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CAUSES OF CATALYST DEACTIVATION DURING  
QUINOLINE HYDRODENITROGENATION\*

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Introduction

Previous studies (1,2) of catalyst samples from the Wilsonville Advanced Coal Liquefaction R&D Facility have shown that the initial rapid catalyst deactivation was due to the buildup of carbonaceous deposits on the catalyst. Greater than 75% of the catalyst's hydrogenation (HYD) activity was lost as soon as coal processing began (2). Variations in the amount of carbonaceous deposits (1) on the catalysts from several different Wilsonville runs, which used two different coals and three process configurations, were due to the process configuration but not the coal type. The heaviest hydrotreater feed (from the Reconfigured Integrated Two-Stage Liquefaction configuration) in the Wilsonville runs, yielded the most accumulation of carbonaceous deposits on the catalyst and therefore the greatest deactivation (1). Hydrotreating this feed resulted in an initial 67% loss of hydrodesulfurization (HDS) activity; hydrotreating the lightest feed (from the Double Integrated Two-Stage Liquefaction configuration) yielded only a 47% decrease in HDS activity.

As a result of the work on Wilsonville catalysts, a program has been initiated to identify the hydrotreater feed components that are most harmful to the catalyst. Previous studies (3) to determine the impacts of the various chemical classes of compounds found in a hydrotreater feed on catalyst activity showed that the aliphatic and neutral polycyclic aromatic compounds yielded much less deactivation than the total hydrotreater feed and the nitrogen polycyclic aromatic compounds (N-PAC) and hydroxy polycyclic aromatic hydrocarbons (HPAH) yielded much greater deactivation. The N-PAC yielded a 95% loss of extrudate activity with 98% of the active sites poisoned. The activity losses for all of these fractions were due to poisoning of active sites and decreased effective diffusivities. Chemical analyses of the HPAH and N-PAC fractions showed that both contained significant amounts of oxygen and nitrogen so that the individual effects of the nitrogen and oxygen compounds could not be separated. Therefore, additional studies (4) were performed using both nitrogen and hydroxy model compounds. Hydrotreating phenol and 1-naphthol yielded only about 35% losses in extrudate activity. Hydrotreating indole, a weak basic pyrrolic nitrogen compound, yielded a 50% loss and carbazole, a neutral pyrrolic compound, yielded a 24% loss. In contrast, pyridinic nitrogen compounds (pyridine, quinoline, acridine) yielded about 75% losses. These results showed that the strong basic nitrogen compounds are most harmful to the catalyst.

The current work involves determining the causes of deactivation due to hydrotreating pyridinic compounds. Quinoline was chosen as the model compound for this study because it represents a type of nitrogen compound present in coal-derived materials, and a hydrodenitrogenation (HDN) reaction network has been proposed for

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this compound (5,6). In the proposed reaction scheme, at low temperatures, quinoline is hydrogenated to 1,2,3,4-tetrahydroquinoline (PyTHQ). PyTHQ is cracked to o-propylaniline (OPA), and then the nitrogen is removed, as ammonia, to give propylbenzene (PBz). At high temperatures, the hydrogenation of quinoline to 5,6,7,8-tetrahydroquinoline (BzTHQ) also becomes important. BzTHQ is further hydrogenated to decahydroquinoline (DHQ), which is then cracked and denitrogenated to yield mostly propylcyclohexane (PCH). PyTHQ can also be hydrogenated to DHQ and OPA can also be hydrogenated and denitrogenated to PCH.

The initial work reported here on the causes of deactivation due to hydrogenating quinoline will cover the impact of process conditions on deactivation and the determination of the effects of the reaction scheme intermediates and products on deactivation.

### Experimental Procedures

Quinoline was hydrogenated under a variety of conditions to determine the effects of process variables on catalyst deactivation. In addition, each of the intermediates formed during quinoline HDN was catalytically hydrotreated and the resultant deactivation measured. The aged catalysts were characterized and the intermediate compounds and products reported for the HDN reaction scheme (5) were quantified.

