

## LOW TEMPERATURE LIQUEFACTION CATALYSIS

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### AUTOCLAVE LIQUEFACTION STUDIES

Molybdenum sulfide catalysts have been prepared by incipient wetness impregnation of Illinois No 6 coal with precursors, either ammonium heptamolybdate or ammonium thiomolybdate. The impregnated precursors become active catalysts when heated under liquefaction conditions - 350° C, 2000 psig H<sub>2</sub> - in the presence of a coal-derived solvent. Catalyst-bearing residues recovered following the THF extraction of the liquefaction products, when mixed with fresh coal, were found to perform in a second liquefaction cycle as well as or even better than the catalyst precursors themselves. Improved performance is thought to derive from the activity possessed by the preformed catalysts, especially during the period of the initial heating to liquefaction temperatures when retrogressive reactions may already begin to play a role. Preliminary results indicate that low temperature performance may be improved by direct transfer of liquefaction products from a small reactor for catalyst preparation to a larger liquefaction reactor. Thus, an active catalyst was formed by loading 20,000 ppm Mo on 3.5 g. coal, and subjecting it to liquefaction conditions (350° C, 2000 psig H<sub>2</sub>, 60 min. 3.0 g V-178 solvent). The entire reaction product was then transferred to a 0.5 L. stirred autoclave with 67 g. fresh coal and 115 g. solvent, then subjected to a temperature staged liquefaction under ca. 2000 psig H<sub>2</sub>. The catalyst loading in this liquefaction performance test was 1000 ppm Mo. Temperature programming was found necessary in order to minimize temperature excursions that begin as the temperature approached 325° C. These exotherms are increased by the presence of an active catalyst. Temperature programming allows the time-temperature profile of individual experiments to be controlled in a more consistent fashion, enabling the performance of a variety of catalysts to be better compared. When programmed from 300-375° C, enhanced coal conversion and hydrogen uptake were found when catalysts prepared in the microautoclave were added to the stirred autoclave. Changes in total pressure indicate that catalytic hydrogenation began as the reactor approached 300° C. Thus, an activated, dispersed catalyst is able to participate in liquefaction chemistry at the beginning of coal dissolution.

### PULSE-FLOW MICROREACTOR STUDIES

Reactions between coal and molecular hydrogen are

fundamentally important to coal liquefaction. Despite the large number of studies concerned with coal hydrogenation, details about the actual mechanisms of reactions between coal and hydrogen, particularly those involving catalysts, are still not available. One of the prime stumbling blocks in this area is the basic fact that coal and many of the catalysts used are both solids. In the approach presented here, the catalytic exchange of hydrogen on coal with molecular deuterium has been used to monitor the interaction of solid coal and solid catalyst derived from  $\text{MoS}_3$ .

A pulse-flow microreactor was conceived as an instrument to study coal-catalyst interactions by means of exchange reactions between coal and deuterium gas. Its construction and demonstration as a useful way to study this chemistry has already been described<sup>1</sup>. The micro-flow reactor is simple in design. It allows a pulse of deuterium to be carried in an inert gas through a heated bed of coal. The gas stream is sampled by a capillary tube at the exit of the tubular reactor and analyzed by a quadrupole mass spectrometer. The influence of a well known liquefaction catalyst was explored by making physical mixtures of dispersed  $\text{MoS}_3$  with coal and comparing the extent of exchange obtained with and without catalyst.

The catalytic exchange of hydrogen sulfide and of hydrogen with deuterium on molybdenum disulfide has been reported<sup>2</sup>. This work was performed in a static (not flowing) system using both  $\text{H}_2$  and  $\text{D}_2$ . The exchange reaction,  $\text{H}_2 + \text{D}_2 = 2\text{HD}$ , was found to be facile over  $\text{MoS}_2$  at 150-200° C. Sorption studies<sup>3,4,5</sup> have also shed light on the character of the sites on  $\text{MoS}_2$  that take up hydrogen. From these results, it could be anticipated that exchange between hydrogen on coal and deuterium gas might occur if a pathway for hydrogen existed between coal and catalyst.

## EXPERIMENTAL

A block diagram of the pulse-flow microreactor is given in Fig. 1. The reactor was a 7.5 x 0.25 inch (O.D.) 316 stainless steel column lying horizontally in a tube furnace. A manually operated zero-dead volume injection valve with a sample loop of approximately 150  $\mu\text{L}$  was used to form pulses of deuterium. A dry ice trap was used to trap condensable gases. The reaction products were analyzed with a Dycor Model M100MD quadrupole gas analyzer. Reaction gases exited the cold trap and were sampled by a fused silica capillary tube attached to the inlet of the mass spectrometer.

