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Zinc Promoted Mo–Al Hydrodesulfurization Catalysts

Catalytic hydrodesulfurization processes are used in virtually every modern petroleum refinery. Other hydrotreating processes such as hydrocracking can be used to convert heavy oils and bitumens into synthetic crude oil. Recent work in our laboratory (*1*) is related to both areas of application. Commercial catalysts for hydrotreating and hydrorefining are usually Co–Mo or Ni–Mo on alumina. Some combinations of Ni–W are also used. Recently De Beer and co-workers (*2*, *3*) have evaluated Zn–Mo on alumina catalysts using thiophene at atmospheric pressure (1.013×10^5 N/m^2). This note describes experiments which were performed to extend the evaluation of Zn–Mo on alumina catalysts to high pressures and to an industrial type feedstock. The heavy gas oil used in these studies was the 345–525°C portion of the product obtained by thermally hydrocracking Athabasca bitumen. Typical compounds in this gas oil contain from three to six condensed aromatic rings rather than the single ring thiophene used by De Beer and co-workers (*2*, *3*). Properties of the feedstock are listed in Table 1.

The catalysts were prepared by adding appropriate amounts of distilled water, trace quantities of nitric acid, and aqueous solutions of ammonium paramolybdate and of zinc nitrate to alpha alumina monohydrate powder (Continental Oil Co., 80 wt% Catapal N, 20 wt% Catapal SB) in a mix muller. A detailed description of the catalyst preparation procedure is available elsewhere (*4*). The powder was mulled, dried at 120°C, calcined at 500°C and pressed into cylindrical pellets ($L = D = 3.18$ mm). The final form of the catalyst consisted of zinc and molybdenum oxides on γ-alumina. The catalyst pellets were evaluated in a bench-scale fixed bed reactor having a volume of 155 ml and a length to diameter ratio of 12. The reactor was filled sequentially from the bottom with 75 mm of berl saddles, 200 mm of catalyst pellets and 25 mm of berl saddles. The heavy gas oil, mixed with hydrogen (purity = 99.9 wt%) flowed continuously into the bottom of the reactor and up through the catalyst bed. The product leaving the top of the reactor flowed to receiver vessels where the liquid and vapor were separated. Each experiment was performed at a pressure of 1.39×10^7 N/m^2 (2000 psig), a liquid volumetric space velocity of 0.556 ks^{-1} (2.0 hr^{-1}) based on the reactor volume occupied by the catalyst pellets, and a hydrogen flow rate of 0.0718 liters/s at STP (5000 cf/bbl). When an experiment at one temperature was completed the reactor temperature was changed and the next experiment was started using the same charge of catalyst. The reaction system was maintained at steady-state conditions for 3.6 ks (1 hr) prior to, and for 7.2 ks (2 hr) during the period in which the sample of liquid product was collected. The amount

TABLE 1

Properties of Heavy Gas Oil

Boiling range	345–525°C
Sp Gr 60/60°F	0.992
Conradson carbon residue	0.97 wt%
Sulfur	3.59 wt%
Nitrogen	0.38 wt%
Vanadium	<1 ppm

TABLE 2

S(wt%) in Hydrodesulfurized Product[a]

Order in which experiments performed	Temp (°C)	Sulfur removed (wt%)
1	400	Presulfiding
2	420	65.7
3	400	48.8
4	380	35.9
5	435	76.9
6	450	86.9
7	420	64.9

[a] Catalyst = 9.0 wt% MoO_3 on γ-alumina.

of sulfur in the product sample was determined using an X-ray fluorescence technique. A description of the experimental equipment and procedures used for catalyst evaluation has been given previously (*1e*).

Table 2 shows the results obtained during a typical series of experiments performed on a single charge of catalyst pellets. The purpose of the first experiment at 400°C was to stabilize and presulfide the catalyst. Gas oil and hydrogen contacted the catalyst for 25.2 ks (7 hr) prior to the beginning of the first 420°C experiment (No. 2). The similarity of the results for both experiments at 420°C (Nos. 2 and 7) indicated that no appreciable change in catalyst activity occurred during the operating period. The catalyst was in the presence of hydrocarbon for 25.2 ks (7 hr) prior to Expt. 2 and for 79.2 ks (22 hr) prior to Expt. 7. This indicates that the initial 25.2 ks period was adequate to convert the oxide form of the catalyst into its sulfided working state.

