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AND HYDRODENITROGENATION IN A LIQUID PHASE REACTOR

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by

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Presulphiding of hydrodesulphurization catalysts used in top feed reactors is known to produce higher catalyst activity and longer catalyst life (1). Studies in our laboratory (2) have shown that, for hydrodesulphurization and hydrodenitrogenation of high boiling hydrocarbon feedstocks, much better results are obtained with bottom feed reactors than with top feed trickle bed reactors. When the mixture of hydrogen and hydrocarbon feedstock enters the bottom of a fixed bed reactor, the low boiling compounds vaporize and flow up through the bed of catalyst particles relatively quickly with the hydrogen. In contrast, the high boiling hydrocarbon material which remains in the liquid phase at reaction conditions will have a much longer residence time in the reactor. Therefore, the liquid holdup will be greater in a bottom feed reactor than in a top feed trickle bed reactor. This means that the high boiling compounds, which are generally the most difficult to desulphurize and denitrogenate, will have greater contact with the catalyst in a bottom feed reactor. Bottom feed reactors have recently been used in other laboratories for hydrocarbon hydrotreating (3) and for other liquid phase reactions (4). The purpose of the present study was to investigate the effect of catalyst presulphiding using bottom feed reactors.

EXPERIMENTAL

The catalyst was made by adding appropriate amounts of distilled water, trace quantities of nitric acid, and aqueous solutions of ammonium paramolybdate and nickel nitrate to alpha alumina monohydrate powder (Continental Oil Company, 80 wt % Catapal N, 20 wt % Catapal SB) in a mix muller. The powder was mulled, dried at 120°C, calcined at 500°C and pressed into cylindrical pellets (L = D = 3.18 mm). The final catalyst was composed of 2.1 wt % NiO and .5.4 wt % MoO_3 supported 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 42 ml of berl saddles, 100 ml of catalyst pellets, and 13 ml of berl saddles.

Presulphiding experiments were performed with carbon disulphide, with hydrogen sulphide and with the hydrocarbon feedstock. The conditions used in the presulphiding experiments are listed in Table 1. At the conclusion of each presulphiding experiment, the catalyst was removed from the reactor while being kept in a nitrogen atmosphere and analyzed for sulphur (5, 6) using the Eschka technique. Precautions were taken to prevent air from contacting the catalyst while it was being removed from the reactor and mixed with the Eschka powder. This was necessary since air is known to react with sulphided catalysts partially converting them to their oxide form. The results obtained using the Eschka method were calibrated by analyzing mixtures of the oxide form of the catalyst which had been mixed with known amounts of different sulphur containing compounds.

For each set of conditions shown in Table 1, a second batch of catalyst was presulphided and then used in reaction experiments at 400°C and 450°C. The heavy gas oil hydrocarbon feedstock used in the reaction experiments had a boiling range of 345–525°C, a specific gravity ($16/16^{\circ}$C) of 0.987, a Conradson Carbon Residue of 0.97 wt %, and contained 3.64 wt % sulphur and 0.38 wt % nitrogen. 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 vapour 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 l/s at STP (5000 cf/bbl).

Several analyses were performed. The amounts of sulphur and of nitrogen in the hydrocarbon product were measured using an X-Ray fluorescence technique and a hydrogenation micro-coulometric apparatus respectively. At the conclusion of the reaction experiments the distillable oil adhering to the catalyst particles was removed at 525°C in a stream of flowing hydrogen. One sample of the catalyst was then analyzed for sulphur using the procedure described above. Another sample of the catalyst was placed in a furnace at 500°C and its weight change measured. After correcting for the conversion of metal sulphides in the catalyst to metal oxides, the balance of the weight change was ascribed to coke formation. All of the experimental details, catalyst preparation, presulphiding and reaction procedures and analytical techniques have been described elsewhere (6).

RESULTS AND DISCUSSION

The amount of sulphur incorporated in the catalyst after presulphiding was found to be a function of the presulphiding conditions, as may be seen

in Table 1. However, variations in the amount of sulphur in the catalyst did not have much effect on the catalyst activity. This is apparent in Figure 1 where the product specific gravity, the wt % sulphur removed from the hydrocarbon and the wt % nitrogen removed from the hydrocarbon are shown. The results obtained at 400°C suggest that there is a slight improvement in sulphur and nitrogen removal with sulphur content after presulphiding. In contrast the 450°C results appear to be independent of sulphur in the catalyst after presulphiding. Furthermore, the presulphiding material, carbon disulphide, hydrogen sulphide or heavy gas oil feedstock did not appear to influence any of the quantities shown in Figure 1.

The amount of sulphur and the amount of coke in the catalyst after the second reaction experiment, the one at 450°C, are shown in Figure 2. All of the results, except those obtained with H_2S presulphiding, appear to be independent of the amount of sulphur in the catalyst after presulphiding. The formation of MoS_2 and Ni_3S_2 from MoO_3 and NiO during sulphiding of hydrodesulphurization catalysts has been suggested by Brewer and Cleavens (7) and supported by the data of de Beer (8). If all the molybdenum and nickel were converted to the above sulphides, the catalyst used in this study would contain 2.97 wt % sulphur, which is close to the measured values shown in Figure 2. The association of two sulphur atoms with each molybdenum atom is consistent with both the formation of bulk MoS_2 and the formation of a sulphided epitaxial layer of molybdenum on the surface of the alumina.

