase, in which it is hypothesized that the Co-promoter atoms lie at the edges of the MoS_2 layers. More recent EXAFS work has provided evidence in support of this edge-decorated MoS_2 species (9). Other researchers (10) have put forward the notion that cobalt sulfide alone might have favor-

able HDS characteristics. This concept was surprising since in previous studies the promoter sulfides had shown little activity (7, 8). More recently Prins and co-workers have expressed doubt about the importance of a Co sulfide phase as the active phase (11). Theoretical work by Harris and Chianelli (12) has indicated that the promoter atom plays a role in determining the electronic state of the MoS_2. Consequently, the increased HDS activity has been attributed to an electronic contribution from the promoter atom. According to this model, only Ni and Co showed a positive activity effect as they increased the electron density on Mo. Fe displayed little effect and Cu acted as a poison, essentially oxidizing Mo. Recently Ledoux et al. (13, 14) proposed the existence of two types of Co species at the edges of the MoS_2 structure, a distorted tetrahedral phase responsible for HDS activity and a rapid octahedral which they think acts as a glue, anchoring the tetrahedral phase to the MoS_2. However, Prins et al. presented EXAFS work which does not support this hypothesis (11).

The present note reports the results of our attempt to grow unsupported bulk P–Mo–S (where P is Fe, Co, or Ni) phases. The synthesis of these phases was based on solid-state reactions of elemental sulfur with metallic promoter and Mo powders. These bulk phases are easier to characterize than those in conventional supported HDS catalysts. Therefore, they offer a better opportunity for establishing correlations between stoichiometry, structure, and activity.

A series of samples with a limited P/Mo ratio and a general stoichiometry of $P_{0.05}$

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Catalyst	BET surface area (m^2/g)
$Fe_{0.05}Mo_{0.975}S_2$	14
$Co_{0.05}Mo_{0.975}S_2$	26
$Ni_{0.05}Mo_{0.975}S_2$	15
$MoS_{1.95}$	20
MoS_2	1

Mo_xS_2 (with x being 0.975 or 0.95) was prepared by combining stoichiometric amounts of the elemental promoter and molybdenum powders with elemental sulfur, all three chemicals used being Fluka products (purum). The powders were thoroughly mixed by grinding them together to insure intimate contact between the components. The mixtures were placed into quartz tubes which were then evacuated to about 0.1 Pa and sealed. The tubes containing the mixtures were heated at a heating rate of 10 K per minute from room temperature to 783 K, held at this temperature for 24 h and then rapidly quenched. Once the treatment was finished, the quartz tubes were opened. The contents of the tubes, generally dark grey or black materials, were removed and, if necessary, ground into fine powders. Based on their nominal composition the samples were named $Fe_{0.05}Mo_{0.975}S_2$, $Co_{0.05}Mo_{0.975}S_2$, and $Ni_{0.05}Mo_{0.95}S_2$. Unpromoted MoS_2 and a nonstoichiometric sample, $MoS_{1.95}$ were also prepared from a mixture of metallic molybdenum and elemental sulfur following the procedure mentioned above. The surface areas of the freshly prepared samples were determined by using the BET method and a Monosorb Quantachrome Single Point Instrument with nitrogen as adsorbate (Table 1).

The catalytic activity for the hydrodesulfurization of thiophene (Aldrich 99+%, Gold Label) was measured in a ¼-in. diameter stainless-steel continuous-flow reactor. The powdered catalyst (0.25–0.35 g) was loaded into the reactor and the temperature

raised to 673 K under a flow of high-purity helium at 20 ml per minute and held at 673 K for 30 min. Then, the temperature was lowered to the desired reaction temperature, typically between 473–673 K. The He flow was replaced by a gaseous feed stream containing 2.7% (by volume) of thiophene, the balance being hydrogen, at a flow rate of 10 ml/min and atmospheric pressure. The high-purity He and H_2 (<49 ppm impurities) were further purified by passage through a commercial oxygen trap (Matheson) and a bed of molecular sieves (5 Å) to remove moisture.

The effluent from the reactor was analyzed by gas chromatography. Product separation and analysis were performed by using an n-octane/Porasil C column in a Varian 3700 gas chromatograph equipped with a thermal conductivity detector. Peak areas were determined by a Hewlett–Packard 3390A integrator.

