The Sulfided Co-Mo/γ-Al_2O_3 Catalyst: Evidence of Structural Changes During Hydrodesulfurization of Dibenzothiophene

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Introduction

The catalyst most often used for hydrodesulfurization (HDS) of petroleum fractions are derived from oxides of Co and Mo supported on γ-Al_2O_3, and their surfaces are sulfided prior to operation. Structures of the oxidic and sulfidic forms of the catalyst are incompletely understood and much debated (1-3), and since the available structural information has been derived from studies of catalysts at conditions far removed from those of commercial operation (about 50-200 atm and 350-320°C), it is not clear how operating variables influence the catalyst structure and activity in practice.

The hydrodesulfurization kinetics data reported here were measured to characterize the catalyst operating at about 100 atm and 300°C; the reactant stream contained dibenzothiophene (DBT) and hydrogen dissolved in n-hexadecane carrier oil. The results provide the first evidence of structural variations in the Co-Mo/γ-Al_2O_3 catalyst brought about by changes in the reaction environment.

Experimental Methods

The catalyst used in all experiments was American Cyanamid HDS 16A having the following properties (prior to sulfiding): surface area, 176 m^2/g; pore volume, 0.50 cm^3/g; Co content, 4.4 wt%; and Mo content, 7.5 wt%. A sample of 10 mg of catalyst powder (80-100 mesh particles, demonstrated experimentally to be small enough to ensure the lack of intraparticle diffusion resistance) was charged to the reactor, and the catalyst was sulfided at 400°C for 2 h with a flow of about 40 cm^3/min of 10% H_2S in H_2 at atmospheric pressure. Following the sulfiding, the flow of feed liquid was started. The feed contained 0.12 wt% DBT (Aldrich, 95% purity) in n-hexadecane [Humphrey Chemical Co. (redistilled)], and it was saturated with H_2 at 68 atm and room temperature. Occasionally, the feed was saturated with H_2S at various partial pressures before it was saturated with H_2. Experiments were carried out with a flow reactor described in detail elsewhere (4). The reactor operated at 300°C and 104 atm. Under all reaction conditions, the fractional conversion H_2 was < 5%, so the H_2 concentration could be considered to be virtually constant throughout the reactor.

Liquid product samples were collected periodically (without interrupting the reactant flow) and analyzed by glc (5). DBT and H_2 were converted into biphenyl and H_2S. To a first approximation, these were the only products formed; the detailed reaction network is considered separately (6).

Results

Some conversion data are plotted in Fig. 1. They show that the initial conversion at a relatively high inverse space velocity (proportional to reactant-catalyst contact time) increased about 10% over the first 10-20 h of operation, following by nearly constant conversion (referred to as "lined-out conversion") for 150 h or more. When the lined-out conversion was determined for various space velocities, the reaction was found to be pseudo-first-order in DBT (5).

Figure 1 shows the results of variations in the space velocity caused by changes in the feed flow rate. After the first step change in feed flow rate, there was a change in conversion characterized by a transient period of some 50 h before the catalyst achieved another time-invarient activity. After a second change in space velocity at 70 h onstream time, giving again the original value, there followed a transient period, as expected, but, surprisingly, the catalyst failed to return to its original lined-out activity.

In further experiments, each begun with a fresh catalyst charge, increasing concentrations of H_2S were added to the feed. The data of Fig. 2 show that at low H_2S concentrations [$(H_2S)/(H_2)$ in the feed liquid - 0.015], the qualitative pattern of changes mentioned above again occurred. The catalyst activity in the presence of added H_2S at each space velocity appeared to be less than that in the absence of added H_2S, corresponding to the well-known inhibition of reaction by H_2S (1, 6). When higher feed concentrations of H_2S were used, the transient periods of change in the catalyst activity became shorter; when the $(H_2S)/(H_2)$ ratio in the feed was as great as 0.2, the transients in catalyst activity were virtually eliminated.

