

THE IMPACT OF THE CHEMICAL CONSTITUENTS OF HYDROTREATER FEED ON CATALYST ACTIVITY*

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INTRODUCTION

The deposition of carbonaceous material on direct coal liquefaction catalysts is known to cause rapid and significant catalyst deactivation (1,2). Studies of hydrotreater catalyst samples from several different runs at the Wilsonville Advanced Coal Liquefaction R & D Facility have shown that greater than 75% of their hydrogenation activity and 50% of their hydrodesulfurization activity were lost within the first few days of coal processing (3). Hydrotreating light thermal resid from the third stage of the Kerr McGee critical solvent deasher yielded the least deactivation whereas hydrotreating the heavier nondeashed resid yielded the largest buildup of carbonaceous deposits and the greatest deactivation. These trends were due to differences in the compositions of the hydrotreater feeds. Previously reported work (4) has shown that carbonaceous deposits cause homogeneous poisoning of active sites and about a 50% decrease in the catalyst effective diffusivity, which is the diffusion coefficient within the extrudates.

As a result of the work on the Wilsonville catalysts, we have initiated a program to identify the hydrotreater feed components that are most detrimental to catalyst activity. Studies of the effect of hydrotreater feed boiling point cut on catalyst activity (5) have shown that processing a -550F component yields a 23% decrease in extrudate hydrogenation activity whereas hydrotreating an 850F+ component results in an 82% loss. Although hydrodesulfurization activity was not affected by the low boiling fraction, a 70% loss resulted from hydrotreating the highest boiling fraction.

In this paper we report the impacts on catalyst activity of four different chemical classes of compounds found in hydrotreater feeds. These chemical classes included the aliphatic hydrocarbons, neutral polycyclic aromatic compounds (PAC), nitrogen polycyclic aromatic compounds (N-PAC) and hydroxy polycyclic aromatic hydrocarbons (HPAH).

EXPERIMENTAL PROCEDURES

A hydrotreater process stream obtained from the Wilsonville facility and four classes of chemical compounds separated from this stream were each catalytically hydrogenated in microreactors. The starting feeds and used catalysts from these experiments were then characterized and the catalysts were tested for hydrogenation activity.

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Materials

The catalyst was Shell 324M with 12.4 wt% Mo and 2.8 wt% Ni on an alumina support in the form of extrudates measuring about 0.8 mm in diameter and 4 mm in length. Prior to use, the catalyst was presulfided with a 10 mol% H₂S in H₂ mixture at 400C and atmospheric pressure for two hours. The V-178 hydrotreater process stream used in this study was obtained from the Wilsonville facility's run 247, which processed Illinois #6 bituminous coal in the Reconfigured Integrated Two-Stage Liquefaction process configuration(6). The V-178 stream, identified by the number of the storage tank from which it was derived prior to entering the hydrotreater, is the light portion of the hydrotreater feed and comprises about 35 wt% of the total feed. Distillation of the V-178 showed that the initial boiling point was 400F and 96.1 wt% boiled below 850F (5).

The V-178 process stream was separated into four chemical classes by adsorption column chromatography using neutral aluminum oxide (7). A 10 g sample was dissolved in chloroform and adsorbed onto 50 g alumina, which was then dried and placed on top of 100 g alumina in a 22 mm id column. The aliphatic hydrocarbon fraction was eluted first using hexane, then the PAC using benzene, followed by the N-PAC using chloroform and the HPAH using 10% ethanol in tetrahydrofuran. Solvent was removed from each fraction by evaporation under vacuum.

Hydrotreating Experiments

Each chemical class and the V-178 process stream were hydrotreated with presulfided catalyst in 26 cc batch microreactors at 300C for 2 hours with a 1200 psig H₂ cold charge pressure. The microreactors were charged with 0.5 g feed, 0.17 g presulfided catalyst and 1.5 g hexadecane, which was added to provide adequate mixing in the reactors because of the small amounts of feed available. The aged catalysts were Soxhlet extracted with tetrahydrofuran prior to analysis or activity testing. Elemental analyses of the V-178 stream, the four fractions and the aged catalysts were performed using standard methods.

Activity Testing

Hydrogenation activities of fresh and aged catalysts were determined by measuring the rate of hydrogenation of pyrene to dihydropyrene (4) in 26 cc microreactors at 300C with 450 psig H cold charge pressure. Experiments with catalyst ground to -200 mesh and whole extrudates enabled determination of the losses of both intrinsic and extrudate activities respectively.

RESULTS AND DISCUSSION

Feed and Catalyst Compositions

The compositions of the V-178 stream and the amounts and compositions of the four separated chemical classes, given in Table 1, show that the V-178 contains significant amounts of aliphatic hydrocarbons and the PAC fraction, and only low concentrations of nitrogen and hydroxy compounds. The 95% total recovery for the four chemical classes is good for this type of

separation. The high quality of the separations of the aliphatic hydrocarbons and PAC fraction is indicated by the much higher H/C ratio of the aliphatic fraction (1.70) compared to the PAC fraction (1.16) and the low concentrations of nitrogen and oxygen in these two fractions. In contrast, the N-PAC and HPAH fractions both have significant amounts of oxygen and nitrogen indicating the presence of compounds that contain both heteroatoms or possibly some overlap of the fractions.

