Novel Nanodispersed Coal Liquefaction Catalysts: Molecular Design Via Microemulsion-Based Synthesis

Technical Progress Report
January - March 1991

by

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Date Published, April 1991

Prepared for the United States Department of Energy
Under
Contract No. DE-AC22-90PC90054

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ABSTRACT

The work performed during the second quarter of the first year of this three-year project is briefly described. In Task 1 (Catalyst Preparation), the pH dependence of the aqueous chemistry of molybdenum sulfide, the particle synthesis in microemulsions, and microemulsion phase equilibria and solubilization are discussed. In Tasks 2 and 3 (Catalyst Characterization and Catalyst Testing), the design of the chemisorption equipment to be constructed and the preliminary liquefaction experimental procedures are described.
PROJECT OBJECTIVES

The objective of this project is to pursue the development of highly dispersed and inexpensive catalysts for improved coal solubilization and upgrading of coal liquids. A novel study of the synthesis of liquefaction catalysts of nanometer size will be carried out. It is based on the molecular design of reverse micelles (microemulsions). These surfactant-stabilized, metal-bearing microdrops offer unique opportunities for synthesizing very small particles by providing a cage-like effect that limits particle nucleation, growth and agglomeration. The emphasis will be on iron- and molybdenum-based catalysts, but the techniques to be developed should also be generally applicable. The size of these very small and monodispersed particles will be accurately determined both separately and after in situ and ex situ coal impregnation. The as-prepared nanoparticles as well as the catalyst-impregnated coal or char matrix will be characterized using the following techniques: dynamic light scattering, x-ray diffraction, x-ray photoelectron spectroscopy, scanning and/or transmission electron microscopy, and selective chemisorption. Catalytic activity tests will be conducted under standardized conditions in both hydrogenation and hydrodesulfurization reactions. The effect of particle size of these unsupported catalysts on the product yield and distribution during liquefaction of a bituminous and a subbituminous coal will thus be quantitatively determined.
STATEMENT OF WORK

The following task activities are being carried out under this project.

Task 1: Formulation, Characterization and Synthesis (Catalyst Preparation)

Subtask 1.1: Microemulsion Formulation and Characterization

We shall formulate and characterize suitable microemulsion media wherein the catalyst particles shall be synthesized. Different surface-active agents shall be considered. These shall include ionic and nonionic systems as well as mixtures of surfactants. The use of cosurfactants and additives shall also be investigated. Special emphasis shall be given to the characterization of microemulsions formulated with polynuclear aromatic compounds (model coal liquefaction solvents) as the external nonpolar phase.

The selection of suitable surfactant systems and characterization methods shall be based on well-documented information in the literature. For example, the phase diagrams shall be based on data obtained by accepted titration techniques. At a minimum, we shall use the techniques of steady-state fluorescence spectroscopy, fluorescence lifetime measurements and dynamic light scattering for the determination of microemulsion structural and dynamic properties. Using the fluorescence techniques, the surfactant aggregation numbers and rates of intermicellar exchange shall be
determined. We shall use light scattering techniques to determine the droplet size, polydispersity and intermicellar interactions. In addition, we shall determine the particle size of the nanoparticles produced.

**Subtask 1.2: Catalyst Synthesis**

In this subtask, the focus shall be on the preparation of Fe and Mo sulfide nanosize particles. The particles shall be synthesized in microemulsion media using the following techniques:

(a) mixing two microemulsions containing the metal ion (Fe,Mo) and S anion, respectively;
(b) bubbling H₂S through a microemulsion containing the metal ions;
(c) solubilizing both the metal ion and the sulfur-bearing reactant in a microemulsion and inducing the reaction by thermal decomposition of the sulfur donor.

