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# Effect of Sulfiding on an Unsupported Hydrotreating Catalyst

It is well known that sulfiding plays a very important role in determining the performance of commercial hydroprocessing catalysts (*1, 2, 3*). Recently, Ho and Reyes (*4*) described the sulfiding behavior of an unsupported catalyst derived from tris(ethylenediamine) cobalt molybdate, or $Co(NH_2CH_2CH_2NH_2)_3MoO_4$. A heterometallic metal oxygen complex of this type may be called self-promoted because the primary and promoter metals are all present in a single complex. This water soluble metallate upon sulfiding shows very high volumetric activities for both hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) (*5*). The BET surface area of this catalyst is much less than 100 $m^2/g$. Commercial catalysts, which are in supported form (on $Al_2O_3$), typically have surface areas on the order of 250 $m^2/g$.

A major finding in Ho and Reyes' study is that gas ($H_2S/H_2$) sulfiding of this bulk catalyst is accompanied by significant hot spotting, much more so than sulfiding of commercial catalysts (*6*). They developed a mathematical model for predicting the speed and magnitude of the traveling thermal wave. At the conditions used by Ho and Reyes, the model calculated that the catalyst could be some 20°C hotter than the gas, and the $H_2S$ level could drop from 10% at the reactor inlet to as low as 0.5% at the outlet.

This study was carried out to get some idea on the extent to which the activity of the bulk catalyst is affected by presulfiding conditions. The comparative experiments were done under somewhat "exaggerated" conditions.

## EXPERIMENTAL

The feedstock used was a light catalytic cycle oil, with 16.5 API gravity, 1.35 wt% total sulfur, and 715 wppm total nitrogen. The activity tests were conducted in an automated fixed-bed unit consisting of two independent upflow reactors in a common sand bath. The conditions used were 330 psig hydrogen pressure, 343°C, 0.8–1.0 LHSV, and 1000 SCF/barrel hydrogen treat gas rate. The liquid products were analyzed for total sulfur by X-ray fluorescence using external standards and for total nitrogen by the Antek analyzer.

Prior to the activity tests, the catalyst precursor was divided into two portions, each of which was sulfided in a downflow fixed-bed reactor. One portion was sulfided with a 10% $H_2S$-in-$H_2$ gas mixture, the other with a 1% $H_2S$-in-$H_2$ mixture. For a 40 cc catalyst charge, the sulfiding was carried out as follows. The catalyst precursor was heated under flowing nitrogen at 370°C for two hours and then sulfided at 400°C for two hours with the $H_2S$-$H_2$ gas mixture flowing at 800 cc/min (room temperature). The temperatures were chosen based on such considerations as completeness of amine removal, surface area and degree of crystallinity of the final catalysts. Following this, the reactor was cooled down to room temperature. The sulfided catalyst particles were compressed to wafers, then crushed and sized to 20–40 mesh granulars to ensure adequate particle-to-reactor diameter ratios in the activity tests.

Note that in the 1% $H_2S$ case the amount of $H_2S$ supplied during presulfiding was less

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than that required by stoichiometry for complete sulfiding of both surface and bulk oxides. Thus the catalyst might be sulfided only on and in the surface. (This may represent a worst-case scenario in practice.) Of course, the catalyst would get further sulfided during the break-in period of the activity test, due to the indigenous sulfurs in the feed.

## RESULTS

The activity tests were run for about 200 hours on stream. Samples of liquid products were taken at 24 hour intervals. It took about 80 hours for the catalysts to attain their steady-state activities. During this period, post-sulfiding occurred. After the break-in period, the HDS activity was determined by calculating the average of second-order rate constants (assuming plug flow) for liquid products collected at different times. The HDN activity was determined by the rate constant of first-order kinetics. The following Table lists the averages of lined-out rate constants for both HDS and HDN.
As can be seen, for HDS the activity difference can be two fold. The difference in HDN, on the other hand, is relatively small. This observation is consistent with the common belief that the sulfur vacancies used for HDN are not entirely the same as those used for HDS. Despite the occurrence of on oil post-sulfiding, the final activity (or sulfided state) is indeed affected by the presulfiding treatment. In fact, presulfiding may be used for control of catalyst selectivity, which is important in some practical situations (e.g. Ref. 7).

TABLE 1

Effects of $H_2S$ Concentration

| Sulfiding agent | $k_{HDS}$ | $k_{HDN}$ |
|---|---|---|
| 10% $H_2S$ | 13.0 | 0.59 |
| 1% $H_2S$ | 5.7 | 0.42 |

## CONCLUDING REMARKS

When exploring new catalysts, one should keep in mind that each catalyst is different. Its presulfiding protocol should be carefully tailored to avoid potential underutilization of the catalyst's active ingredients.

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