In summary, these results show that H_2S does more than just inhibit the HDS reaction by adsorbing on catalytic sites in competition with DBT. We infer that when the space velocity was increased, reducing the concentration of H_2S produced in the reaction (Figs. 1 and 2), structural changes took place, reducing the number of catalytic sites. The presumed solid-state reactions were slow, in contrast to the adsorption of H_2S that caused the inhibition of reaction. The loss of catalytic sites was only partially reversed when the concentration of H_2S was again increased by decreasing the space velocity. But when H_2S was present in the feed in sufficient amounts that the H_2S concentration remained nearly constant throughout the reactor, then the catalyst activity (and structure) did not change with space velocity; the data then indicate only the simple competitive hibition of reaction by H_2S, and there was no hysteresis.

The foregoing results suggest that there is an optimum concentration of H_2S [or perhaps a $(H_2S):(H_2)$ ratio] corresponding to a catalyst structure which has a maximum HDS activity. Experiments were carried out to test this suggestion. In one series, catalyst were brought on stream with initially low space velocities, producing initially high activities; the experiments were done with various feed H_2S concentrations. The pseudo-first-order rate constants (determined from linear semilogarithmic plots of fraction unconverted vs. inverse space velocity) are represented by curve B in Fig. 3; they indicate that in these experiments the H_2S was simply a reaction inhibitor.

In the complementary series of experiments, each new catalyst charge was brought on stream at a high space velocity and, correspondingly, with a relatively low conversion and a low H_2S concentration; H_2S concentration in the feed was varied systematically. The rate constants scatter around curve A in Fig. 3. These results confirm that increasing the H_2S concentration increased the activity of the catalyst when it was brought on stream in such a way that its initial activity was relatively low.

The important conclusion is that the catalyst achieves a lined-out activity which is dependent on the reactor startup procedure (and probably on the presulfiding procedure as well). This conclusion may be important to the technology of HDS, and we suggest that the industrial art may include the application of presulfiding and reactor startup procedures which maximize the catalyst activity; the optimum startup would ensure that some H_2S contacted the catalyst initially.

Discussion

The observed changes in catalytic activity and, by inference, catalyst structure, are suggestive of Farragher's (7) observations of the activity of Ni-W/γ-Al_2O_3 catalyst for benzene hydrogenation. Farragher presented evidence of hysteresis effects similar to those reported here, but caused by temperature variations; he explained the results in terms of solid-state reactions influencing catalyst structure and activity. The suggested reactions were the following:

$$3V_s + Ni_3S_2 + 2H_2 \rightleftarrows 3Ni_s + 2H_2S \qquad (1)$$

$$2W^{4+} + Ni_s \rightleftarrows 2W^{3+} + Ni_s^{2+} \qquad (2)$$

The former reaction involves conversion of Ni from bulk Ni_3S_2 on the catalyst; it becomes intercalated in interstitial octahedral holes at the surface of WS_2 crystallites on the catalyst surface. The latter reaction is believed to produce W^{3+} ions at the surface, which Voorhoeve et al. (8,9) have characterized by esr and identified as the catalytic sites for benzene hydrogenation. Farragher showed that both the rate constant for benzene hydrogenation and the esr signal indicative of W^{3+} were dependent on the P_{H_2S}/P_{H_2}

ratio in a way that is consistent with the catalyst stoichiometry suggested in Eqs. (1) and (2).

There is much evidence (1, 11) [but not a consensus (2, 3)] supporting the view that the Co-Mo/γ-Al_2O catalyst is similar to the Ni-W/γ-Al_2O_3 catalyst, consisting of MoS_2 and Co_9S_8 on the Al_2O_3 surface, and esr evidence supports the idea that the catalytic sites are Mo^{3+} ions intercalated at the edges of the MoS_2 crystallites (1, 7, 12).

Following Farragher, and assuming the validity of the edge intercalation model for the Co-Mo catalyst, we suggest the following speculative interpretation of the structural changes in the catalyst brought about by changes in the reaction environment. The fully active catalyst is supposed to consist of MoS_2 crystallites intercalated with Co^{2+} ions, and H_2S can bond to the surface at anion vacancies in competition with DBT, causing inhibition of the HDS reaction. When only little H_2S is present, however, intercalated MoS_2 may be converted into a sulfur-deficient layer structure which may lack catalytic activity. We speculate that $CoMo_2S_4$ may be the sulfur-deficient structure, since it is known to lack HDS activity and to have the layer structure shown in Fig. 4 (10). Here both Co^{2+} and Mo^{3+} ions are octahedrally surrounded by S^{2-} ions, whereas in MoS_2 the surrounding is trigonal prismatic.

