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A PULSED MICROREACTOR STUDY OF CATALYST USED IN THE SYNTHOIL PROCESS

David M. Heinze

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ABSTRACT

In studying the deactivation mechanisms of the Harshaw 0402T cobalt and molybdenum oxide catalyst used in the SYNTHOIL coal liquefaction reactor, a pulsed microreactor with a gas chromatography detection system has been found useful in measuring catalyst activity. Five types of catalyzed reactions important to the SYNTHOIL process were represented in the experiment: hydrodesulfurization (thiophene to C_4 hydrocarbons), cracking (diphenylmethane to benzene and toluene), dehydrogenation (tetralin and Napthalene), hydrodeoxygenation (m-cresol to toluene), and hydrodenitrogenation (pyrrole to C_4 hydrocarbons). It has been determined that exposure of the catalyst in the SYNTHOIL reactor definitely lowers activities in these five reactions, particularly in catalyst pellets taken from the middle and outlet of the reactor. Regeneration is effective in restoring used catalyst to levels of activity comparable to new oxide and presulfided catalyst. It was determined that in situ presulfidation resulted in little difference in catalyst activity from that of an externally-presulfided catalyst and a decrease in some cases.

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Introduction

The Pittsburgh Energy Research Center's (PERC) SYNTHOIL[1] is a process in which coal is dissolved in a recycle oil at elevated temperature and pressure and passed through a fixed bed catalytic reactor along with a turbulent flow of H_2. Sandia Laboratories is conducting research on the process which includes studies of catalyst deactivation, the effects of coal mineral matter, and reactor kinetics. This study contributes to the determination of the deactivation mechanism(s) for the Harshaw 0402T cobalt and molybdenum oxide catalyst used in the SYNTHOIL reactor. Experimental catalyst samples included pellets in the new oxide (Pitt. #1), presulfided (M-17),[2] used and regenerated (heating to 500°C for 3 hours in air) conditions. Used and regenerated pellets were taken from PERC SYNTHOIL reactor run number FB-44 and reactor inlet (loop 1), middle (loop 4), and outlet (loop 7) from runs FB-30, FB-31, and FB-35. Operating conditions for these runs are shown in Table 1.

Gas chromatography was used to measure activities of the catalyst in reactions similar to those that occur in the SYNTHOIL reactor. By introducing pulses in model reactant compounds into the carrier stream flowing across the catalyst pellet at 450°C, product compounds were monitored using the basic chromatography technique. The system also allowed the presulfiding of the fresh oxide catalyst pellet in situ so the above analysis could be performed without removing the sample from the oxygen-free atmosphere.

The major objectives of this study were: 1) to identify reactions compatible with the chromatography techniques that are representative of the SYNTHOIL catalyzed reactions and, 2) to measure the extent to which these reactions take place with the new, used, regenerated, and presulfided (air exposed and in situ) catalysts.

TABLE 1

Operating Conditions for SYNTHOIL Reactor Experiments

Run	Pressure	H_2 Flow Rate	Coal Feed Rate	Duration
FB-30	4000 psi	125 std. ft^3/h	1.5 lb/h	155 h
FB-31	4000	125	2.25	20
FB-35	2000	500/125/500	1.5	168
FB-44	4000	1300	8.75	400

Experimental Apparatus

A Hewlett-Packard Model 7620 gas chromatograph was used with a thermal conductivity detector. The columns were 12' long, 1/8" stainless steel packed with 100/120 mesh Supelcoport coated with 5% by-weight SP-1200 and 1.75% by-weight Bentone-34. The thermal conductivity detector operates with two flow systems; the sample side (A-side) and the reference side (B-side). The sample-side flow system was extended externally to accommodate the pulsed microreactor. In progressive order toward the column, this arrangement consisted of a flow controller, stainless steel tubing with an injection port, a quartz sample tube running through a platinum wound furnace, and stainless steel tubing connecting to the existing injection block on the sample-side (see Figure 1). All external lines were wrapped with heat tape to provide a preheater. Microreactor temperature was monitored and kept within 5°C of 450°C and oven (column) temperature was 150°C (programming was not necessary). Hydrogen was used as the carrier gas necessitating exhaust venting. The basic technique consisted of injecting a model compound into the preheater and starting the electronic integrator so as to maintain constant retention times and receive the integrated peak areas and recorder presentation. As the model compound flows over the sample, conversion products are emitted and undergo column separation. Thermal conductivities of these gases (A-side) are measured with reference to the hydrogen carrier gas (B-side) in the detector yielding peaks representing individual compounds.