#### 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% H<sub>2</sub>S in H<sub>2</sub> mixture at 400°C and atmospheric pressure for 2 hours. The structures of the model compounds used in this study are shown in Table 1.

#### Hydrotreating Experiments

Each hydrotreating experiment was performed in 26 cc batch microreactors with 1200 psig H<sub>2</sub> cold charge pressure. Runs were made for either 5 minutes or 120 minutes at either 300°C or 400°C. Unless otherwise stated, experiments were performed with 1.5g of model compound and 0.5g presulfided catalyst. The aged catalysts were Soxhlet extracted with tetrahydrofuran prior to activity testing. Elemental analyses were performed on the extracted aged catalysts.

#### Activity Testing

Hydrogenation activities of fresh and aged catalysts were determined by measuring the rate of hydrogenation of pyrene to dihydropyrene in 26 cc microreactors at 300°C with 450 psig H<sub>2</sub> cold charge pressure (7). Experiments with whole extrudates and catalyst ground to -200 mesh enabled determination of the losses of extrudate and intrinsic activities (8) respectively. Loss of intrinsic activity is proportional to the loss of active sites.

#### Liquid Product Analyses

Intermediates and products reported for the quinoline HDN reaction network (5) were identified using GC/MS and quantified using GC analysis with commercially available compounds as standards.

## Results and Discussion

### Activity Testing

The measured extrudate and intrinsic activity losses for the runs with quinoline at 300°C and 400°C for 5 minutes and 120 minutes are given in Table 2. The catalysts from all these runs had extrudate activity losses ranging from 73 to 84% and intrinsic activity losses from 85 to 94%. The differences in the measured extrudate activities of the catalysts from the two times at a given temperature are not significant. However, the catalyst from the 400°C run for 120 minutes is slightly more deactivated than the catalyst from the 300°C run for 5 minutes. The intrinsic activity losses for the catalysts from the quinoline runs are all the same within experimental error. These results show that deactivation occurs very rapidly and that significant changes in time and temperature have little effect on the extent of deactivation.

Effects of variations in the catalyst to reactant ratio were tested using quinoline at 300°C for 120 minutes. A run with a 1:1 ratio yielded a 64% extrudate activity loss, whereas runs with 1:3 and 1:9 ratios gave 76% and 77% losses respectively. These results suggest that a higher catalyst to quinoline ratio yields less deactivation, which is probably due to the greater number of active sites relative to the amount of deactivating compound.

The four intermediate compounds (PyTHQ, OPA, BzTHQ, DHQ) and the two products (PBz, PCH) were each hydrotreated with catalyst at 300°C for 5 minutes and 120 minutes. The measured extrudate and intrinsic activity losses are given in Table 3. The results show that for the 5 minute runs, the three hydrogenated species (PyTHQ, BzTHQ, DHQ) yielded comparable deactivation (about 70% extrudate activity loss) to hydrotreating quinoline. For the 120 minute runs, quinoline, DHQ, and BzTHQ yielded comparable activity losses to the 5 minute runs; PyTHQ yielded significantly less deactivation (53%). With both run times, OPA caused less deactivation than the other intermediates and PCH caused the least deactivation. PBz caused deactivation by a different mechanism than quinoline, PCH or the intermediates as indicated by the low amount of active sites poisoned. The 52% extrudate activity loss caused by PBz may be due to diffusional limitations caused by the deposition of carbonaceous material in the outer regions of the catalyst. This is a different mechanism than observed for quinoline so that this compound is not important in quinoline deactivation. The results of the hydrotreating experiments with the intermediate compounds and products indicate that greater deactivation is correlated with the hydrogenated intermediates (PyTHQ, BzTHQ and DHQ) and quinoline. It is not known why PyTHQ causes less deactivation at the longer time; it may be due to the greater reaction of PyTHQ at the longer time (see below).

