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**KINETICS AND MECHANISM OF DESULFURIZATION
AND DENITROGENATION OF COAL-DERIVED LIQUIDS**

Annual Report, June 20, 1975—June 19, 1976

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July 15, 1976

Work Performed Under Contract No. E(49-18)-2028

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DENITROGENATION OF COAL-DERIVED LIQUIDS

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III. SUMMARY OF PROGRESS

This summary is organized to follow the task statements of the contract. The summaries are very brief, containing only the most significant results and conclusions; the interested reader can obtain further information including the primary data obtained from the quarterly reports.

A. Microreactor Development

Two high-pressure liquid-phase flow microreactors have been built in this laboratory during the first year of this study of catalytic hydroprocessing reactions. The first reactor was built with University of Delaware funding, and the second was constructed under support from ERDA. These reactors provide hydrogen to the catalyst by saturating a carrier oil with hydrogen; the reactant is carried in this oil at low concentration. It is thereby possible to operate without a gas phase of hydrogen but with a substantial hydrogen excess.

These microreactors are unique in that meaningful kinetic measurements can be made with as little as 25 milligrams of catalyst and small amounts of reactants over a broad range of operating conditions. These microreactors have been operated in the continuous mode, but pulse operation is possible. These microreactors are being used to determine the reaction networks and reaction kinetics of dibenzothiophene hydrodesulfurization and quinoline hydrodenitrogenation and will be used to study the hydrotreating behavior of a range of sulfur- and nitrogen-containing compounds found in coal-derived liquids.

The operating success of these units has exceeded the expectations of the contract. In addition to their application to studies of hydroprocessing, these reactors should be of general interest to catalytic research.

B. Catalytic Hydrodesulfurization

The major objective of this research is to determine reaction kinetics and relative reactivities for catalytic hydrodesulfurization of sulfur-containing compounds found in coal-derived liquids.

The microreactor described in the previous part was used to determine kinetics and product distributions of hydrodesulfurization of dibenzothiophene in a paraffinic oil. The experiments were carried out at temperatures of 300-350°C and space velocity 1-4 hr⁻¹, which are characteristic of expected commercial conditions. The catalyst used was cobalt molybdate on alumina. The analysis of the product was carried out by a gas chromatograph equipped with a sulfur-specific detector and flame ionization detector. Greater resolution is expected from a gas chromatograph equipped with a coated open-tubular column; this unit has just been installed.

Results of the study of the kinetics and reaction network for hydrodesulfurization of dibenzothiophene can be summarized as follows:

*- At relatively high hydrogen saturation pressure (approximately 1000 psig), molar ratio of H₂/dibenzothiophene $\approx$ 10, T = 350°C and L.H.S.V. = 4, 100% conversion based on sulfur removal occurs, suggesting that the reactivity level of dibenzothiophene is considerably higher than what is expected from industrial experience.

*- Hydrodesulfurization of dibenzothiophene produces biphenyl as an almost exclusive primary product (over 75% selectivity). No thiol type compounds or partially hydrogenated dibenzothiophenes were detected.

*- Based on these results, the reaction network for hydrodesulfurization of dibenzothiophene is very simple, involving cleavage of C-S bonds with formation of thiol as a postulated surface intermediate. Sulfur removal then occurs with biphenyl formation as the only primary product. Hydrogenation of the aromatic ring adjacent to the thiophene ring is not necessary to obtain easier sulfur removal.

C. Catalytic Hydrodenitrogenation

The main objective of this task is to study the reaction kinetics and mechanism of hydrodenitrogenation of multi-ring aromatic nitrogen-containing compounds under industrial

temperature (300-450°C) and pressure (1000-5000 psig) conditions. During this first year, two autoclave reactors (batch reactors) have been assembled. The autoclaves have been used to evaluate and establish the necessary operating procedures for the hydrodenitrogenation studies. The relative catalytic activity for quinoline hydrodenitrogenation of five commercially available catalysts including cobalt molybdate, nickel molybdate and nickel tungstate was determined. Nickel molybdate was the most active catalyst for the hydrodenitrogenation of quinoline. A Ni-Mo/Al₂O₃ catalyst (Cyanamid HDS-9A) was chosen for the further hydrodenitrogenation studies. High-temperature gas chromatography using flame-ionization and nitrogen-specific detectors is used for product analysis. The identification of reaction intermediates is performed by on-line gas chromatography-mass spectroscopy.

The reaction network for quinoline hydrodenitrogenation has been determined in both the autoclaves and in the high-pressure liquid-phase flow microreactor. Hydrodenitrogenation of quinoline involves equilibrium hydrogenation to 1,2,3,4-tetrahydroquinoline; other ring hydrogenation steps are much slower and do not reach equilibrium. The saturated nitrogen-containing ring is then cracked forming *o*-propylaniline and *γ*-phenyl-*n*-propylamine which then undergo denitrogenation. The reactions appear to be first order in the nitrogen compound concentration. A reaction model has been developed which allows the first-order rate constants for each step in this reaction network to be quantitatively determined. Since hydrodenitrogenation involves a complex reaction network which may require two catalyst functions (hydrogenation and cracking), it is highly desirable to develop quantitative kinetic information on each step so that the exact role of the catalyst surface in the reaction network can be defined. This will allow the effect of catalyst modifications to be quantitatively interpreted and should lead to the more rational design of hydrodenitrogenation catalysts.