Incorporation of the catalyst particles into the coal matrix shall be achieved using both *ex situ* and *in situ* techniques. The *ex situ* techniques shall involve the impregnation of the coal matrix with nanoparticles prepared by one of the routes described in Subtask 1.1. If the solvent used as the external phase in the microemulsion synthesis does not have the desired wetting characteristics, experiments shall be conducted using particles resuspended in a suitable solvent. By *in situ* technique is meant catalyst synthesis and incorporation into the coal matrix in a single step. One of the *in situ* methods shall involve impregnation of a coal with a metal-ion/sulfur-
donor-loaded microemulsion, followed by heat treatment to promote metal sulfide formation. Other in situ methods shall be attempted to identify the best technique to obtain a coal matrix incorporating homogeneously distributed nanosize catalyst particles.

Task 2: Catalyst Characterization

A detailed characterization of the catalyst materials produced in Task 1 shall be performed using the following techniques: dynamic light scattering, UV/visible absorption and fluorescence spectroscopies, x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), scanning and/or transmission electron spectroscopy (SEM/TEM), Mössbauer effect spectroscopy (MES), and selective chemisorption.

For particles developed by ex situ techniques, particle size and size distribution shall be determined prior to impregnation into the coal matrix. The change in particle size after introducing the particles into the coal matrix shall be determined. The particle size and particle size distribution after in situ impregnation shall be determined. In order to better assess the characterization technique, a limited number of experiments shall be performed on catalyst particles impregnated onto the char derived from the parent coal.
Task 3: Catalyst Testing

Liquefaction tests shall be carried out in stainless steel tubing bomb reactors under standard conditions: 275-400 °C, 7 MPa H₂ (cold), 30 min. Both a hydrogen-donor solvent (e.g., tetralin) and a non-donor solvent (e.g., naphtalene) shall be used. The solvent/coal ratio shall be 2/1. For each catalyst developed in Task 1, liquefaction tests shall be conducted on one bituminous and one subbituminous coal. The coals chosen (with the concurrence of the DOE Project Manager) shall have a sufficiently extensive liquefaction database to permit a meaningful evaluation of the catalysts developed in Task 1. If requested by the DOE Project Manager, samples (up to 5 grams) of catalyst or catalyst-impregnated coal will be provided for independent testing.

A limited number of gasification experiments on catalyst-impregnated coal shall be performed to provide a measure of the coal/catalyst interface area. In selected cases, the kinetics of hydrodesulfurization of a model compound shall be determined to provide a relative comparison of the effectiveness of the catalysts developed in Task 1 in coal dissolution vs. liquid upgrading.
DESCRIPTION OF TECHNICAL PROGRESS

Task 1: Catalyst Preparation

1.1 Aqueous Chemistry of Molybdenum Sulfide: pH Dependence

Colloidal particles of molybdenum sulfide have been prepared in aqueous solution using the method reported by Haruta et al. (1984). A basic solution containing \((\text{NH}_4)_2\text{MoO}_4\), thioacetamide (TAA) and ammonia solution, is aged for 1 h under nitrogen gas atmosphere at 50-90 °C. Tetrathiomolybdate ions are formed at a pH below 9 and will precipitate as molybdenum trisulfide when the solution is acidified with sulfuric acid (Prasilova and Burclova, 1972). The chemistry pertaining to the formation of \(\text{MoS}_3\) is summarized below:

\[
\begin{align*}
\text{MoO}_4^{2-} + 4\text{S}^{2-} + 4\text{H}_2\text{O} &= \text{MoS}_4^{2-} + 8\text{OH}^- \\
\text{MoS}_4^{2-} + 8\text{OH}^- + 5\text{H}_2\text{SO}_4 &= \text{MoS}_3 + \text{H}_2\text{S} + 8\text{H}_2\text{O} + 5\text{SO}_4^{2-}
\end{align*}
\]

