

MODEL REACTIONS AS A MEASURE OF MoS₂ ACTIVITY

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ABSTRACT The activity of dispersed molybdenum sulfide liquefaction catalysts was studied using a high-temperature ($\leq 400^\circ\text{C}$), low-pressure (≤ 400 kPa) micro-flow reactor. Model compounds were introduced by one of three methods: injection, continuous flow, or injection into a continuous flow. The dehydrogenation of tetralin, the hydrodesulfurization of benzothiophene, and the hydrodeoxygenation of benzofuran were used as examples of reaction types thought to be important for coal conversion. Transient effects, such as the adsorption of the model compound, could be seen in the injection mode of operation. Under steady-state flow conditions, the catalytic conversion of the reactant could be measured. Injection into the continuous flow demonstrated transient and longer lasting effects of quinoline on the catalytic activity. Two dispersed MoS₂ catalysts were compared in terms of their activity, selectivity, and sensitivity to temperature change.

INTRODUCTION This work employed the known catalytic reactions of model compounds to compare the effectiveness of two dispersed MoS₂ liquefaction catalysts. The HDS of benzothiophene, the dehydrogenation of tetralin, the reaction of benzofuran, and the effect of quinoline on activity were used as the basis of the comparison. The reaction mechanisms of these and other model compounds under hydroprocessing conditions have been critically reviewed recently.¹ One of the catalysts studied was a MoS₂ sample recovered as part of the residue from a liquefaction experiment; the other was a MoS₂ formed under dispersing conditions in the absence of coal. This work used a packed column heated in the oven of a GC as a reactor. Although only low hydrogen pressures could be employed, the GC was used to differentiate transient from steady-state behavior and allowed for the rapid adjustment of reaction temperature. This provided an experimental technique which allowed kinetic data to be obtained within a reasonable time period.

EXPERIMENTAL A Hewlett-Packard 5890 gas chromatograph was used as the basis for a high-temperature, low-pressure reactor. A packed column injection port was used to provide a large volume for the expansion of the vaporizing model compound solution. The catalyst was packed into a stainless steel tube and connected to the injector. The amount of catalyst or catalyst-containing residue was adjusted to give 90 mg of molybdenum in the reactor. Reactor pressures up to about 400 kPa of hydrogen were obtained by adding lengths of metal-clad capillary tubing to the end of the reactor. The total effluent flow was monitored using the Hewlett-Packard TCD detector. Model compound solutions were injected into the hydrogen carrier gas in the usual manner except that a slow injection speed was used. Reactants and products were recovered by condensation upon exiting the reactor. The eluant was analyzed by GC-FID and/or GC-MS to determine the identity and quantity of the products. An alternative method of introducing the model compound solution used a Hewlett-Packard Series 1050 pump to provide a continuous stream of solution. In a third type of experiment, a pulse of material was injected into the continuous stream. Regardless of the technique used to introduce the sample, all of the material was vaporized in the injection port of the GC before entering the reactor. Three types of catalytic materials have been studied. The first was a coal liquefaction residue recovered from a batch reaction which had been prepared using a Blind Canyon coal (DECS-17). The residue (IK87-5) contained 50% by weight MoS₂. The remaining 50% was coal ash and organic matter insoluble in THF. Recycling IK87-5 in a second liquefaction experiment with fresh coal showed it was still active for coal conversion and hydrogen up-take. Only a preliminary report has appeared on this material,² but its preparation and recycle activity are similar to those found for an Illinois No. 6 coal.³ IK87-5 was used as an example of a used dispersed catalyst. The second material was an MoS₂ formed by heating ammonium molybdate and tetralin under liquefaction conditions but in the absence of coal or other added solid support (BCP-287). It was used as an example of a fresh, dispersed catalyst. Third, a commercial (Harshaw 0402T) alumina-supported CoMo catalyst was sulfided *in situ* using injections of dimethyldisulfide into the flowing hydrogen. To date, the majority of the work has been done using the first catalyst.