The *in situ* presulfiding experiment required the addition of a valve system to the pulsed microreactor. This apparatus is shown schematically in Figure 2. The hydrogen carrier by-passed the sample tube while the hydrogen-hydrogen sulfide mixture flowed over the fresh-oxide catalyst pellet. Upon completion of presulfiding the H_2-H_2S source was cut off and carrier flow was re-established through the reactor, restoring the analysis mode. Presulfidation conditions are included with the data in Table 4 (see below). The H_2S exhaust was scrubbed through a 50% sodium hydroxide solution to remove sulfur and the entire external system was enclosed in a plastic exhaust hood to guard against even small leaks.

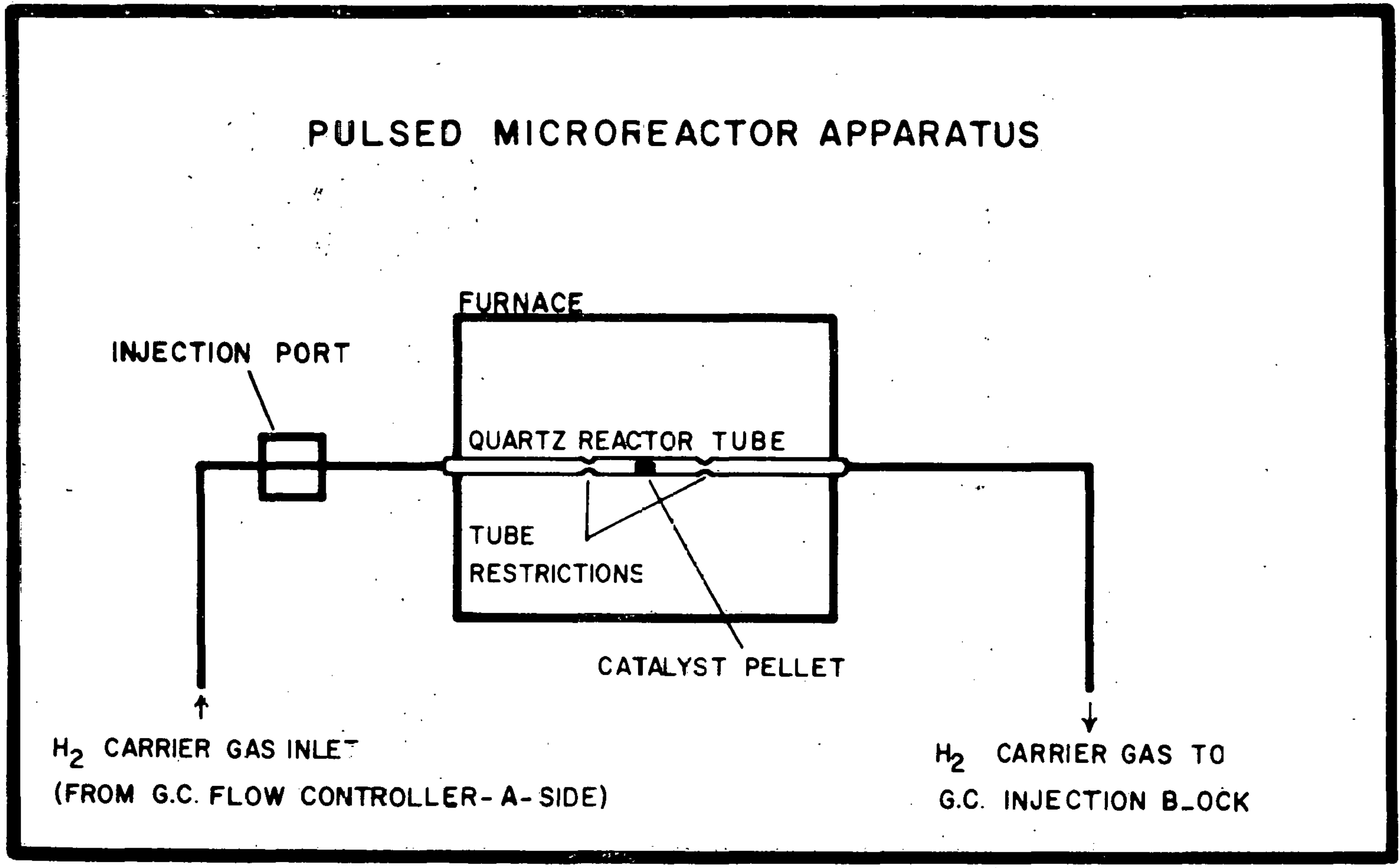


Figure 1. Schematic representation of the pulsed microreactor apparatus showing connecting points to the gas chromatograph. All lines shown were wrapped with heat tape for preheating.