The results in Fig. 1 show how sulfur removal varied with the Zn/Mo ratio in the catalyst. Slight promotional and poisoning effects might be attributed to the catalysts which initially contained 12 and 9 wt% MoO_3, respectively. Whatever the trend it is clear that variations in zinc content only changed the weight percent sulfur removed from the gas oil by a few percent at the most. In contrast, previous work in our laboratory (*4*) using the same feedstock and processing conditions showed that the addition of cobalt to molybdenum on alumina catalysts increased the sulfur removed from the gas oil by an additional 33 wt%. This comparison indicates that the promotional effect of zinc is at least an order of magnitude smaller than cobalt.

These findings are in agreement with some of the results obtained by De Beer and co-workers (*3*) but contradict others (*2*). In the first paper by De Beer and coworkers (*2*) catalytic activity was shown to vary with metal/molybdenum ratio for cobalt, manganese, nickel and zinc. Although not stated explicitly it was implied that the measurements were made after the thiophene had contacted the catalyst for 6 ks (100 min) and that this represented a steady-state period. They found that at optimum metal/molybdenum ratios, all of the metals were good promoters, and that zinc was the best. De Beer's data (*2*) have

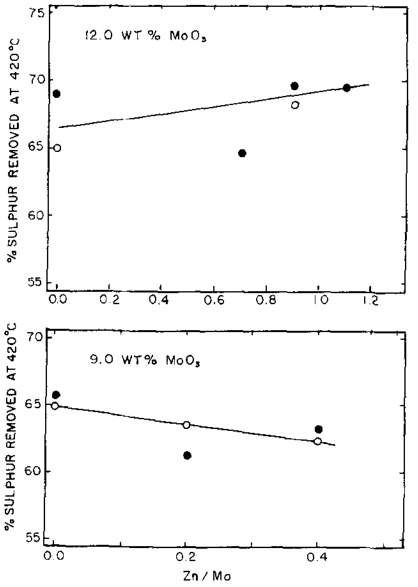

FIG. 1. Percent sulphur removal at 420°C vs zinc to molybdenum ratio. (●) Expt. 2 in each series; (○) Expt. 7 in each series.

been given additional exposure by their presentation in two recent reviews of hydrodesulfurization (*5*, *6*). Our data (as shown in Fig. 1) do not agree in any way with those presented by De Beer *et al.* (*2*) in their first paper. In a second paper by De Beer and co-workers (*3*) an extensive decrease in activity of a zinc promoted catalyst (12 wt% MoO_3, Zn/Mo = 0.59) was reported as the time increased to 28.8 ks (8 hr). Furthermore the steady-state activity of their zinc promoted catalyst was only slightly better than their equivalent unpromoted Mo on alumina catalyst. This second set of results tends to be consistent with our data in Fig. 1. Therefore, we conclude that Zn–Mo catalysts are much less active for hydrodesulfurization than either Co–Mo or Ni–Mo on alumina catalysts.

All of the above results can be explained by the conversion of the initial oxide form of the catalyst to its sulfided working state. The oxide form of the zinc promoted catalyst has a high activity for sulfur removal. After it has been converted to the sulfide form, its desulfurization activity diminishes considerably. Evidence for the above phenomenon is apparent in presently used technology. A zinc oxide desulfurization catalyst, not containing molybdenum, has been manufactured for over 20 yr (*7*). In use the oxide is gradually converted to sulfide. When the catalyst has been fully sulfided, it must be replaced to maintain the desired degree of sulfur removal.

Completely sulfided catalysts appear to have been obtained in our high pressure experiments with a commercial type gas–oil and in the second study by De Beer and coworkers (*3*) at atmospheric pressure using thiophene. In both sets of experiments, comparable results were achieved after the catalyst had been in contact with hydrocarbon for periods of 25.2 ks (7 hr). The fact that these two sets of results agree constitutes strong evidence that thiophene is a good model compound for studying hydrodesulfurization of hydrocarbon mixtures. The inconsistency with the earlier results of De Beer and coworkers (*2*) was probably caused by their catalysts being only partially sulfided.

The present work with zinc promoted Mo on alumina catalysts illustrates the need for hydrodesulfurization experiments to be performed with fully sulfided catalysts in their working states. Continuous flow experiments should be of sufficient duration to ensure that the catalyst has reached its steady-state condition. If a pulse method or other transient technique is to be used for catalyst evaluation, it is imperative that the catalyst be in its working state prior to the introduction of the transient.

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