At a pH of 3-11 the following thiomolybdates are formed: \(\text{MoO}_3\text{S}^{2-}\), \(\text{MoO}_2\text{S}_2^{2-}\), \(\text{MOO}_3\text{S}_3^{2-}\) and \(\text{MoS}_4^{2-}\). Yatirajam et al. (1976) have suggested that molybdenum trisulfide precipitation is more complete if all the molybdenum in aqueous solution is in the form of tetrathiomolybdate prior to acidification. Extensive formation of tetrathiomolybdate has been shown to depend on the S/Mo molar ratio and on the solution pH. In the work by Prasilova and Burclova (1972), it was shown that the formation of tetrathiomolybdate is more complete at a pH of 3-9. Thus, to get a more complete precipitation of \(\text{MoS}_3\), one will have to age the solution of
ammonium molybdate and thioacetamide at a pH of 9 or below for 1 h to obtain appreciable amounts of the tetrathiomolybdate ions before acidifying to a pH of 3 or below to precipitate MoS₃. A TEM micrograph of MoS₃ obtained by this method is attached (Figure 1A).

Advantage will be taken of this method in the in situ technique of the liquefaction catalyst preparation. Here, by use of UV/visible spectroscopy, one will be able to track the formation of the tetrathiomolybdate ion because it absorbs at 4700 cm⁻¹. The tetrathiomolybdate ions will be solubilized in the NP-5 cyclohexane microemulsion (see below). Acidified coal will then be impregnated with MoS₄²⁻, which has been solubilized in a microemulsion, followed by heat treatment to promote molybdenum sulfide formation. The solubilization of the tetrathiomolybdate ions has been achieved and experiments are being designed for the in situ technique.

Molybdenum trisulfide has also been prepared by reacting sodium sulfide and ammonium molybdate. The initial solution consists of ammonium molybdate and sodium sulfide at a pH of 12. After aging the solution for about ten minutes, the solution is gradually acidified with sulfuric acid. The solution turns yellow after a few drops of the acid are added and then finally turns wine red. At this stage, the solution is believed to be made up of tetrathiomolybdate ions. Further acidification precipitates MoS₃.

1.2 Particle Synthesis in Microemulsions

The selection of a suitable microemulsion for the preparation of the molybdenum sulfide catalyst is still in progress. Among the
Figure 1. Transmission electron micrographs of molybdenum sulfide particles.
microemulsions tried are the cyclohexane-polyoxyethylene phenyl ethers (the NP series) and the cyclohexane AOT microemulsion system. So far NP-5 and NP-9 have been used in our experiments. For the NP-5 cyclohexane system, the following techniques have been investigated:

(a) Aging solutions of ammonium molybdate, thioacetamide and ammonia solution in the microemulsion for 1 h followed by acidification with sulfuric acid.

(b) Acidifying the NP-5 cyclohexane microemulsion with sulfuric acid, followed by addition of a microemulsion which contains an aged solution of ammonium molybdate, thioacetamide (TAA) and ammonia solution.

Since molybdenum sulfide will precipitate at a pH below 3, an attempt has been made to saturate the microemulsion with enough acid before adding the aged solution of ammonium molybdate and TAA. It has been found that even though the acid dissolves in the microemulsion at room temperature, there is phase separation at temperatures above 50°C. Sulfuric acid has been solubilized in the microemulsion at very low H₂O/surfactant (R) values; the question yet to be answered definitively is whether the pH is low enough at these low R values for molybdenum trisulfide to precipitate.

TEM micrographs of some particles obtained by the above methods are attached (Figure 1B,C). The particles will be characterized to determine the nature of the solid materials obtained in the microemulsion. At this time, it is believed that the particles may contain substantial amounts of elemental sulfur, since the initial orange yellow color of the microemulsion turned yellow after a week.

Molybdenum sulfide has also been prepared in the NP-5 and NP-9 cyclohexane microemulsion system using an aged solution of sodium
sulfide and ammonium molybdate in place of TAA and ammonium molybdate. Here care was taken to age the solution to a wine red color before adding it to an acidified solution of the microemulsion. The color of the resulting solution is brown, believed to be due to particles of MoS3 dispersed in the microemulsion. Figure 1D is a TEM micrograph of molybdenum sulfide particles produced by this method.