Samples of coal, catalyst, or blends of coal and catalyst were prepared by grinding thoroughly with an agate mortar and pestle under a gentle stream of  $\text{N}_2$ . The samples were loaded into the microreactor column and glass wool plugs were inserted into both ends of the packed column. The maximum mass of coal charged was 2.0 g. An optimum sample mass was found to be 1.0 g. The column was placed in the tube furnace and connected to the loop injection valve and cold trap. The system was flushed with high purity argon at a flow rate of 3 cc per minute. The flow of argon was continued at this rate throughout the experiment. After the air was flushed from the system, the sample was heated to 120° C to dry the coal.

When the baseline mass spectrum displayed only the masses associated with argon, the sample was pulsed with deuterium at 25° C temperature increments until a temperature of 425° C was reached. In experiments that monitored exchange reactions during a regulated cooling cycle, the sample was pulsed with D<sub>2</sub> each time there was a 25° C decrease in temperature. The temperature in the reactor column was monitored with a digital thermometer equipped with a Type K thermocouple probe located inside the tube furnace.

The coals used were obtained from the Argonne National Laboratories Premium Coal Bank. Both samples, the Illinois No. 6 and the Pittsburgh No. 8, were high volatile bituminous coals. The MoS<sub>3</sub> used as a catalyst precursor was prepared as a precipitate by acidifying an aqueous solution of ammonium tetrathiomolybdate with formic acid following a published procedure<sup>7</sup>.

## RESULTS

A series of experiments was carried out to determine whether hydrogen in coal is accessible for hydrogen exchange reactions. The curves in Figure 2 represent the detector response to a series of deuterium pulses carried by argon through a sample of Pittsburgh No. 8 coal in the heated reactor. At 130° C, the deuterium pulse emerged virtually unchanged. The small amount of HD observed is probably due to the hydrogen present in the D<sub>2</sub> itself. By comparing the response at 390° C with that at 130° C, it may be seen that a relatively small amount of HD and H<sub>2</sub> was produced at the higher temperature. Thus, in the absence of an added catalyst, only a minor amount of exchange was observed, and only at the higher temperature. It may also be noted that a small amount of methane was evolved from the coal at this temperature. Thus, indications are that a modest amount of thermal chemistry takes place at the higher temperature, as would be expected, but the amount of exchange is small.

Molybdenum sulfides are among the more commonly used catalysts for direct liquefaction. It was therefore of interest to examine the interaction of these catalysts with coal in the pulse-flow microreactor. For the initial experiments, MoS<sub>3</sub> was selected as a precursor to the usual form of the active catalyst, MoS<sub>2</sub>. The particular sample of MoS<sub>3</sub> used in these experiments had previously been shown by others at our center to provide a liquefaction catalyst of high activity in batch liquefaction experiments using Illinois No. 6 coal and tetralin under a pressure of hydrogen<sup>6</sup>. A series of experiments was carried out to determine whether or not this catalyst precursor could be a source of H<sub>2</sub> or HD in the absence of coal under the conditions used in subsequent experiments to probe for exchange with coal. The results indicate that it is not.

Next, a physical mixture of Pittsburgh No.8 coal and MoS<sub>3</sub> was prepared by grinding the two together with a mortar and pestle. The mixture, 1.9g coal and 0.1g MoS<sub>3</sub>, was loaded into the reactor and the temperature was increased while a series of deuterium pulses was passed through the tube. The results are shown in Fig. 3. The D<sub>2</sub> pulses emerged unchanged as the temperature increased up to about 275-300° C. Then, the size of the D<sub>2</sub> pulses that emerged

began to decrease until they disappeared at about 325-350<sup>0</sup> C. Evidence of a pulse reappeared when the temperature reached 425<sup>0</sup> C. However, the pulse that emerged was due to hydrogen, not deuterium. No evidence for D<sub>2</sub> or HD was found. The pulse of H<sub>2</sub> was superimposed on a continuous level of H<sub>2</sub> that was apparently evolved from the coal on heating to this temperature. Observation of a pulse of hydrogen emerging after a pulse of deuterium was injected indicates that, in conjunction with a catalyst, the coal may serve as a source of hydrogen. It is evident that both coal and catalyst must be present for extensive exchange to occur, because the prior experiments of heating either the coal or the catalyst separately gave little or no indication of exchange. The emergence of only H<sub>2</sub> and not D<sub>2</sub> nor HD shows that the pool of hydrogen that participates in the exchange must be large compared to the size of each pulse of deuterium injected. Also, the rate of the exchange reaction must be fast enough to permit this replacement of D<sub>2</sub> with H<sub>2</sub> to be essentially total and complete.