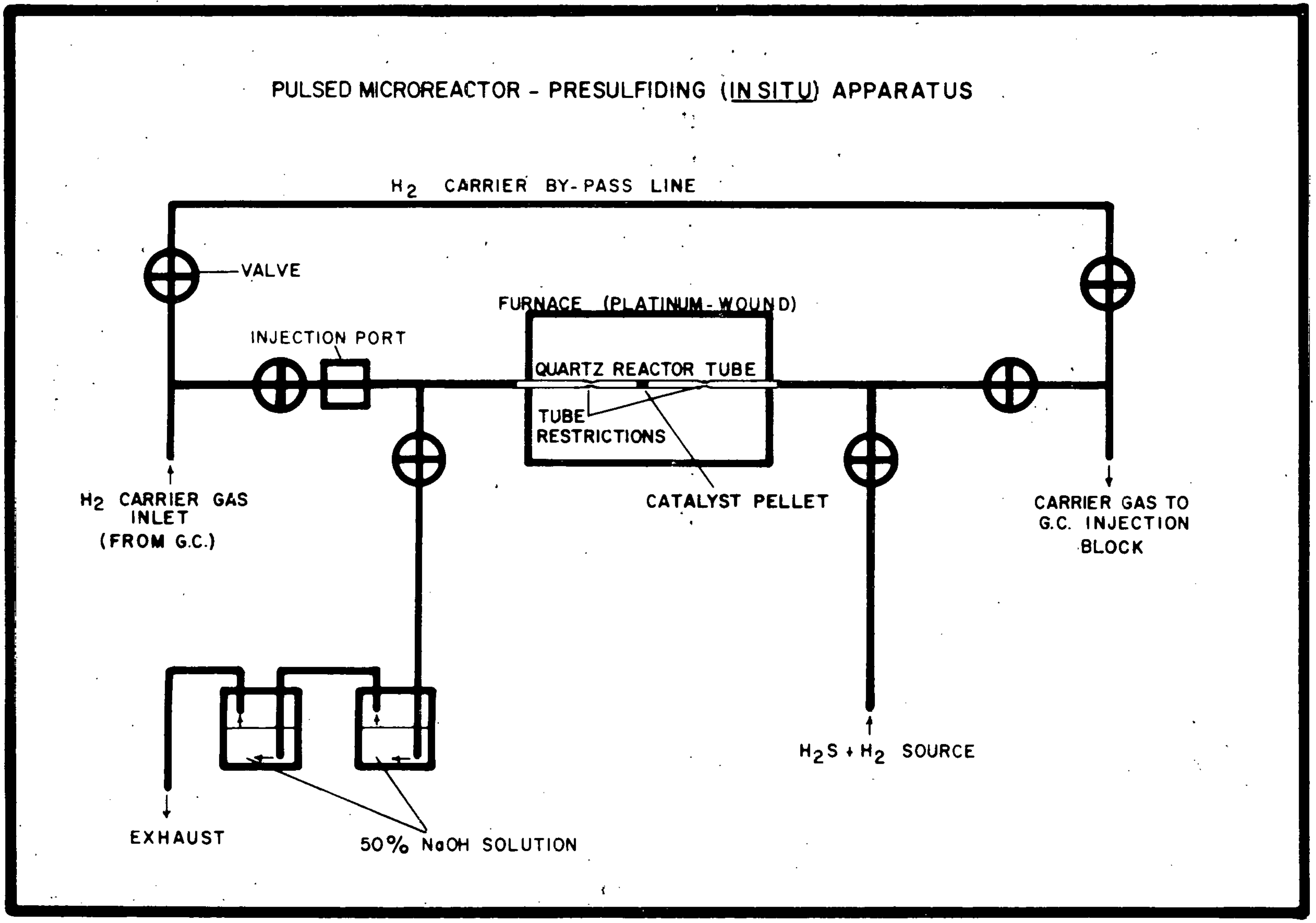


Figure 2. Schematic representation of the <u>in situ</u> presulfiding apparatus and pulsed microreactor showing the valve system allowing carrier by-pass and sulfidation.

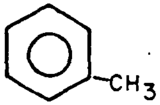
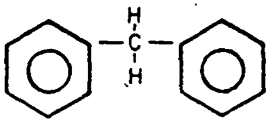
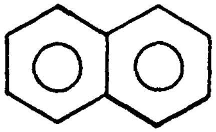
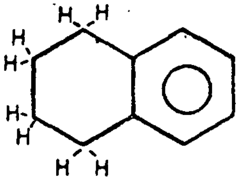
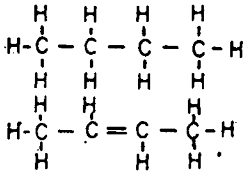
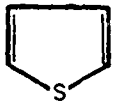
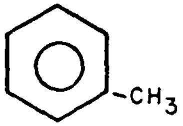
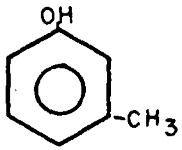
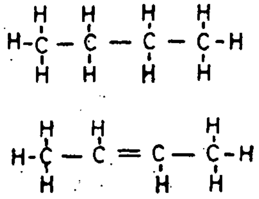
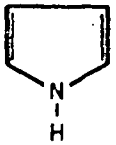
Results and Discussion

In the SYNTHOIL process heteroatoms such as sulfur, nitrogen, and oxygen are removed from the coal slurry. In addition, the reduction of the average molecular weight (hydrocracking) is important in converting the coal to a liquid. Therefore, five major reactions are of particular interest: hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation, cracking, and hydrogenation. Model compounds were selected which represented, to a reasonable degree, those in the coal. All reactions took place at 450°C. Thiophene was used successfully as the model compound in hydrodesulfurization yielding C_4 hydrocarbons and H_2S. This reaction was very easily detected in all of the catalyst conditions studied. Hydrodenitrogenation was initially achieved with pyridine yielding pentane and ammonia, but detection was significant only in the unused catalyst. In search of a similar model compound for nitrogen removal, pyrroline, pyrrolidine, and pyrrole were tested. The bonding structure of pyrrole allowed the reaction to take place sufficiently above detection limits of the instrument with all catalyst conditions. Hydrodeoxygenation was clearly observed in the conversion of m-cresol to toluene. It was difficult to find a model compound which allowed sufficient cracking with the used catalyst. Cumene, biphenyl, and diphenylmethane were tested and the latter was found to meet the sensitivity requirements although experimental resolution was poor because of product retention(toluene and benzene) on the catalyst. Tetralin (tetrahydronaphthalene) reacted with all catalysts to produce naphthalene in the dehydrogenation reaction. Chemical structure representations of these model compound reactants and products are shown in Table 2.