1.3 Microemulsion Phase Equilibria and Solubilization

The solubility domains of water and ammonium hydroxide solutions in the NP-5 surfactant system were determined by two methods. In one set of experiments, the surfactant/oil molar ratio was fixed, and the phase behavior of a number of samples with different contents of aqueous phase was observed as a function of temperature. A solution of NP-5 in cyclohexane and the required amounts of water (or ammonium hydroxide solutions) were weighed and sealed in glass ampoules (5 mL, Thomas). After thorough hand-mixing, the ampoules were placed in a thermostatted water chamber. While subjected to slow temperature changes (at a rate of 1 °C/h), the number of phases present at a given temperature in each sample was recorded.

In a separate set of experiments, the phase behavior was determined at 22 °C for samples of variable surfactant and aqueous phase content. In this case, the solubilization limits were determined by inspection of the mixture upon small, sequential additions of aqueous phase to a given surfactant/oil solution. Once permanent turbidity was observed (indicating the onset of phase separation), a few samples were back-titrated with surfactant/oil solution to double-check the transition points.
The solubilization diagram of water and ammonium hydroxide solutions as a function of temperature in cyclohexane containing 5.83 wt% NP-5 (ca. 0.1 M) is shown in Figure 2. The region between the solubilization and solubility curves is a homogeneous transparent phase where water-swollen NP-5 reverse micelles are dispersed in the continuous cyclohexane phase.

As seen in Figure 2, upon replacement of water by ammonium hydroxide solutions, the solubilization curve is shifted to lower temperatures. Such an effect is stronger for concentrated ammonium hydroxide. For both concentrated and dilute ammonium hydroxide solutions, only the solubilization curve (i.e., upper temperature limit) was observed for a 5.83 wt% NP-5 solution. These samples remained clear upon cooling to about 5 °C, where cyclohexane freezes.

The effect of ammonium hydroxide on the phase equilibria may be interpreted as the result of the competition between hydroxyl ions and the oxyethylene groups of the surfactant for interaction with water molecules, i.e., ammonium hydroxide is acting as a lyotropic salt reducing the mutual solubility between water and the surfactant (Firman et al., 1985). Similar results were obtained by Kon-no and Kitahara (1970), who studied the effects of sodium hydroxide and salt additions in NP-8/tetrachloroethylene microemulsions.

1.4 Instrumentation

A dynamic light scattering instrument, which was ordered from Malvern Instruments (Photon correlation spectroscopy system 4700PS/MW), has arrived and is being set up. The main components of the
Figure 2. Ternary phase diagram for the NP-5/cyclohexane/H₂O-NH₄OH systems at 22 °C.
system are: (a) variable angle spectrometer goniometer, (b) multi-bit correlator, (c) dedicated computer, (d) operating and size analyzing software, (e) a laser light source, and (f) a laser table. A refrigerated heat exchanger capable of removing 13 kW of heat is needed before the set-up could be completed.

**Task 2: Catalyst Characterization**

As shown in the Project Work Plan, the experimental work on this task is to begin in the third quarter of this year. We are in the process of critically assessing the most appropriate catalyst characterization techniques. We have designed the selective chemisorption addition to an existing adsorption apparatus. The schematic representation of the apparatus is shown in Figure 3. For the chemisorption studies to be performed under the present contract, the pulse technique will be used (Anon., 1990). The experiments will be carried out at atmospheric pressure and ambient temperature in a flow system. The coal/catalyst sample (0.1-1.0 g) is placed in a small diameter cell. After appropriate treatment to provide a clean catalyst surface, the sample is subjected to a flow of inert gas (e.g., argon). A pulse of chemisorbed gas is injected (via the gas injection valve) into this carrier gas before it flows over the catalyst. The composition of the stream exiting the sample cell is monitored quantitatively either by a thermal conductivity detector or a quadrupole mass spectrometer, and this signal is compared to that produced by the injected pulse of chemisorbing gas flowing through the cell in the absence of the sample. With each pulse, the size of the detector signal increases until it becomes constant and equal to
Figure 3. Schematic Representation of the Pulse Chemisorption Apparatus.
the blank cell pulse signal. If the amount of chemisorbing gas in the injected pulse is known, the uptake by the catalyst can be calculated.