When coal was mixed with MoS<sub>3</sub> and heated, a certain temperature was reached before appreciable exchange of deuterium with hydrogen was observed. However, Wilson, Kemball, and Galwey<sup>2</sup> report a study of the exchange reaction between H<sub>2</sub> and D<sub>2</sub> over MoS<sub>3</sub> in the range of temperature of from 140<sup>0</sup> to 200<sup>0</sup> C. The following question then arises: is this temperature required to render the catalyst precursor active, or is the exchange itself limited to higher temperatures? To investigate this point, the reactor was cooled to room temperature in a flow of argon without disturbing its contents, and the same heating cycle was begun again the next day. The results are shown in Figure 4. Evidence for the exchange reaction was seen by the time the temperature reached 225<sup>0</sup> C. All three isotopic species, D<sub>2</sub>, H<sub>2</sub>, and HD, emerged after a D<sub>2</sub> pulse. At 250<sup>0</sup> C and higher temperatures, only H<sub>2</sub> emerged after a D<sub>2</sub> pulse. Apparently, the higher temperatures required for observation of the exchange in the first heating cycle were necessary for the activation of the catalyst precursor. Once activated, the coal/catalyst mixture exhibits the exchange property at much lower temperatures.

It was also noted that the system behaved similarly during the time when the reactor was again cooled down. After reaching 425<sup>0</sup> C, deuterium pulses were injected at several temperatures as the reactor cooled. Only H<sub>2</sub> pulses emerged until the reactor reached about 210<sup>0</sup> C, when HD was observed again along with H<sub>2</sub>. As the temperature declined further, the relative size of the D<sub>2</sub> peak increased until only D<sub>2</sub> was observed at 80<sup>0</sup> C. Increasing the temperature again brought about the same pattern of exchange as seen in Figure 4. Thus, the behavior of the system with regard to changes in temperature seems to be regular, at least in major respects. This is further evidence that the behavior of the catalyst may be more sensibly defined and characterized after it is activated.

The initial experiments with coal and catalyst were done with a relatively high catalyst loading. These conditions were picked arbitrarily because the facility of the catalytic reactions was not known. A few experiments of the same kind were done at lower catalyst loading to determine if catalyst activity could be

detected at concentrations closer to those typically used in liquefaction experiments. Figure 5 shows the results for a mixture of 1g of Pittsburgh No. 8 coal with 0.008g of  $\text{MoS}_3$  (about 4000 ppm of Mo based on coal). The pattern of activity is similar to that seen at the higher catalyst loading. In the first heating cycle, no exchange is seen until the temperature reached  $400^{\circ}$ - $425^{\circ}$  C. The degree of exchange observed at  $425^{\circ}$  C is somewhat less than that seen at the higher catalyst loading. The pulse that emerges now contains a mixture of  $\text{H}_2$ , HD, and  $\text{D}_2$  (Figure 5a). The predominant species is  $\text{H}_2$ . When the sample was subjected to a second heating cycle, as was performed in the previous experiments at higher loading, exchange was again found at lower temperatures. However, in contrast to the results at higher loading, the exchange reaction was far from complete at  $250^{\circ}$  C. At this temperature,  $\text{D}_2$  is the predominant species (Figure 5b), whereas at the higher loading the exchange was essentially complete (Figure 4c). At higher temperature, the exchange reaction proceeds to a greater degree. The major component emerging is now  $\text{H}_2$ , along with a minor amount of HD. Thus, the system behaves the same with regard to the need to activate the precursor, but the rate of the exchange reaction has been reduced by using a lesser amount of catalyst.

#### CONCLUSIONS

An experimental method has been developed that permits investigations of the interactions of solid, dispersed catalyst with coals in the absence of a solvent. The method has been used to examine the exchange of gas phase deuterium with the hydrogen in coal. It seems reasonable that other probes of catalytic activity could be used by simple extensions of the method. The results indicate that at least some of the hydrogen on coal is in a pool readily accessible to an activated catalyst. The catalyst precursor,  $\text{MoS}_3$ , required heating to temperatures commonly used in direct liquefaction to become active, in accord with the generally held belief that  $\text{MoS}_2$  or a closely related sulfide must be formed before activity in liquefaction is observed. Once activated, the catalyst may operate at temperatures considerably below those generally used in direct liquefaction. Thus, an important result is the finding that the best conditions for in situ activation of a catalyst precursor may not be the same as the best conditions for its use. These preliminary findings indicate that the study of catalyst/coal interactions using a pulse-flow microreactor is profitable, and further work is in progress.