Results of analyses of the aged catalysts, given in Table 2, show that catalytic hydrotreating of the aliphatic and PAC fractions yielded lower carbon accumulations on the catalysts than hydrotreating the V-178 or the N-PAC and HPAH fractions. Likewise, the catalysts used to hydrotreat the N-PAC and HPAH fractions have significantly higher accumulations of nitrogen than the catalysts used to hydrotreat the aliphatics and the PAC fractions. The 0.6 and 0.5 wt% accumulations resulting from our two hour experiments are comparable to the levels (0.5 to 0.6 wt%) observed on the first catalysts, with catalyst ages of about 20 lb resid/lb catalyst, withdrawn from Wilsonville runs. These results show that the nitrogen buildup on the catalyst under process conditions must be very rapid.

Hydrogenation Activity

The measured intrinsic activity losses (α) and the measured remaining extrudate activities (F) are given in Table 3. A quantitative mathematical expression, reported previously (8), relates F to α and effective diffusivity. Use of this equation enabled us to determine the catalyst effective diffusivities. The catalysts used to hydrotreat the V-178 and the aliphatic hydrocarbon and PAC fractions showed a 20% decrease in effective diffusivity from the fresh catalyst value of 5×10^{-6} cm²/sec/cm³, whereas those used to hydrotreat the HPAH and N-PAC fractions had greater than a 50% decrease. Recalculating the F values without these changes in effective diffusivity (i.e. with fresh catalyst effective diffusivity) (Table 3) shows that less than 10% of the loss of fresh extrudate activity is due to the changes in effective diffusivity.

The relationship between F (corrected for changes in effective diffusivity) and α also enabled us to differentiate the two limiting modes of deactivation -- homogeneous and shell-progressive poisoning. A plot of F vs α for the results from the hydrogenation activity testing of the V-178 and the four chemical classes is shown in Figure 1. Since the α values increase more rapidly than the F values, the dominant mode of deactivation for these catalysts is homogeneous poisoning of active sites (9). As can be seen in Figure 1, the aliphatic hydrocarbons and the PAC fraction caused less deactivation than the V-178, whereas the N-PAC and HPAH caused more deactivation. This trend in deactivation is inversely correlated with the carbon contents of the aged catalysts given in Table 2. The catalysts used to process the aliphatics and the PAC fraction have lower carbon contents than the catalyst used to hydrotreat the V-178, whereas the catalysts used to hydrotreat the N-PAC and HPAH fractions have higher carbon contents. Hydrotreating the N-PAC fraction yields the greatest deactivation with about an 87% loss of extrudate hydrogenation activity and 98% of the active sites poisoned.

CONCLUSIONS

Separation of a light hydrotreater process stream into four chemical classes has shown that about half of the stream is composed of aliphatic hydrocarbons. There are also small amounts of N-PAC and HPAH fractions. Hydrotreating each of these four fractions and the whole process stream with catalyst has shown that all four fractions cause deactivation. The greatest deactivation is due to the N-PAC fraction, although the HPAH fraction also yields greater deactivation than the whole process stream. The deactivation is caused primarily by active site poisoning, with a lesser amount due to a decrease in effective diffusivity.

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Table 1. Compositions of the V-178 stream and the four chemical classes in weight percents.

		<u>C</u>	<u>H</u>	<u>N</u>	<u>O</u>	<u>H/C</u>
V-178		87.69	10.05	0.23	1.08	1.38
	<u>Wt % of V-178</u>					
Aliphatic hydrocarbons	46	87.27	12.36	< 0.10	0.10	1.70
Neutral polycyclic aromatic compounds (PAC)	35	90.15	8.70	0.10	0.17	1.16
Nitrogen polycyclic aromatic compounds (N-PAC)	5	83.60	7.93	3.61	2.81	1.14
Hydroxy polycyclic aromatic compounds (HPAH)	9	78.18	8.25	1.13	9.44	1.27

Table 2. Analyses of aged catalysts from microreactor runs (reported as weight percents).

<u>Catalyst</u>	<u>C</u>	<u>N</u>
V-178 run	3.87	0.3
Aliphatic hydrocarbon run	2.36	0.1
PAC run	2.71	0.1
N-PAC run	4.53	0.6
HPAH run	5.02	0.5

Table 3. Results of activity testing experiments
(for fresh catalyst $F = 1.00$, $\alpha = 0.0$)

<u>Reactor Feed</u>	<u>F</u> <u>measured</u>	<u>α</u> <u>measured</u>	<u>F*</u>
V-178	0.44	0.72	0.52
Aliphatic hydrocarbons	0.72	0.39	0.78
PAC	0.59	0.58	0.64
N-PAC	0.05	0.98	0.13
HPAH	0.19	0.92	0.26

* Corrected for changes in effective diffusivity.

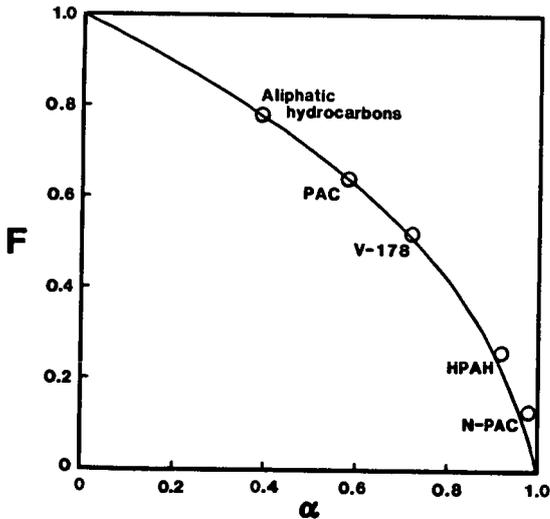


Figure 1. F vs α plot for V-178 and the four chemical classes.