RESULTS AND DISCUSSION The three methods of sample introduction provide different types of information. The injection technique provides a limited amount of material which passes through the reactor as a nearly Gaussian-shaped peak. Strong adsorption on the catalyst and/or support may appear as a peak tail if desorption is fast

relative to the time the material is in contact with the catalyst, or as a loss of peak intensity due to material losses if the desorption is relatively slow. Although significant peak tailing was not seen in our experiments, the preferential loss of material from some samples was seen. Material balances were determined by quantitative GC analysis of the condensed eluant. The preferential adsorption of diphenylether from injections of a 10% solution in *n*-undecane is shown in Figure 1. The recovered material contained *n*-undecane, diphenylether and a small amount of benzene amounting to about 3% of the diphenylether injected. No phenol was detected. The recovery of undecane in these experiments averaged 90% and was fairly constant from injection to injection. In contrast, the diphenylether recovery ranged from 65% to 80% and appeared to increase with injection number. A similar though less severe loss of a different oxygenate was seen when aliquots of a 10% solution of benzofuran were injected under the same conditions. In this case, the undecane recovery was 97% while the benzofuran recovery was only 91%. Although the loss of oxygenate in the presence of catalysts dispersed in coal solids has been fairly small, the extent of adsorption can become large in some cases. This can be seen in Figure 2 where the loss of benzofuran is shown for a commercial supported catalyst. In these experiments, benzofuran was introduced as 10 μ L injections of a 10% solution, 5 μ L injections of the neat material, or 10 μ L injections of the neat material. The three sets of data form a single curve showing increased recovery as a function of the total amount of benzofuran injected. Thus, the catalyst appears to adsorb only a certain amount of model compound. Once its capacity has been reached, no further adsorption occurs. Such phenomenon may be important for the proper interpretation of batch data, especially when the amount of model compound is comparable to the amount the catalyst can adsorb. However, they would be expected to disappear in flow experiments where steady-state can be attained. This is the second type of experiment conducted with this reactor.

Steady-state flow conditions were attained by continuously introducing the model compound solution into the injection port of the GC using an HPLC pump. Flows of less than 20 μ L/min were necessary to prevent overloading the packed-column injection port. Injector overload caused a decrease in recovery. A similar effect is seen when too much material is injected into an analytical gas chromatograph.⁴ In addition to alleviating the problems associated with model compound adsorption, steady-state operation allows for kinetic measurements. For example, the conversion of tetralin to naphthalene at 400°C in the presence of residue IK87-5 is shown in Figure 3. At the lowest flow rate of 2 μ L/min, a naphthalene yield of nearly 15% was obtained, well above the amount attributable to a thermal reaction. Increasing the flow rate produced less conversion and the rate appears to be first order in tetralin. Similar measurements at 375°C and 350°C were used to determine the temperature coefficient for the reaction. A value of 300 kJ/mol was obtained. Thermolysis reactions typically have values of this magnitude.

Benzothiophene was also used as a model compound to investigate the effectiveness of the residue for HDS reactions. A solution containing 1% benzothiophene yielded recovered starting material along with ethylbenzene as its only product. No styrene was detected in any of the product solutions. When the initial concentration of benzothiophene was raised to 10%, an additional product was also found. The material produced a mass spectrum consistent with dihydrobenzothiophene, C₈H₈S. The recoveries of the benzothiophene and its two products are shown in Figure 4. The amount of C₈H₈S obtained in these experiments decreased with increasing residence time. The presence of dihydrobenzothiophene has been observed in some^{5,6}, but not all⁷ reports on the MoS₂ catalyzed HDS of benzothiophene. Benzothiophene desulfurization by a molybdenum naphthenate derived material has been proposed to follow a pathway dominated by the initial hydrogenation to form dihydrobenzothiophene.⁵