The advantage of this technique over the more conventional volumetric methods lies in its easier standardization, because there are fewer parameters to set. Furthermore, for microporous materials such as coals, the establishment of equilibrium in a low-pressure volumetric apparatus may take a very long time.

Task 3: Catalyst Testing

As shown in the Project Work Plan, the experimental work on this task is to begin in the third quarter of this year. In the current quarter, we have initiated the preliminary liquefaction experiments using conventional catalyst preparation techniques. One such experiment is described below.

The sample of coal used was a Wyodak subbituminous B coal (PSOC 1401). Table 1 is a summary of its properties. The coal was ground to -80 mesh particle size. The catalyst precursor used was ammonium heptamolybdate (AHM). The catalyst preparation was designed to take advantage of the chemistry of the coal surface (Solar et al., 1990). The necessary amount of Mo precursor for preparing 1 wt% Mo-catalyst (0.14 g) was dissolved in deionized water. The pH of this solution was then adjusted to 2.5 (using litmus paper) under constant stirring. Ten grams of coal were added to this solution of AHM and the mixture was stirred overnight at 60 °C. After this process of catalyst impregnation, the mixture was dried under vacuum at room temperature for 48 hours.

The liquefaction procedure was similar to that used previously at Penn State (Derbyshire et al., 1986; Davis et al., 1991). Catalyst-impregnated
Table 1 Composition and Characteristics of Coal

<table>
<thead>
<tr>
<th>Penn State Sample Number</th>
<th>PSOC - 1401</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seam</td>
<td>Lower Wyodak</td>
</tr>
<tr>
<td>State</td>
<td>Wyoming</td>
</tr>
<tr>
<td>ASTM Rank</td>
<td>subB</td>
</tr>
<tr>
<td>Mean - Maximum Reflectance of Vitrinite ( % )</td>
<td>0.42</td>
</tr>
</tbody>
</table>

**Ultimate Analysis ( % daf )**

<table>
<thead>
<tr>
<th>Element</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>72.23</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.59</td>
</tr>
<tr>
<td>Oxygen ( by difference )</td>
<td>21.83</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.06</td>
</tr>
<tr>
<td>Total Sulphur</td>
<td>0.29</td>
</tr>
</tbody>
</table>

**Proximate Analysis ( a.r.% )**

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>16.33</td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>37.74</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>41.14</td>
</tr>
<tr>
<td>Ash</td>
<td>4.79</td>
</tr>
</tbody>
</table>

**Petrographic Composition ( vol %, mineral - free )**

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitrinite</td>
<td>85</td>
</tr>
<tr>
<td>Liptinite</td>
<td>2.0</td>
</tr>
<tr>
<td>Inertinite</td>
<td>13.0</td>
</tr>
</tbody>
</table>
coal (2.5 g), tetralin (5 g) and carbon disulfide (0.12 g) were charged into a 25 cc tubing bomb reactor. The reactor was sealed and pressurized with hydrogen. It was purged with hydrogen three times and finally pressurized to 1000 psig. It was then immersed into a preheated fluidized sand bath at 350 °C, and agitated vertically at a rate of 200 cycles/min and an amplitude of 2.5 cm. The reaction temperature was maintained at 350 °C. After 30 min the reactor was removed from the unit and quenched in cold water. The gases formed during the reaction were collected into an evacuated glass bulb system and thus stored for GC analysis. The tubing bomb was vented, opened and rinsed with hexane into a weighed ceramic thimble. The residue filtered into the thimble was extracted with hexane in a Soxhlet extractor assembly for 12 to 18 hours, till the solvent falling back into the flask was absolutely colorless. The hexane was removed in a rotary vacuum evaporator and the product left behind (referred to as oils) was stored in a vial. The thimble with the residue was subsequently extracted with toluene and then with tetrahydrofuran (THF) in a similar fashion. The toluene-solubles are referred to as asphaltenes and the THF-solubles are referred to as preasphaltenes. These are dried in a vacuum oven and the solids are stored in vials. The samples are all weighed and the product yield is determined.
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