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CATALYTIC COAL LIQUEFACTION

Final Technical Report for the Period June 1, 1981—May 31, 1984

By
Sol W. Weller

July 1984

Work Performed Under Contract No. FG22-81PC40781

State University of New York
Buffalo, New York

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I. OBJECTIVES AND SCOPE OF WORK

This research program was established with the following two objectives (tasks):

1. To characterize supported molybdena catalysts, in the sulfide as well as in the oxide form, with respect to total surface area, specific surface area by oxygen chemisorption, and catalytic activity in a standardized test reaction. High area unsupported MoS_2 will be synthesized and used as a reference material, and catalysts regenerated after use in coal liquefaction will also be characterized.
2. To study the effect of preparational variables in the liquefaction of coal with efficient catalysts, with particular emphasis on molybdenum catalysts employed in very small amount. Problems of catalyst recovery and recycle will also be examined.

These tasks were pursued in parallel during the three years of the program. Emphasis in the program was on molybdenum catalysts for coal liquefaction. As is evident from the above statement of objectives, the first task centered on the characterization of conventional supported catalysts, the second on the use of small amounts of efficient molybdenum catalysts prepared in unusual ways. Research on the second task has led to filing of a patent application by DOE on microencapsulated catalysts.

II. TECHNICAL ACCOMPLISHMENTS

A. Task No. 1: Surface Area of Active Components

1. Amocat 1B

An extensive series of measurements has been carried out on Amocat 1B, as representative of molybdena-alumina catalysts useful in coal liquefaction. Total (BET) surface areas and low temperature oxygen chemisorption (LTOC) were measured as a function of reduction, reductive sulfiding, re-oxidation, and sintering in air. The principal results are these:

(a) The reduced-only catalyst has a total surface area consistent with the presence of small crystallites of molybdenum dioxide. Re-oxidation returns the molybdena to a molybdenum trioxide monolayer.

(b) The reductively-sulfided catalyst may also contain small crystallites of molybdenum disulfide, not a monolayer.

(c) Reductive presulfiding decreases the subsequent LTOC value by a factor of 2-3, compared with that of reduced-only Amocat 1B. The extent of this decrease depends on the duration of the hydrogen treatment after sulfiding. A maximum in the LTOC value seems to be reached with 4 hours of hydrogen treatment at 500°C.

(d) Air-sintering of Amocat 1B at 725°C results in a much greater decrease in total surface area than in LTOC value. Our concomitant research on the heat treatment of

II. Technical Accomplishments (continued)

molybdena-alumina pellets indicates that an important macro-redistribution of molybdena in shell catalysts occurs at temperatures around 750°C.

(e) As had been observed in our previous work on oxide catalysts, a dynamic system for LTOC measurements is as suitable for sulfided catalysts as a static, gas-volumetric apparatus. The dynamic system is more convenient for sulfiding in situ, but precautions must be taken to have the presulfiding gas stream bypass the thermal conductivity detector during sulfiding.

2. Unsupported, high surface area molybdenum disulfide

For the quantitative interpretation of LTOC measurements on molybdena-alumina catalysts, it is necessary to have data for the total (BET) surface area and for LTOC of unsupported molybdenum disulfide samples. These serve as "calibration samples" for the measurements on supported catalyst. The ratio of total surface area to LTOC value for unsupported sulfide can be considered as a "conversion factor," by use of which the LTOC value for a supported catalyst can be translated into an "equivalent molybdena area" (EMA). If the pretreatment conditions are standardized, the EMA values give at least relative values for the apparent specific surface areas of the molybdenum phase in different supported catalysts. This is analogous to the use of hydrogen

II. Technical Accomplishments (continued)

chemisorption to characterize the specific surface area of platinum in platinum-alumina catalysts.

Samples of high surface area ($40 \text{ m}^2/\text{g}$) unsupported "molybdenum disulfide" have been prepared by flash decomposition of ammonium thiomolybdate in flowing helium. This procedure gives " MoS_x " with $x = 2.2$ to 2.3 . These samples have been employed for a variety of tests:

(a) Demonstration of the large effect of pretreatment on LTOC.

(b) Temperature-programmed reduction (TPR) in hydrogen, from 20°C to 500°C . These show that sulfur species of different stability are present in the starting sulfide: several H_2S peaks are observed in the TPR spectrum.

(c) Temperature-programmed surface reduction (TPSR), in which hydrogen chemisorbed at 20°C is removed as hydrogen sulfide on programmed heating in flowing helium.

(d) Reduction, followed by exposure to hydrogen sulfide at 20°C and temperature-programmed desorption of hydrogen sulfide in helium.

(e) Activity testing (pulsed microreactor) for the dehydrogenation of cyclohexane and hydrogenation of propylene.

The important results obtained to date with the samples of unsupported sulfide may be summarized as follows:

II. Technical Accomplishments (continued)

(a) The samples of sulfide prepared directly by decomposition in helium have the following characteristics: relatively high total area; no appreciable sintering on being re-heated in helium to 450°C; no appreciable LTOC; no low-temperature activity for olefin hydrogenation.

(b) The ability to chemisorb oxygen and to catalyze olefin hydrogenation is developed when these samples are pretreated in hydrogen. However, severe sintering (loss of total surface area) occurs during this hydrogen pretreatment.

(c) After hydrogen pretreatment to 450°C, the composition of the solid is close to MoS_2 .