In the third type of experiment, an injection of a second material is made into a steady flow of model compound in solution. An example of this type of experiment is shown in Figure 5 where the TCD trace resulting from injections into a flowing solution is simulated. The recovery data from experiments in which a 10% solution of quinoline was injected into a continuous flow of 1% benzothiophene in tetralin are displayed in Figure 6. The first three determinations in Figure 6 correspond to samples taken on the plateau prior to the first injection of quinoline, roughly between 50 and 100 time units in Figure 5. These determinations consistently gave the conversion of benzothiophene to ethylbenzene to be 50% and the overall material balance to be 91%. The fourth determination results from the collection of the material that elutes with the quinoline pulse from about 110 to 130 time units. The quinoline recovered from the pulse amounted to 80% of that injected. No tetrahydroquinoline or further reduction products were detected. The major effect of the

pulse was to inhibit the production of ethylbenzene. The total recovery of benzothiophene remained constant but the proportion of HDS product decreased to less than 43%. Determination 5 represents a sample taken on the plateau after the quinoline pulse had passed, roughly in the area of 150 to 175 time units. This sample contained neither quinoline nor its reduction products. Figure 6 shows that the conversion of benzothiophene to ethylbenzene had regained about half of the activity lost during the pulse but had not yet fully recovered. Sample 6 contained the material eluting with the second pulse of quinoline and sample 7 contained the material eluting on the plateau after the quinoline pulse. The same results as were obtained with the first pulse are repeated in the second pulse. This indicates that at least two mechanisms of nitrogen base inhibition are operative in this residue. Competitive inhibition in which the quinoline competes with the benzothiophene for adsorption at catalyst active sites may account for a portion of the lost activity seen during the pulse. However, the loss in activity that persists after the quinoline pulse has passed more likely arises from a poisoning of catalyst HDS sites by the base. This poisoning is thought to result from an adsorption mechanism similar to that seen for the diphenylether.

In summary, the liquefaction residue IK87-5 has shown only moderate catalytic activity in the model compound studies. Dehydrogenation and HDS reactions occurred but were significant only when the reaction temperature approached 400°C. Adsorption of heteroatom species occurred and, in the case of quinoline, appeared to be associated with a loss in catalytic activity. The temperature coefficient for the dehydrogenation was quite large and may reflect a thermal rate limiting step.

Work using the fresh, dispersed catalyst BCP-287 is just beginning. Preliminary results indicate much higher rates of tetralin dehydrogenation and benzothiophene HDS than were seen with the liquefaction residue.

CONCLUSIONS Model compound reactions have been used to investigate the catalytic activity of a coal liquefaction residue. The poor dehydrogenation effectiveness of the residue makes it a poor candidate for a hydrogenation catalyst at higher hydrogen pressures. However, in liquefaction experiments at 375°C, this material has been shown to be effective at inducing the uptake of hydrogen gas by coal and the conversion of coal.² On the basis of the above results, this ability must be related to some activity other than aromatic hydrogenation.

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DISCLAIMER Reference to a brand or company name is made to facilitate understanding and does not imply endorsement by the U.S. Department of Energy.

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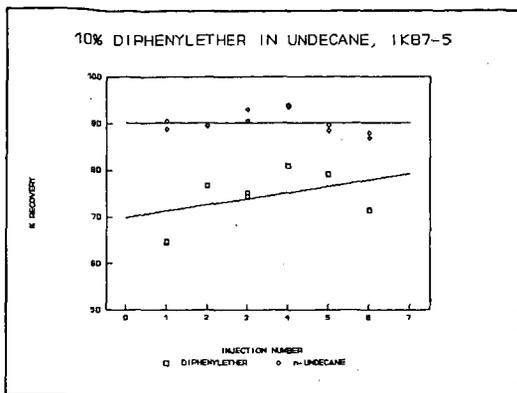


Figure 1. Coal Residue Containing MoS_2 Exhibiting Preferential Adsorption of Diphenylether at 300°C , 100 kPa Hydrogen.