### Elemental Analyses of the Catalysts

There is a correlation between the carbon contents of the aged catalysts (Table 4) and deactivation. Quinoline, PyTHQ, BzTHQ and DHQ caused the most deactivation and gave the highest carbon contents. PCH yielded the least deactivation and gave the lowest carbon content. However, it appears that above a certain carbon content, when the catalyst is significantly deactivated, additional carbonaceous deposits do not have much effect on activity. For example, aged catalyst from the 120 minute run with quinoline at 300°C has about a 30% higher carbon content than the catalyst from the 5 minute run and yet they both are equally deactivated.

### Liquid Product Analyses

Quantitative analyses of the liquid products from the quinoline runs performed at 300°C and 400°C for 5 minutes and 120 minutes are given in Figure 1. The amount of unidentified components (components that are not intermediates or products in the reported quinoline HDN reaction scheme (5)) is equal to 100% minus the height of the bar. The quantity of unidentified compounds increased with both time and temperature. At 300°C for 5 minutes, 19% of the liquid product was unidentified whereas at 400°C for 120 minutes 86% was unidentified. These results indicate that side reactions occur to a greater extent under more severe reaction conditions. The product distribution for the 300°C run for 5 minutes also shows that the hydrogenation of quinoline to PyTHQ was very rapid. Increasing time and/or temperature yielded more OPA. None of these runs yielded significant concentrations of PBz or PCH. The 400°C run products show a higher concentration of BzTHQ than the 300°C runs in agreement with previous results (5).

The product distributions for the run with a 1:1 quinoline to catalyst ratio had 54% unidentified product, whereas the runs with 1:3 and 1:9 ratios had 44% and 24% respectively. Therefore, a higher catalyst to quinoline ratio yields more side reactions. The product distributions also showed increasing concentrations of OPA and PCH with increasing catalyst to quinoline ratios.

The product distributions for the 5 minute runs with the intermediates and products showed no significant amount of unidentified material. In addition, the only significant reaction that occurred in any of these runs was the hydrogenation of BzTHQ to about 15 wt% DHQ. In the 120 minute runs (Figure 2), PyTHQ, DHQ and BzTHQ yielded 29%, 19% and 9% unidentified product respectively. In addition, PyTHQ formed more OPA, DHQ and PCH. OPA yielded more PCH. PBz was hydrogenated to a significant amount of PCH, and BzTHQ was hydrogenated to DHQ.

There is no correlation between the amount of deactivation and the amount of unidentified material in the liquid product. This is shown by the results of the quinoline runs in Table 2 and Figure 1. In addition, the 1:1 catalyst to quinoline run yields less deactivation than the 1:3 run, but yields more unidentified material.

The rapid deactivation due to hydrotreating quinoline and the hydrogenated heterocyclic intermediates may be due to the low reaction rates of the intermediate compounds to denitrogenated products at 300°C. Some of the intermediates (PyTHQ and DHQ) are strong basic compounds (9). Therefore, these compounds would be strongly adsorbed on the catalytic sites causing site blockage. Additional studies are underway to evaluate the effects of hydrotreating the intermediates and products at 400°C and to characterize the deposits on the aged catalysts.

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Table 1. Model compounds.

Quinoline	PyTHQ	OPA	PBz
			
BzTHQ	DHQ	PCH	
			

Table 2. Fraction of measured extrudate and intrinsic activity losses for the runs with quinoline. Results are relative to fresh presulfided catalyst.

TEMPERATURE(°C)	EXTRUDATE		INTRINSIC	
	5 min	120 min	5 min	120 min
300	0.73	0.76	0.89	0.89
400	0.80	0.84	0.85	0.94

Table 3. Fraction of measured extrudate and intrinsic activity losses for the 300°C runs with the intermediates and products. Results are relative to fresh presulfided catalyst.

REACTANT	EXTRUDATE		INTRINSIC	
	5 min	120 min	5 min	120 min
PyTHQ	0.70	0.53	0.85	0.80
OPA	0.54	0.47	0.66	0.66
PBz	0.52	0.53	0.22	0.27
BzTHQ	0.75	0.66	0.88	0.83
DHQ	0.68	0.67	0.82	0.78
PCH	0.14	0.21	0.37	0.35

Table 4. Carbon contents of the aged catalysts from the 300°C runs reported as weight percents.