Model compounds and reaction products transit the gas chromatograph column and detector producing peaks identified by their retention times and measured by their integrated areas.[3] The relative activity for a sample was taken to be the ratio (designated R) of the integrated areas of the chosen reaction product to that of the model compound. Weight percent corrections for different detector responses to different compounds were not necessary for relative measurements between catalysts in a given reaction. The R value from the externally presulfided M-17 catalyst

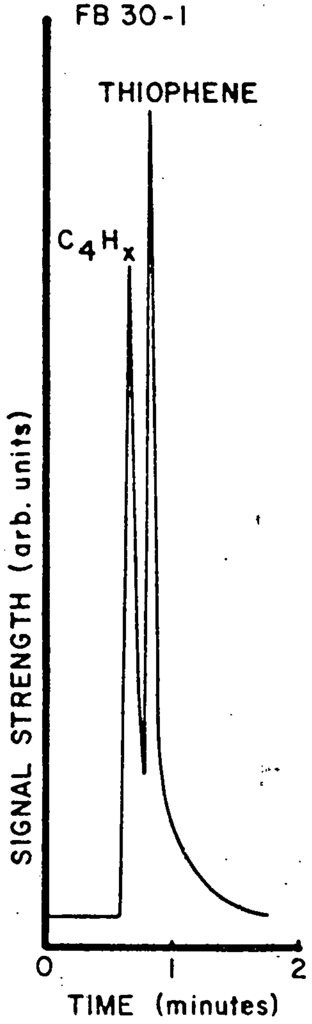
Table 2

Model Compcunds and Products Used to Measure Catalytic Activity

Reaction Studied	Product		Model Compound Reactant	
Cracking	Benzene + Toluene	 	Diphenylmethane	
Dehydrogenation	Napthalene		Tetralin (Tetrahydro- naphthalene)	
Hydrodesulfurization	C_4H_x, e.g.	 $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$ $H-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\underset{H}{C}-\underset{H}{\overset{H}{C}}-H$	Thiophene	
Hydrodeoxygenation	Toluene		m-Cresol	
Hydrodenitrogenation	C_4H_x, e.g.	 $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$ $H-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\underset{H}{C}-\underset{H}{\overset{H}{C}}-H$	Pyrrole	

(R presulfided)^3 was used as a standard measure of activity. R values for the other catalysts (e.g., used) were divided by the R presulfided values to obtain an activity ratio A; i.e., $A = \frac{\text{R used}}{\text{R presulfided}}$. A typical conversion chromatogram for hydrodesulfurization is shown in Figure 3 along with the method used to derive the activity ratio. Table 3 compiles these activity ratio or A values for oxide, used, regenerated (FB-44), and presulfided (in situ) catalyst. These values are averages of two or more measurements. Tests to evaluate data reproducibility on the same sample showed the ratios to seldom vary more than a factor of two and generally agree within 1 to 20%. Measurements on "equivalent" samples show the accuracy of the data to be only within a factor of three. While some error was undoubtedly the result of technique and carrier flow deviances, repeated measurements indicated that most variance in data (on "equivalent" samples) is due to actual catalyst activity differences from sample to sample. It is reasonable to suggest that the proposed deactivation mechanisms could take place in the varying degrees suggested by the data at slightly different reactor locations and pellet orientations in the reactor. Also random breakage of the pellets upon removal from the used reactor tubes certainly could affect measurements of deactivation (e.g., coking). Acknowledging the above uncertainties, definite trends are shown in Table 3 (average values). Particularly evident is the decrease (by a factor ∿ 100) in cracking activity of the catalyst after use in the reactor. The decrease in the other catalyst activity functions is not so profound as in the cracking activity; dehydrogenation is decreased by factors of 10 to 100, hydrodesulfurization by factors of 2 to 20, hydrodeoxygenation by factors of 2 to 50, and hydrodenitrogenation by factors of 2 to 10.