(d) The changes in surface area, LTOC, and hydrogenation activity depend on the temperature and time of hydrogen pretreatment.

(e) The ratio of BET surface area to oxygen chemisorption is about $1660 \text{ \AA}^2/\text{O}_2$ molecule chemisorbed for the helium-decomposed sample. The ratio decreases dramatically to $61 \text{ \AA}^2/\text{O}_2$ molecule chemisorbed for a sample hydrogen-treated for one hour at 450°C.

(f) If the reduction is performed with hydrogen sulfide/hydrogen rather than with pure hydrogen, the extent of sintering, the oxygen chemisorption, and the hydrogenation activity are all less than those obtained after reduction in pure hydrogen. This behavior seems to be the result of smaller hydrogen sulfide evolution (and fewer anion vacancies)

II. Technical Accomplishments (continued)

when hydrogen sulfide is present in the reducing gas.

(g) A method has been developed for deducing Langmuir-Hinshelwood kinetic parameters from pulsed microreactor data. Apparently the sites developed by hydrogen treatment, and able to chemisorb oxygen, show a wide spectrum of hydrogenation activity. This variation arises from detailed differences in the catalyst pretreatment.

B. Task No. 2: Coal Liquefaction with Efficient Catalysts

1. Tubing bomb experiments

Possible catalysis of hydrogen transfer from tetralin to coal, in the absence of added hydrogen gas, was studied with a series of impregnated metal salts and two acids, all at 1% loading based on coal. On the basis of production of naphthalene in the liquid products, many metals apparently increased the extent of hydrogen transfer. However, blank runs with tetralin and catalyst, but no coal, showed that only ammonium heptamolybdate (AM) and stannous chloride (SC) have a large incremental effect. Even in the case of AM, the apparent catalysis of hydrogen transfer seems to be an artifact. The reason for this conclusion is the following: Coal itself, when present, acts as a high-area carrier for the impregnated AM, which then acts as a catalyst for the dissociation of tetralin (T) to naphthalene (N) and gaseous hydrogen. Blank runs with AM

II. Technical Accomplishments (continued)

on alumina (no coal) show the same catalytic effect. It follows that hydrogen transfer calculated only from analysis of N in the reaction products can be in gross error.

2. Thermodynamic considerations: tubing bomb vs. autoclave experiments on hydrogen transfer

Significant differences are observed when coal liquefaction and hydrogen transfer from tetralin is studied in tubing bombs or autoclaves, with a good catalyst such as AM. Consideration of thermodynamic equilibrium has permitted an explanation for these differences between tubing bomb and autoclave. In a tubing bomb, the ratio of gas volume to liquid volume (at reaction conditions) is typically rather low. As a result, even when equilibrium is reached in the dissociation of T, the extent of dissociation is relatively small, but the equilibrium partial pressure of hydrogen (resulting from T dissociation) is relatively high. The reverse situation typically exists in autoclave experiments: the gas:liquid volume ratio is relatively high, T dissociation is relatively high, but the equilibrium hydrogen pressure is relatively low. These considerations lead to a prediction that higher coal conversion, at the same conditions, should be observed in tubing bomb than in autoclave experiments. This prediction has been experimentally confirmed.

II. Technical Accomplishments (continued)

3. Fate of ammonium molybdate

X-ray diffraction has been used to identify the fate of ammonium heptamolybdate (AM) in a typical one hour autoclave experiment at 400°C or 450°C. AM calcined in air at 450°C yields crystalline MoO_3 . AM heated in tetralin, under nitrogen, for one hour at 450°C in an autoclave yields only MoO_2 by x-ray analysis. Interestingly, only MoO_2 was observed when the same experiment was repeated in the presence of a stoichiometric amount of powdered sulfur. Experiments with AM in the presence of coal have not shown evidence for crystalline Mo compounds. The only x-ray diffraction pattern observed in our experiments was that of pyrrhotite, derived from pyrite in the coal mineral matter.

4. Microencapsulated liquefaction catalysts

The liquefaction of a bituminous coal has been studied in the presence of AM catalyst added in a novel form: as microcapsules. These can be prepared by in-situ encapsulation of an emulsion of AM in tetralin. Average diameter of a typical preparation of polymeric microcapsules, resulting from reaction between a diisocyanate and a polyfunctional amine, was about 6 micrometers. Autoclave testing of the catalytic effect on liquefaction showed, both in terms of coal conversion and hydrogen

II. Technical Accomplishments (continued)

consumption, that at 450°C the microencapsulated catalyst is at least as good as AM pre-impregnated on the coal from aqueous solution, and far better than powdered AM. Micro-encapsulated catalysts of this kind should offer advantages of convenience in use, stability in storage, and flexibility.

5. Autoclave tests of surfactants and of zeolite supports

Autoclave tests have been performed in which surfactants of various types were added to coal-tetralin mixture before liquefaction. Contrary to a literature report, none of the surfactants tested resulted in any significant improvement in coal liquefaction.

Preliminary experiments have been done to compare the effectiveness, in liquefaction of (a) Mo supported on an acidic, shape-selective zeolite (HZSM-5) with (b) Mo supported on alumina, or (c) Mo impregnated on coal. Early results, which will have to be replicated, suggest that 0.1% Mo on HZSM-5 may be an attractive catalyst: the liquefaction was almost as high as Mo impregnated on coal, H_2 consumption was less, and the ratio of (oil + gas): asphaltene was higher.

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IV. PATENT APPLICATIONS

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