The effect of H₂S concentration, H₂ concentration, catalyst type and quinoline concentration on the first-order rate constants for the important steps in the reaction network for quinoline hydrodenitrogenation has been determined. The relative behavior of each of the steps can be rationalized on the basis of whether it is a hydrogenation step or a cracking step along with an analysis of nitrogen-carbon bond reactivity. Hydrogenation steps exhibit a positive order with respect to hydrogen pressure; cracking reactions exhibit

a negative or zero order in hydrogen pressure. Studies of hydrodenitrogenation of carbazole and acridine have been initiated. The reaction networks appear to be very complex, and carbazole reactivity appears to be very low.

D. Characterization of Aged Hydroprocessing Catalysts

Three samples of spent catalyst taken from the Synthoil pilot plant were examined physically and chemically via scanning microscopy to determine the fate of the catalyst activity. The samples were prepared as polished cross-sections of catalyst particles cleaned in a variety of ways. Broken cross sections which reveal the surface structure of the deposited material quite well also were used.

The samples were examined qualitatively with a scanning electron microscope equipped with energy dispersive X-ray analysis (EDAX). The EDAX was used to provide qualitative identification of the elements above sodium deposited on the surface. EDAX also was used with calibration and correction to identify the atomic ratio of Fe/S in FeS crystals. The electron microprobe is equipped with X-ray ^xfluorescence detection. This mode can measure elements above nitrogen with a series of diffraction crystals. The electron microprobe was used to map element density for a 200 by 300 μm section near the surface of the catalyst particles and to measure the radial concentration profile along a 100 μm line aligned parallel to the exterior surface of the catalyst. The pore volume and surface areas were measured by the mercury penetration method.

These studies show that coal mineral matter is cemented to the surface of used catalyst. The fraction of the surface covered varies with position in the reactor; the catalyst toward the front of the reactor is more densely decorated with deposits than the catalyst toward the end of the unit.

The deposited material included (1) clay minerals from the coal, which were apparently little changed in the process; (2) deposits of mineral matter which evidently had undergone significant change (e.g., FeS); and (3) deposits (e.g., titanium compounds) which might have originated from organometallic components of the coal matrix.

The penetration studies showed that the spent catalyst lost approximately 60 percent of the original surface area and pore volume. The loss was found to be confined to the micropore volume.

These scanning microscopy studies demonstrate the critical importance of mineral matter in coal to catalytic processing. Some of the mineral matter is reactive (indeed FeS_2 is reduced easily without catalyst), some may even be catalytic, but even the non-reactive material can foul the catalyst.

E. Microreactor Engineering

The object of this task is to maximize the fundamental information gathered in the microreactor studies of tasks B, C, and D. In the first subtask models for recovering adsorption equilibrium and transport parameter estimates from pulse microreactor experiments have been developed.

In a pulse microreactor experiment the products and the reactants are not separated as the reaction charge passes through the reactor. Consequently with conventional equipment the experimentalist knows the shape of the pulse of reactants entering the system, the form of this pulse after passing through the microreactor assembly, and the overall composition of the two pulses.

Analysis of the inlet and outlet pulses by moments is appropriate because the data then are transformed into a simple set of numbers which can be compared with kinetic models. The analysis by moments can be found from the Laplace-transformed version of the governing set of partial differential equations. The analysis is straightforward but tedious.

This method has been used to develop a set of models which range from simple engineering approximation to highly

quantitative models. The models are often equivalent for wide ranges of parameters of general interest. Thus some direct schemes have been found for extracting rate data from pulse experiments. Some preliminary experiments with thiophene have been conducted to provide a critical test of the theory. These experiments show the power of the overall approach and also show the critical need for developing more accurate experimental technique. A recent review commented that the moment analysis of reacting systems is quite difficult. On the other hand these efforts show that the method is fairly direct and powerful.

Table I is the actual milestone chart and time plan prepared for the work at the beginning of the grant period (in the Proposal). Hatching on the chart indicates that the activity (task) indicated is under active investigation; the number in the hatched region is an estimate of the percentage completion of this particular activity. Crosshatching on the chart indicates that an activity (task) has been completed. Table II gives the cumulative expenditures.

TABLE I TIME PLAN* AND MILESTONE CHART**

C. CATALYST DEACTIVATION

SYNTHOIL

CATALYST:

D. REACTION ENGINEERING

* Time Plan and Milestone Chart as Presented in Proposal

** Hatching indicates that activity indicated is under active investigation;
 number in hatched region indicates the percentage completed;
 crosshatching indicates that the task has been completed.

TABLE II
CUMULATIVE EXPENDITURES

	First	Second	Third	Fourth
Personnel	\$ 5,807	20,740	37,396	53,418
Travel	28	528	1,152	1,152
Supplies & Expenses	4,674	10,007	19,582	25,735
Occupancy & Maintenance	6,110	9,208	10,108	10,634
Equipment	610	17,978	30,704	34,930
Information Processing	--	--	--	97
Transfers (Overhead)	--	10,202	20,035	38,710

IV. PUBLICATION

Stanulonis, J. J., Gates, B. C., and Olson, J. H.,
"Catalyst Aging in a Process for Liquefaction and Hydro-
desulfurization of Coal," A.I.Ch.E. Journal, Vol. 19, No. 3,
pg. 417-438 (1976).