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NOTES

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

The catalysts 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 not completely 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 350–420°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 an indication of structural variations in the Co–Mo/γ-Al_2O_3 catalyst brought about by changes in the reaction environment.

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- to 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 hr 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, designated 95% purity; no impurities were detected by glc) 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 conversion of H_2 was $<5\%$, and therefore the H_2 concentration was 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*).

The conversion data (Fig. 1) 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 hr of operation, followed by nearly constant conversion for 150 hr or more.

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

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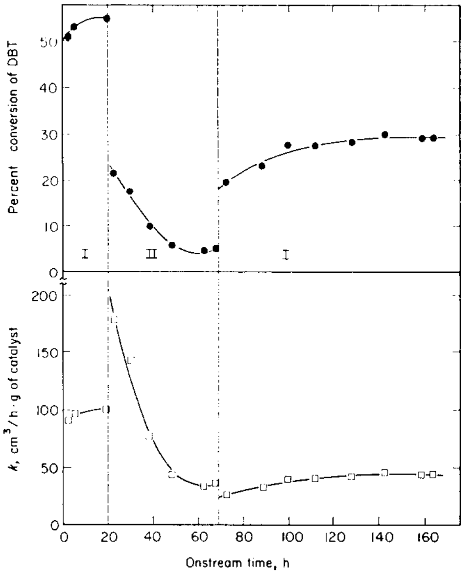

FIG. 1. Conversion and pseudo-first-order rate constants (k) for HDS of DBT. (I) Space velocity = 128 cm³/hr·g of catalyst. (II) Space velocity = 730 cm³/hr·g of catalyst. Feed was 0.12 wt% DBT in n-hexadecane which had been saturated with H_2 at 25°C and 68 atm. The catalyst was American Cyanamid HDS 16A. Reaction conditions: 300°C and 104 atm.

conversion characterized by a transient period of some 50 hr before the catalyst achieved another time-invariant activity. After a second change in space velocity at 70 hr onstream time, giving again the original space velocity, there again followed a transient period, but, surprisngly, the catalyst failed to regain its original time-invariant activity.

In further experiments, each begun with a fresh catalyst charge, increasing concentrations of H_2S were added to the feed. The data in 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, but the transients were shorter. The activity of the catalyst 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 the $(H_2S):(H_2)$ ratio in the feed was as great as 0.2, the transients in activity were sharply reduced.

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 presumed 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 amounts sufficient for the H_2S concentration to remain nearly constant throughout the reactor, the activity (and structure)

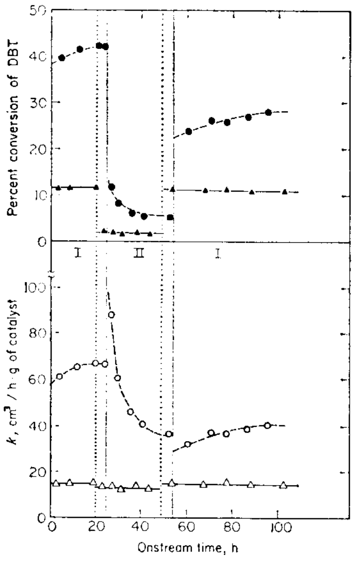

FIG. 2. Conversion and psuedo-first-order rate constants (k) for HDS of DBT. (I) Space velocity = 124 cm³/hr·g of catalyst. (II) Space velocity = 705 cm³/hr·g of catalyst. Concentration ratios [$(H_2S):(H_2)$] = 0.2(-△-) and 0.015(-○-). The feed, catalyst, and reaction conditions were the same as those described in the legend to Fig. 1, except for the added H_2S.

of the catalyst did not change with space velocity; the data then suggest only the simple competitive inhibition of reaction by H_2S.

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 some experiments, catalysts 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 are represented by curve B in Fig. 3; they indicate that in these experiments the H_2S was simply a reaction inhibitor.

In other 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. Conversions determined with catalysts initially brought on stream at low space velocity and subsequently allowed to attain steady state at high space velocity also gave points scattering around curve A. The results show that increasing H_2S concentrations correspond to increasing activities of catalysts which have attained steady activity at low H_2S concentrations. There was an apparent irreversibility: These catalysts did not attain the activities associated with curve B, even when the $(H_2S):(H_2)$ ratio was increased into the range of overlap of curves A and B.

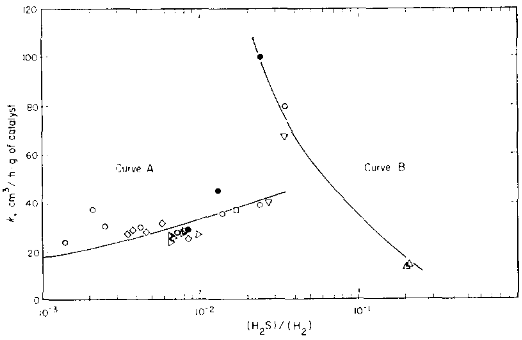

FIG. 3. Effects of H_2S on activity of the catalyst for HDS of DBT under the reaction conditions given in the legend to Fig. 1. The points on curve A represent conversion measured at various space velocities and with various feed [$(H_2S):(H_2)$] ratios for catalysts which had previously attained time-invariant activities at high space velocities (700–750 cm^3/hr·g of catalyst). These results imply that the catalyst which attained time-invariant activities at high space velocities were 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 catalysts which had previously attained time-invariant activities at low space velocities (90–100 cm^3/hr·g of catalyst). These results indicate competitive inhibition of reaction by H_2S. See text for details.

The important conclusion is that the catalyst achieves a time-invariant activity which is dependent on the reactor start-up 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 start-up procedures which maximize the activity of the catalyst; the optimum start-up would ensure that some H_2S contacted the catalyst initially.

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 changes in catalytic activity influenced by $(H_2S):(H_2)$ ratio and temperature variations. He explained the results in terms of solid-state reactions converting Ni from bulk Ni_3S_2 on Al_2O_3 to intercalated Ni^{2+} in interstitial octahedral holes at the surface of WS_2 crystallites. Farragher showed that both the rate constant for benzene hydrogenation and the ESR signal indicative of W^{3+} [presumably produced upon intercalation of Ni (*8, 9*)] were dependent on the $P_{H_2S}:P_{H_2}$ ratio. There is much evidence (*1, 11*) [but not a consensus (*2, 3*)] supporting the view that the Co–Mo/γ-Al_2O_3 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 located next to Co^{2+} ions intercalated at the edges of the MoS_2 crystallites (*1, 7, 12*).

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, intercalculated 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 a layer structure (*10*). In this structure, 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. Clearly the model is rough and speculative and in need of experimental evaluation.

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