Since the data for the catalysts presulphided with H_2S differed significantly from the other data in Figure 2, an additional set of experiments was performed. The catalyst was presulphided with H_2S and then four reaction experiments were performed at 400°C, 420°C, 380°C, and 400°C. At the conclusion of this set of experiments the amount of sulphur and the amount of coke

in the catalyst were 3.23 and 2.75 wt % respectively.

The results obtained after H_2S presulphiding and four reaction experiments can be compared with those in Figure 2 obtained after H_2S presulphiding and two reaction experiments. As the number of reaction experiments increased from two to four, the catalyst sulphur content became lower and the catalyst coke content became higher. This suggests that the amounts of sulphur and coke in the catalyst would approach the horizontal lines in Figure 2 if a sufficient number of reaction experiments were performed. Increasing coke content with decreasing sulphur content is consistent with the results of Aoshima and Wise (9) who reported that a carbonaceous residue was formed when their catalyst had a low sulphur content and a high electrical conductivity. Also, Massoth (10) stated that hydrogen chemisorption on sulphided $Mo-Al_2O_3$ catalysts was due to the sulphided metal phase. When the findings of Massoth and of Aoshima and Wise are related it would appear that raising the catalyst sulphur content increases hydrogen adsorption which in turn decreases coke formation. This would account for the relationship between sulphur and coke which we observed in our H_2S presulphiding experiments. It would also be consistent with our CS_2 presulphiding results in Figure 2. Because the catalyst sulphur content after reaction was similar in all cases, the catalyst coke content would also be expected to be similar.

It may be that catalyst sulphur content is controlled by the relatively high concentration of sulphur species in the reaction mixture, particularly in the liquid phase material, which surrounds the catalyst pellets. Presumably in this environment the catalyst pellets will gradually attain the same steady state sulphur content regardless of their sulphur content after presulphiding. If the catalyst had not attained its steady state sulphur level until the first reaction experiment was at least partially completed,

then the catalyst activity results could be affected by the catalyst sulphur content after presulphiding. The results in Figure 1 for the first reaction experiments at $400^{\circ}C$ show this trend. In contrast the results for the second reaction experiments at $450^{\circ}C$ are independent of the catalyst sulphur content after presulphiding, possibly because the catalyst had attained its steady state sulphur content.

It may be concluded that presulphiding the catalyst using the hydrocarbon feedstock in a bottom feed liquid phase reactor is equivalent to presulphiding with CS_2 or H_2S. The catalyst activity results in Figure 1 were similar in all cases. Furthermore, if catalyst coke content is taken as an indication of catalyst life, then equivalent catalyst lifetimes would be expected in all cases. Thus, unlike top feed reactors, catalyst presulphiding in bottom feed liquid phase reactors does not appear to improve either catalyst activity or catalyst life.

While the reasons for this are as yet not fully understood, one could speculate that the intimate contact of the higher sulphur liquid with the catalyst in bottom feed liquid phase reactors causes the catalyst to be sulphided rapidly. In contrast, if the catalyst were sulphided more slowly, a greater quantity of coke could form while the catalyst was still in its oxidized state. This would decrease both catalyst activity and life. Undoubtedly some of the experience with top feed reactors (1) has involved hydrotreating naphthas which are in the vapour phase at reaction conditions and which contain less sulphur than the gas oil used in our experiments. It is plausible that under these circumstances the catalyst would be sulphided at a slower rate and that initially coke formation would occur to a greater extent.

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TABLE 1

Conditions Used in Presulphiding Experiments

Presulphiding Material	Temperature ^oC	Pressure MPa	H_2 Flowrate ml/s	CS$_2$-Toluene* Solution Flowrate ml/ks	$\dfrac{\text{moles } H_2S}{\text{mole } H_2}$	Hydrocarbon Flow rate ml/ks	wt % S in Catalyst after Presulphiding
CS_2	200	0.172	52.2	137			2.60
CS_2	300	0.172	48.1	140			3.63
CS_2	400	0.172	49.3	134			2.09
CS_2	400	0.172	9.7	136			4.66
CS_2	400	5.27	52.0	136			4.25
CS_2	400	13.9	51.4	138			3.88
H_2S	400	0.102	57.2		0.15		3.00
Gas Oil	400	13.9	57.2			55.6	2.97

*The CS$_2$ was dissolved in toluene to give a solution of 0.818 mole CS$_2$ per litre.

LEGENDS FOR FIGURES

Figure 1   Catalyst Activity (specific gravity, wt % sulphur removed and
            wt % nitrogen removed from the hydrocarbon) Versus Weight Per-
            cent Sulphur in the Catalyst after Presulphiding. Circles,
            triangles and squares are for CS_2, H_2S and gas oil presulphid-
            ing respectively. The open and solid data points were obtained
            at reaction temperatures of $400^{o}C$ and $450^{o}C$ respectively.

Figure 2   Weight Percent Sulphur and Weight Percent Coke in the Catalyst
            after the Reaction Experiments Versus Weight Percent Sulphur in
            the Catalyst after Presulphiding. Circles, triangles, and
            squares are for CS_2, H_2S and gas oil presulphiding respectively.