#### ACKNOWLEDGMENTS

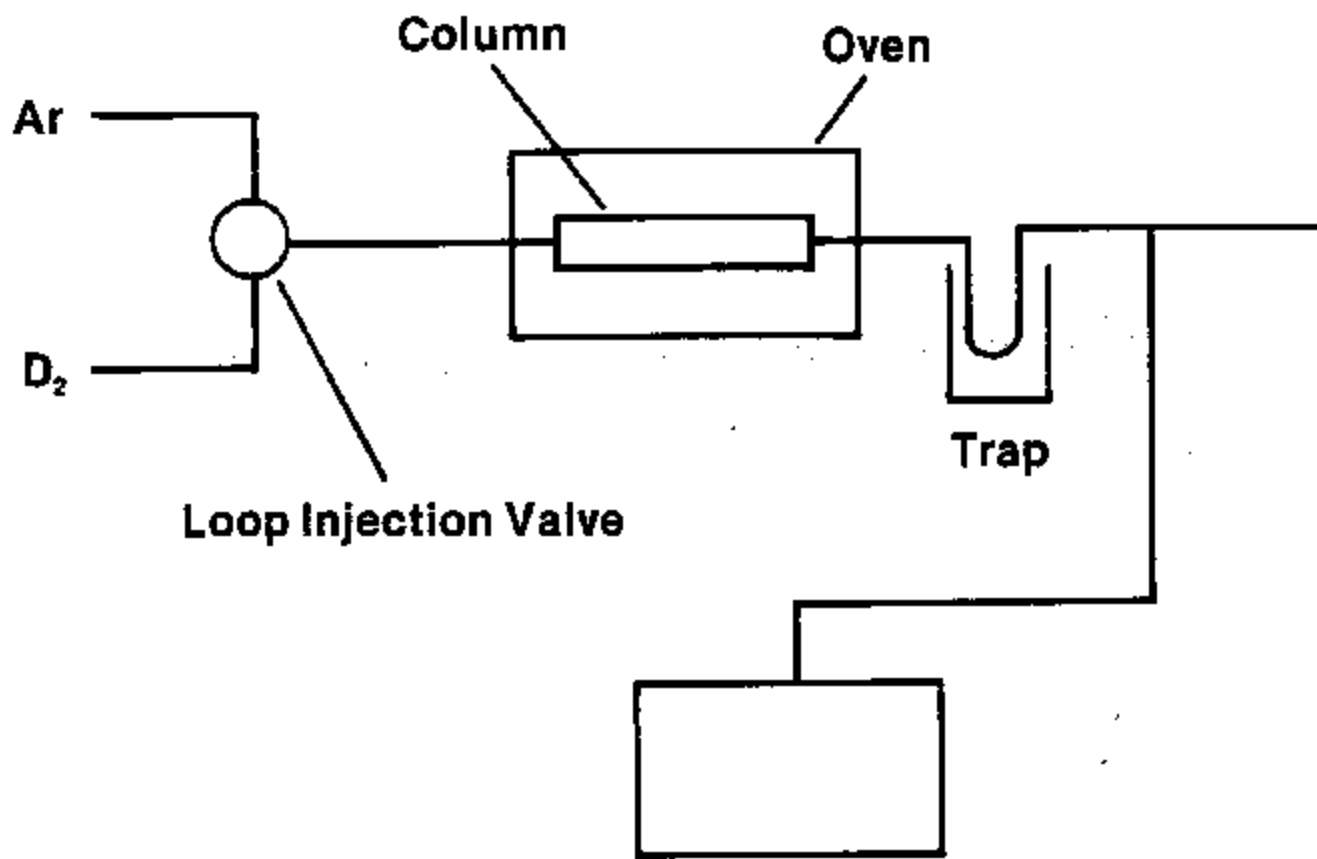
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## REFERENCES

- 1) Finseth, D. H. Proceedings, DOE Direct Liquefaction Contractors Review Meeting, U. S. Dept. of Energy, Pittsburgh, PA. 1988, 378
- 2) Wilson, R. L.; Kemball, C.; Galwey, A. K. Trans. Faraday Soc. 1962, 58, 583
- 3) Wright, C. J.; Sampson, C.; Fraser, D.; Moyes, R. B.; Wells, P. B.; Riekel, C. J. C. S. Faraday I 1980, 76, 1585
- 4) Sampson, C.; Thomas, J. M.; Vasudevan, S.; Wright, C. J. Bull. Soc. Chim. Belg. 1981, 90, 1215
- 5) Badger, E. H. M.; Griffith, R. H.; Newling, W. B. S. Proc. Roy. Soc A 1949, 197, 184
- 6) Utz, B. R.; Cugini, A. V; Frommell, E. A. in 'Novel Materials in Heterogeneous Catalysis' (Eds. R. K. T. Baker and L. L. Murrell), Am. Chem. Soc., Washington, 1990, p. 289

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