

## The Effect of H<sub>2</sub>S on the Hydrogenation and Cracking of Hexene over a CoMo Catalyst

Hydrogen sulfide is known to inhibit the hydrodesulfurization (HDS) of thiophenic compounds over sulfided CoMo catalysts (1). Desikan and Amberg (2) reported that H<sub>2</sub>S also inhibits hydrogenation over these catalysts. They postulated that two types of sites exist: strong sites, showing great affinity for thiophene, H<sub>2</sub>S, and pyridine, and being responsible for hydrogenation and to a limited extent for desulfurization; and weaker sites, for desulfurization alone. Satterfield and Roberts (3), on the basis of thiophene desulfurization kinetic studies, also reported H<sub>2</sub>S inhibition on hydrogenation. Lee and Butt (4) found that H<sub>2</sub>S inhibited butene hydrogenation much more when pure 1-butene was used as the feed compared to its hydrogenation in thiophene HDS, and suggested that hydrogenation in the absence of H<sub>2</sub>S occurs on an incompletely sulfided surface. Goudriaan *et al.* (5) studied the effect of H<sub>2</sub>S on the hydrodenitrogenation of pyridine on a CoMo catalyst and found that an increase in H<sub>2</sub>S concentration increased nitrogen removal and attributed this to enhancement of hydrocracking activity of the catalyst. Satterfield *et al.* (6) also found that thiophene increased hydrodenitrogenation of pyridine and attributed this to some interaction of hydrogen sulfide with the catalyst to increase the hydrogenolysis activity. We wish to report some results dealing directly with the effect of H<sub>2</sub>S on the hydrogenation and cracking activity of a sulfided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst.

Hydrogenation of 1-hexene was carried out in a stirred flow microbalance reactor (7), modified to accommodate liquid feeds (8). The catalyst was a commercial CoMo

formulation (Ketjenfine 124-1 · 5E H.D.), which contained 3.85% CoO and 12% MoO<sub>3</sub> supported on alumina, having 1.09% Si and 264 m<sup>2</sup>/g surface area. The catalyst was sulfided at 400°C for 2 h with 9% H<sub>2</sub>S in H<sub>2</sub>, cooled to 350°C in He, and then subjected to a feed of benzothiophene, *n*-heptane, H<sub>2</sub>, H<sub>2</sub>S for 3 weeks to achieve a steady-state condition. Following this, a solution of 1-hexene in *n*-heptane was substituted for the benzothiophene, maintaining a flow of H<sub>2</sub> and H<sub>2</sub>S. Steady-state conversions were measured at several partial pressures of H<sub>2</sub>S. A minimum concentration of 2% H<sub>2</sub>S was employed to avoid possible catalyst structural changes (9). Products were analyzed by gas chromatography with a flame ionization detector, using an *n*-octane on a Porosil C column at 60°C. The major product was *n*-hexane, but small amounts of propylene were also present.

Rates of hydrogenation divided by the hydrogen partial pressure ( $P_H$ ) for several partial pressures of hydrogen sulfide ( $P_S$ ), at constant hexene partial pressure, were:

$P_S$ (atm)	Rate/ $P_H$ (cm <sup>3</sup> /min · g · atm)
0.015	0.099
0.037	0.100
0.058	0.100
0.071	0.101

The results show that a fivefold increase in hydrogen sulfide concentration has not changed the rate of hydrogenation, indicating that the hydrogenation sites are not inhibited by hydrogen sulfide over the stable sulfided catalyst. The conclusions of Desikan and Amberg (2) and Satterfield and

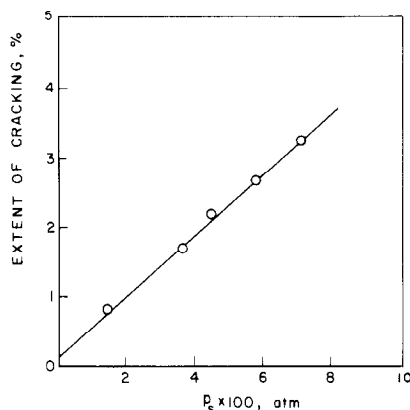
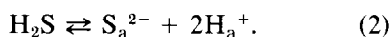
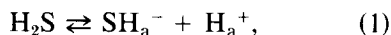


FIG. 1. Effect of hydrogen sulfide on cracking activity.

Roberts (3) are based on conditions in the presence and absence of  $\text{H}_2\text{S}$  and the catalyst state will be different in both situations, as suggested by Lee and Butt (4), and demonstrated by Broderick *et al.* (9).

During the hydrogenation of hexene, some propylene was always formed due to cracking. Interestingly, the cracking activity increased linearly with  $\text{H}_2\text{S}$  partial pressure as shown in Fig. 1. Since the mechanism of cracking is believed to involve carbonium ions, it may be surmised that  $\text{H}_2\text{S}$  has generated some active protons to promote the cracking reaction. This could occur by heterolytic dissociation of  $\text{H}_2\text{S}$ , as, for example,



If the rate of cracking is proportional to the concentration of  $\text{H}_a^+$ , then Eq. (1) would be favored based on the linearity of the plot of

Fig. 1, since Eq. (2) would predict a  $P_S^{1/2}$  relationship.

From our results, we conclude that  $\text{H}_2\text{S}$  has no effect on the hydrogenation function and increases the cracking function of sulfided CoMo catalysts. Since  $\text{H}_2\text{S}$  depresses the hydrogenolysis function, it appears that these three reactions occur on different active sites.

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