It is important that $CoMo_2S_4$ meets the criterion of having a lower sulfur content than the presumed catalyst, Co-intercalated MoS_2; to explain the observed intermediate activities, we suggest that the catalyst may consist of a range of intermediate structures which could be interconverted by local redistributions of Co and Mo ions accompanied by changes in the Mo-S surrounding.

An explicit suggestion is the epitaxial structure shown in Fig. 5. This structure accounts for the observed promotion by Co at higher Co/Mo ratios than can be accounted for by the edge interculation model (11). It might be expected to undergo changes analogous to those postulated by Farragher for the Ni-W catalyst:

$$9V_s + Co_9S_8 + 16H_2 \rightleftarrows 9Co_s + 8H_2S \qquad (3)$$

$$2Mo^{4+} + Co_s \rightleftarrows 2Mo^{3+} + Co_s^{2+} \qquad (4)$$

This model is consistent with the experimental evidence, but it is rough and speculative and in need of experimental evaluation.

Notation

k	pseudo-first-order rate constant, $cm^3/h \cdot g$ of catalyst
P	partial pressure
V_s	interstitial octahedral hole in a layer structure like MoS_2

Acknowledgment

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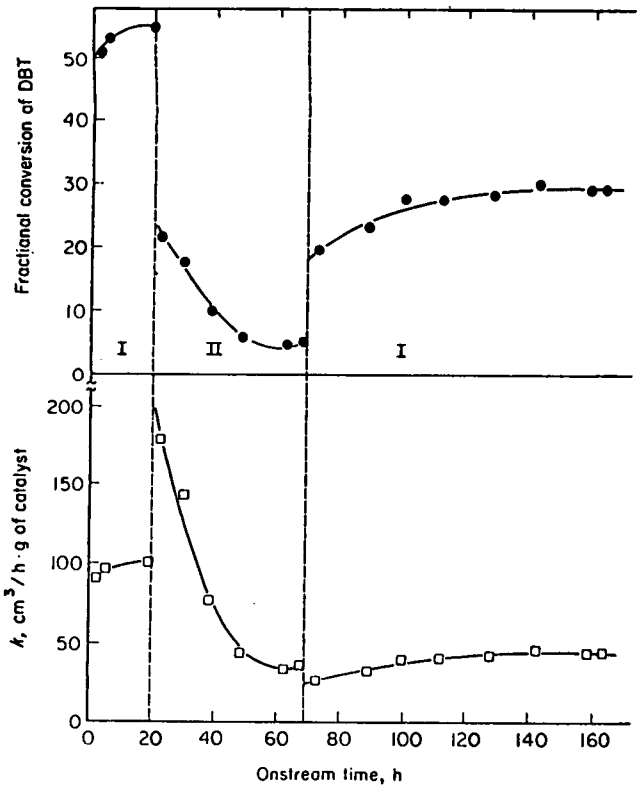

Figure 1. Conversion and psuedo-first-order rate constants for HDS of DBT. I: space velocity = 128 $cm^3/h \cdot g$ of catalyst. II: space velocity = 730 $cm^3/h \cdot g$ of catalyst. Feed was 0.12wt% of DBT in n-hexadecane which had been saturated with H_2 at 25°C and 68 atm. The catalyst was American Cynamid HDS 16A. Reaction conditions: 300°C and 104 atm.