	<u>Quin</u>	<u>PyTHQ</u>	<u>OPA</u>	<u>PBz</u>	<u>BzTHQ</u>	<u>DHQ</u>	<u>PCH</u>
5 min	4.81	4.25	3.86	2.28	5.19	4.07	1.81
120 min	6.36	NA*	3.43	2.49	4.76	4.19	1.99

\* Not analyzed.

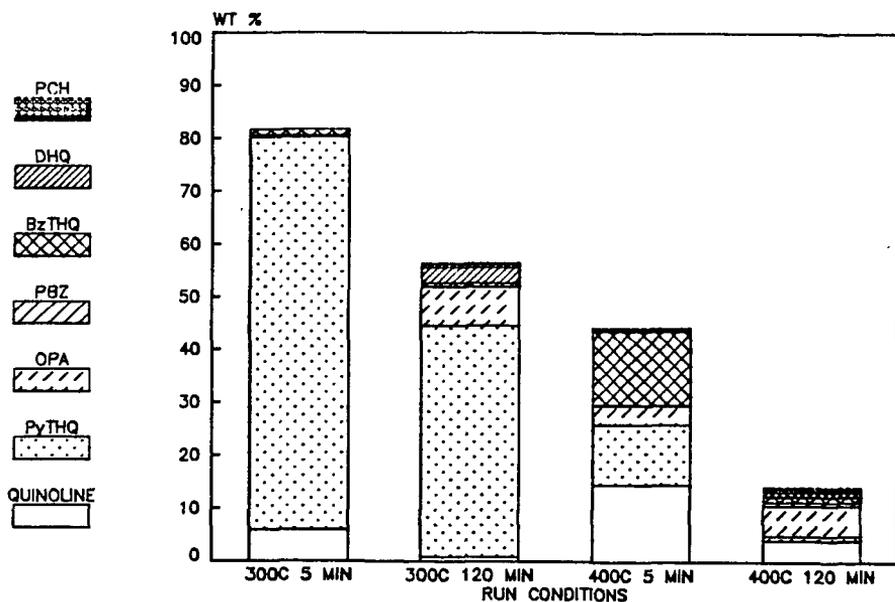


Figure 1. Liquid product analyses from the runs with quinoline.

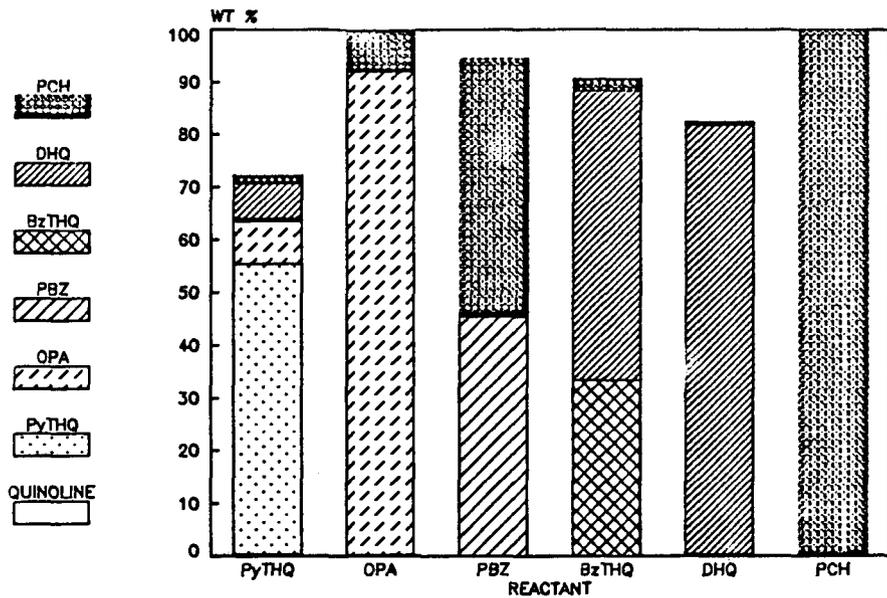


Figure 2. Liquid product analyses from the guns with the intermediates and products at 300°C for 120 minutes.