At 523 K the activity trends for the model catalysts were Ni(30.0%) > Co (6.3%) > Fe (5.7%) > $MoS_{1.95}$ (5.5%) > MoS_2 (<1%). The specific thiophene conversions for these materials are given in parentheses. At 573 K the activity trends for the model catalysts remained, but the differences became more pronounced. After 3 h on stream it was seen that the $Ni_{0.05}Mo_{0.95}S_2$ catalyst had a steady-state conversion just over 60%, the $Co_{0.05}Mo_{0.975}S_2$ was in the mid-50% range, $Fe_{0.05}Mo_{0.975}S_2$ was just over 40%, $MoS_{1.95}$ was near 30%, and MoS_2 was consistently below 1%. At higher temperatures (673 K) conversions in excess of 90% were consistently observed for the promoted samples and $MoS_{1.95}$.

The temperature dependence of the HDS activity for all the model catalysts is presented in Fig. 1a. The turnover frequencies (TOF) were expressed in terms of moles of thiophene converted per gram-atom Mo per second. Again, it may be seen that the promoter trend of Ni > Co > Fe is observed in our solid-state system. Other researchers (15, 16) have reported similar findings, although Fe-promoted catalysts
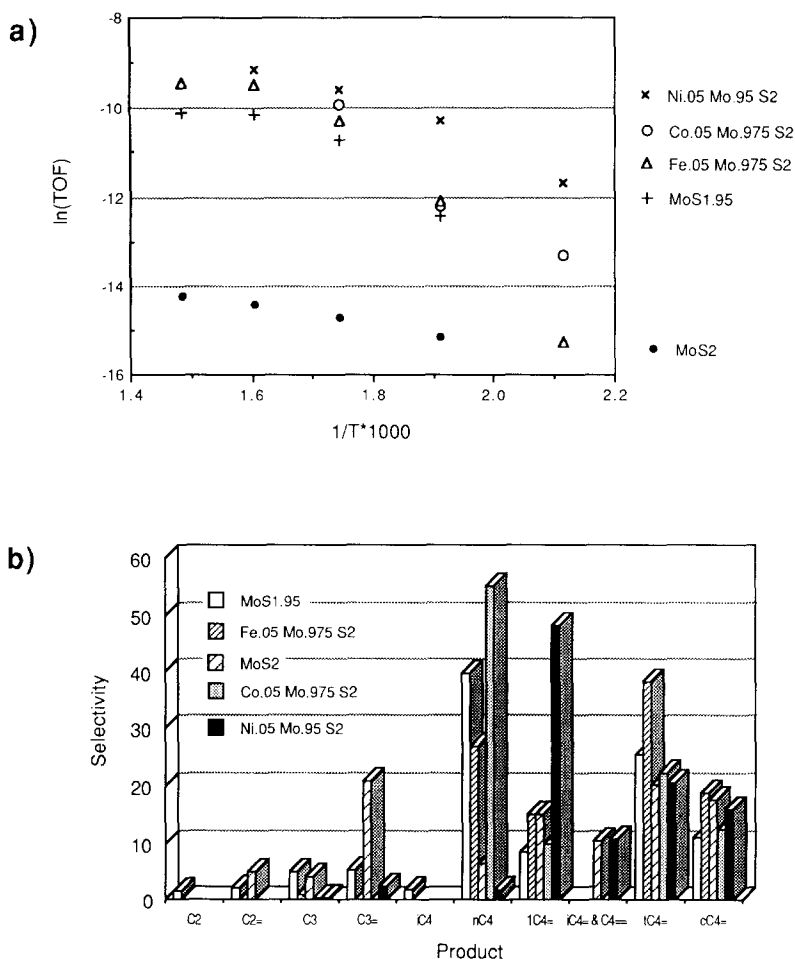
FIG. 1. (a) Temperature dependence of turnover frequencies (molecules of thiophene/mol of Mo/s) for thiophene HDS over the various solid-state catalysts. (b) Product distributions obtained in thiophene HDS. The results shown were collected at 523 K on all samples, except for the Ni-containing catalysts where data are shown for a temperature of 473 K.

tend to have low activities. However, in our solid-state catalysts the promoting effect of Fe is far from negligible and is very close to that of Co. It should be noted that the substantial increase in HDS activity of these solid-state catalysts cannot be attributed solely to the presence of promoters. In fact, even in the absence of a promoter, significant increases in HDS activity could be achieved simply by introducing anionic sulfur vacancies into MoS_2. Hence, one of the predominant roles of the promoter atom in these solid-state catalysts appears to be linked to the creation of sulfur vacancies.