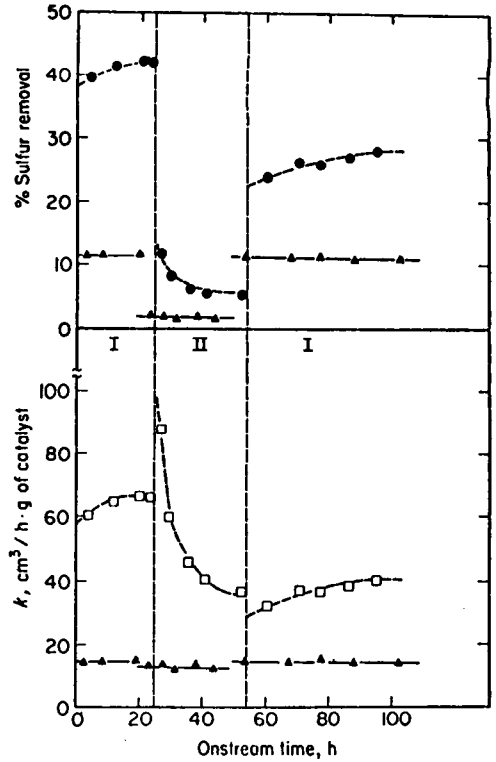

Figure 2. Conversion and psuedo-first-order rate constants for HDS of DBT. I: space velocity = 124 $cm^3/h \cdot g$ of catalyst. II: space velocity = 705 $cm^3/h \cdot g$ of catalyst. Concentration ratios $(H_2S)/(H_2)$ = 0.2 (-Δ-); 0.015 (-O-). The feed, catalyst, and reaction conditions were the same as those described in the caption of Fig. 1, except for the added H_2S.

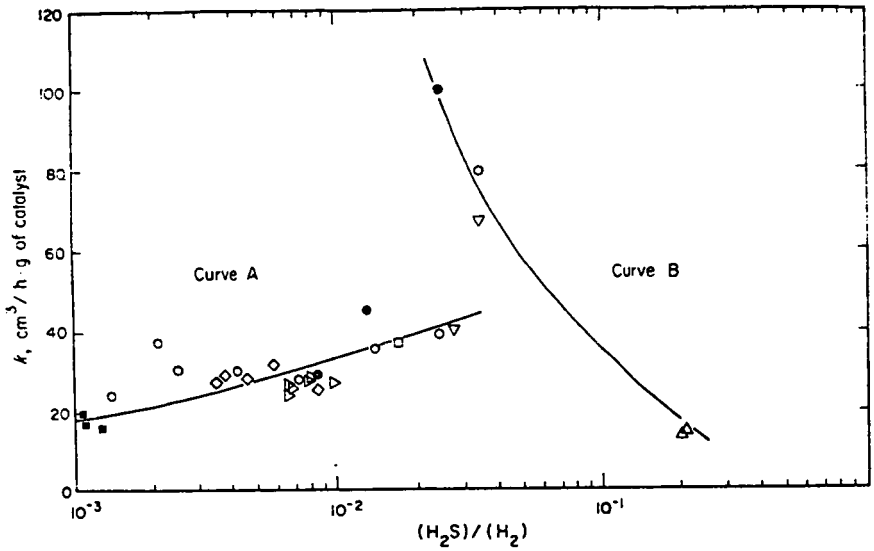

Figure 3. Effects of H_2S on catalyst activity for HDS of DBT at the reaction conditions given in the caption of Fig. 1.

The points on curve A represent conversion measured at various space velocities and with various feed $(H_2S)/(H_2)$ ratios for catalyst which had previously lined out at high space velocities (700-750 $cm^3/h \cdot g$ of catalyst). These results show that the catalyst which lined out at high space velocities was sulfur deficient and relatively inactive, becoming more active on addition of H_2S, as discussed in the text.

The points on curve B represent conversion measured at various feed $(H_2S)/(H_2)$ ratios for catalyst which had previously lined out at low space velocities (90-100 $cm^3/h \cdot g$ of catalyst). These results indicate competitive inhibition of reaction by H_2S.

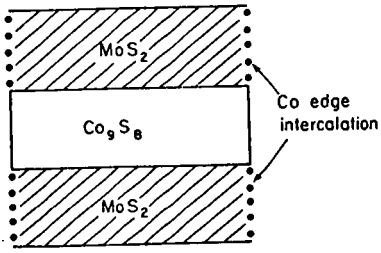

Figure 4. Model of the sulfided Co-Mo/γ-Al_2O_3 catalyst, representing layers of Co_9S_8 and MoS_2 intercalated with Co^{2+} at the crystal edges.

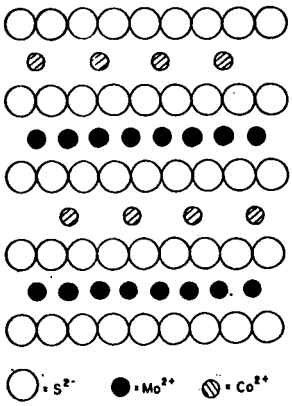

Figure 5. Representation of the layer structure of $CoMo_2S_4$; the actual structure is distorted, as shown by van den Berg (19).