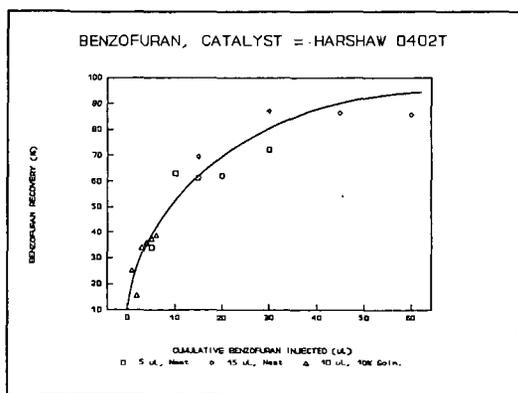


Figure 2. Data Illustrating the Adsorption of Oxygenate by a Supported Catalyst at 300°C , 100 kPa Hydrogen.

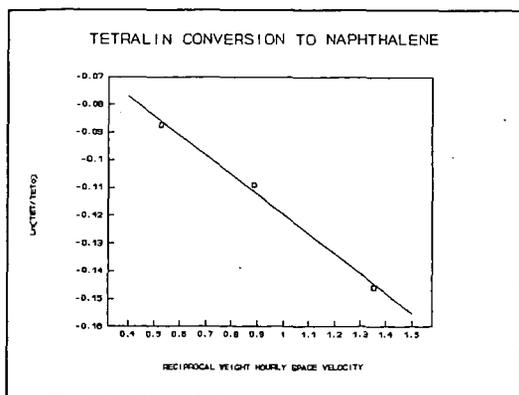


Figure 3. First Order Rate Constant Determination, 400°C , 340 kPa Hydrogen.

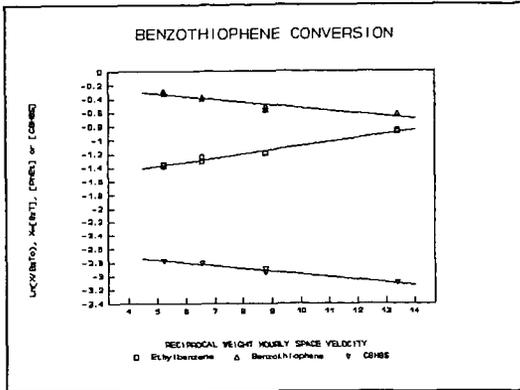


Figure 4. First Order Rate Constant Determination Showing Dihydrobenzothiophene Intermediate Formed at 400°C, 340 kPa Hydrogen.

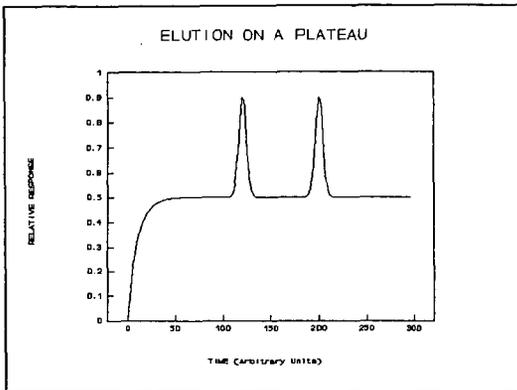


Figure 5. Typical TCD Signal from an Elution on a Plateau Type of Experiment. Units Are Arbitrary.

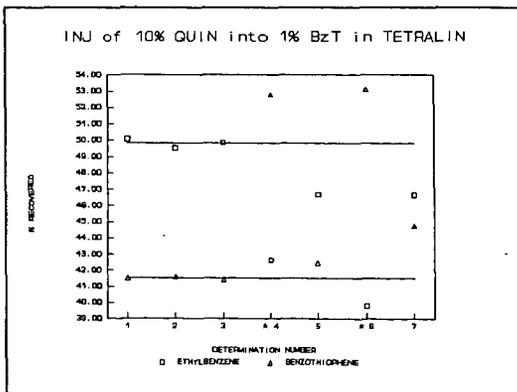


Figure 6. Quinoline Inhibition of the HDS of Benzothiophene, 400°C, 340 kPa. Injection on a Plateau Type Experiment.