Of course, this does not rule out that the promoter may have an additional second-order effect beyond facilitating nonstoichiometry and sulfur deficiency in molybdenum sulfide.

Two possible scenarios for the formation of nonstoichiometric molybdenum sulfide could be envisioned. One is that the incorporation of lower charged promoter ions into the MoS_2 lattice requires the introduction of sulfur vacancies to maintain electroneutrality. The second possibility could be that the promoter acts as a scavenger during catalyst synthesis. The formation of

promoter bulk sulfides could thereby deplete the sulfur pool required for the formation of stoichiometric MoS_2. In support of the second hypothesis, when presulfiding (H_2/H_2S at 673 K for 24 h) a mechanical mixture of Mo and promoter powder bulk promoter sulfides were preferentially formed, leaving most of the Mo unreacted. At this point the relative contribution of each of these two scenarios is not yet clear.

The product distributions of the different hydrocarbons resulting from the hydrodesulfurization of thiophene are given in Fig. 1b. The data shown in this figure were collected at conversions less than 8% of the total thiophene fed. Isobutene and butadiene could not be separated under our experimental conditions and Fig. 1b shows the sum of these two products. Due to the higher activity of the Ni-promoted sample the reaction temperature was 473 K rather than the 523 K used for the other promoted catalysts in order to keep the conversion and TOF values roughly equivalent. It must be noted that product distributions tend to be not only a function of conversion but also of temperature. Therefore, the data shown in Fig. 1b should only be used for illustrating that our catalyst selectivities conform with those found typically in HDS catalysts under comparable reaction conditions.

Although each of the three promoters used in this study provided similar increases in activity, there are subtle differences in the product distributions. $Co_{0.05}Mo_{0.975}S_2$ and $MoS_{1.95}$ preferentially produced n-butane, $Fe_{0.05}Mo_{0.975}S_2$ favored the formation of $trans$-2-butene, $Ni_{0.05}Mo_{0.95}S_2$ made primarily 1-butene, while MoS_2 produced significant quantities of propylene, $trans$-2-butene, and cis-2-butene. Only MoS_2 and $Ni_{0.05}Mo_{0.95}S_2$ yielded any isobutylene or butadiene in the product stream, and only $MoS_{1.95}$ produced any isobutane. Lighter products (<C4) were produced by all samples; however, they were never major (i.e., > 10%) components, except in the case of propylene for

the MoS_2 sample. The high n-butane fractions seen for $Co_{0.05}Mo_{0.975}S_2$ and $MoS_{1.95}$ are likely due to an increased H_2 transport capability resulting from the presence of unreacted Mo in the catalyst synthesis charge. Vrinat et $al.$ (17) have shown that Ni has greater hydrogenation activity than Co. However, in our case the Ni catalyst was run at a lower temperature than the other samples and thus this characteristic hydrogenation trend was not as pronounced. At higher temperatures (i.e., > 523 K) all the promoted samples produced predominantly n-butane. As interesting as these subtle trends may be, they are not the focus of this note and a more detailed kinetic analysis will be required to fully explain the observed differences.