The average activity of FB-30 is generally higher than that of FB-31 which is higher than that of FB-35. Activity data from FB-30 shows no consistent location dependence (loops 1, 4, and 7), however, the inlets of FB-31 and FB-35 are much more active than the middle and outlet. The FB-44 catalyst is, in general, comparable in activity to FB-30, FB-31, and FB-35 as shown in Table 3. Regeneration of this catalyst was accomplished by heating to 500°C over a period of ∿ 3.5h in air. Measurements of activity showed these pellets to be comparable with the M-17 presulfided catalyst and new oxide (Pitt. #1) catalyst.



$$\frac{\text{INTEGRATED AREA } (C_4H_x)}{\text{INTEGRATED AREA (THIOPHENE)}} = R_{FB\ 30\text{-}1}$$

$$\frac{R_{FB\ 30\text{-}1}}{R_{M\text{-}17}} = A_{FB\ 30\text{-}1}$$

Figure 3. Typical conversion spectra for hydrodesulfurization with FB30-1 catalyst. The activity ratio, A, is found by dividing the R value of the sample (calculated as shown above) by the R value of the externally presulfided M-17 catalyst (previously determined).

Table 3

Activity Ratio (A) of Catalyst After Various Treatments(1)

Catalyst	Cracking	Dehydrogenation	Hydrodesulfurization	Hydrodeoxygenation	Hydrodenitrogenation
FB 30-1	.009	.09	.2	.2	.1
30-4	.03	.1	.2	.2	.1
30-7	.02	.1	.1	.1	.1
Average	.02	.1	.2	.2	.1
FB 31-1	.03	.2	.4	.6	.4
31-4	.003	.02	.09	.05	.07
31-7	.03	.006	.04	.02	.04
Average	.02	.08	.1	.2	.2
FB-35-1	.02	.1	.2	.2	.1
35-4	.006	.02	.07	.07	.09
35-7	.009	.04	.09	.09	.1
Average	.01	.05	.1	.1	.1
FB-44	.02	.1	.1	.09	.1
Regenerated(2) FB-44	.5	1.1	1.0	.4	1.0
Pitt #1(3)	.3	1.7	1.6	.4	17.

Note: 1. "A" is a ratio of measured activity on existing catalyst to the activity on PERC's presulfided catalyst (M-17).

2. Regenerated FB-44 - FB-44 heated in air to 500°C in 4.5 h and held at 500°C for 3.5 h.

3. Pitt #1 - Fresh, oxide catalyst.

New oxide (Pitt. #1) catalysts were sulfided in situ, using the apparatus and procedure previously described with four different conditions of temperature, time, and H_2S flow. Table 4 shows the in situ presulfidation results in similar or somewhat lower activities than the M-17 catalyst. This shows that presulfiding (in situ or external) lowers activity as compared to fresh oxide catalyst. This does not necessarily make presulfiding undesirable in the SYNTHOIL process since the literature indicates that sulfiding reduces coking.[4,5]

Summary

By using the pulsed microreactor in conjunction with a gas chromatograph, reactions representative of SYNTHOIL catalyzed reactions were identified and measured. The conversions found to be most successful were: thiophene to C_4 hydrocarbons (hydrodesulfurization), diphenylmethane to benzene and toluene (cracking), tetralin to napthalene (dehydrogenation), m-cresol to toluene (hydrodeoxygenation), and pyrrole to C_4 hydrocarbons (hydrodenitrogenation).

Activity ratios were derived from measurements on new, used, regenerated, and presulfided (air exposed and in situ) catalysts. It was found that after use in the SYNTHOIL reactor catalysts show a definite decrease in activity (as compared to the M-17) for all five reactions. This decrease in activity is generally less at the inlet of the reactor. Regenerated catalysts were comparable in activity to the M-17 externally-presulfided catalyst and the Pitt. #1 fresh oxide catalyst.

It was found that in situ sulfidation produces some reduction in catalyst activity from that of the M-17 catalyst.

Table 4

ACTIVITY RATIO $\frac{\text{PRESULFIDED (in situ)}}{\text{M-17}}$

	Cracking	Dehydrogenation	HDS	HDN	HDO
#1 500°C, 4h 20% H_2S	.2	.9	1.1	.3	.9
#2 245°C, 0.16h 370°C, 3h 10% H_2S	.4	.3	.6	.2	.2
#3 340°C, 0.16h 370°C, 3 h 10% H_2S	.7	1.2	1.2	.6	1.1
#4 450°C, 4h 20% H_2S	.4	1.0	.9	.6	.8

Acknowledgments

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