It is important to note that more active samples consistently had larger surface areas than that of the lower activity MoS_2 (Table 1). However, a normalization of activity based on BET surface area would not be meaningful in view of the lack of correlation between HDS activity and surface area previously reported (18–20). Within the HDS research community, a consensus seems to be developing that a normalization based on edge area might be more desirable. However, to accurately determine the edge area is not a trivial task. In the case of our solid-state catalysts, high-resolution electron microscopy showed that the exposed basal planes of MoS_2 containing the Mo ions remain undisturbed when promoters are introduced. In striking contrast to that, other exposed crystallographic orientations containing sulfur ions, which could be considered "edge areas," show significant structural disorder. From the lack of long-range order in these planes we can infer surface roughening on an atomic scale and the presence of sulfur vacancies. Figure 2 illustrates the structural effect of the promoter ($Co_{.05}Mo_{.975}S_2$) on these planes compared with that of stoichiometric MoS_2. The microscopic observations are in excellent agreement with XRD results showing preferential
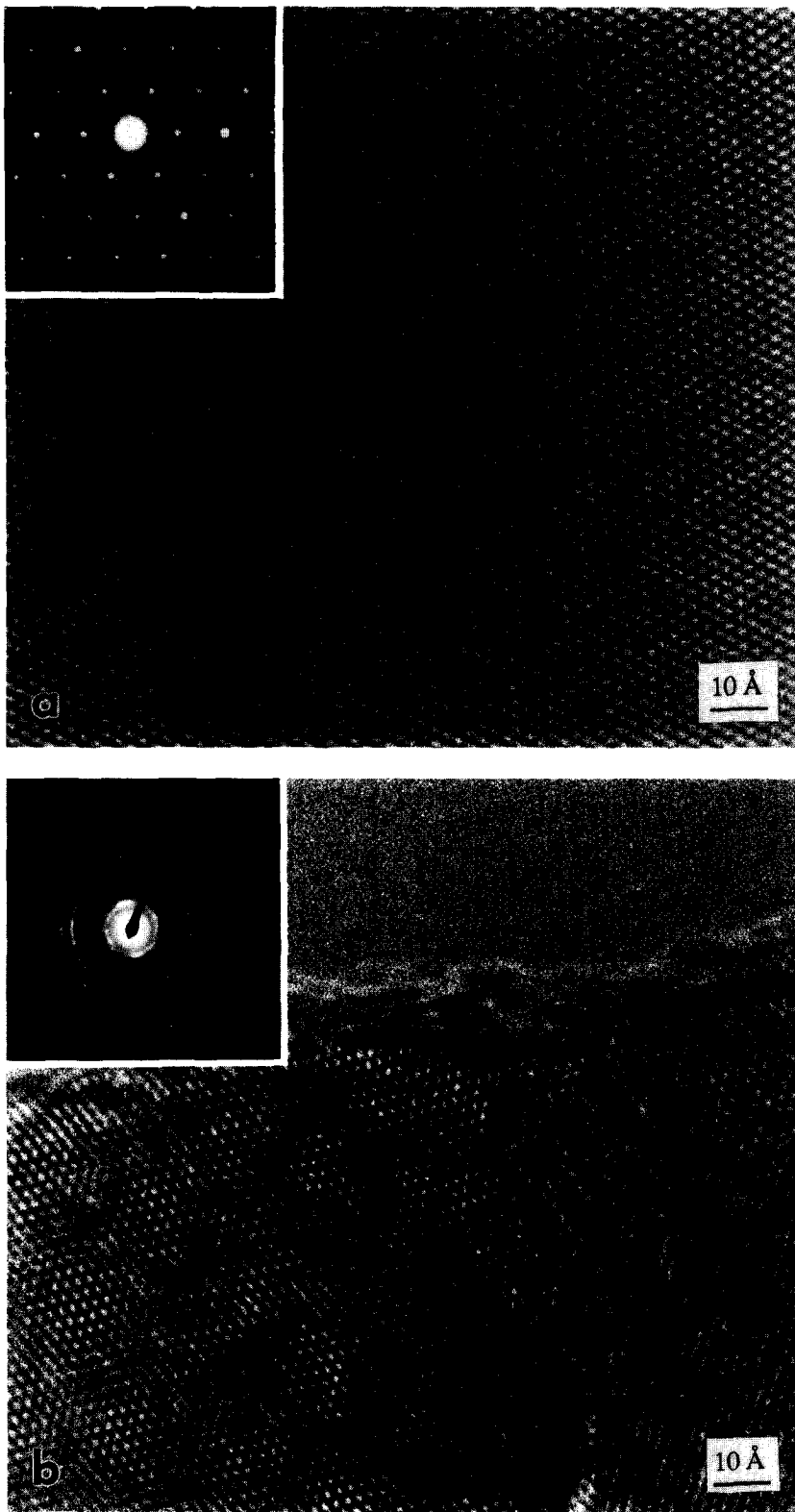
FIG. 2. Examples of high-resolution transmission electron micrographs obtained on a JEOL 4000EX microscope. Inset: Selected area diffraction pattern. (a) Well-oriented MoS$_2$ (stoichiometric) structure showing the 2.74 and 2.69 Å lattice planes. (b) Disordered "edge" structures in the cobalt-containing catalyst.

broadening of reflections arising from sulfur-containing planes.

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