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

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Technical Progress Report

October - December 1990

by

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ABSTRACT

The work performed during the first quarter of the first year of this three-year project is briefly described. A dynamic light scattering system, to be used for the characterization of microemulsion-based catalyst particles, was ordered. The preliminary identification of the phase stability regions of a nonionic microemulsion system of interest in this research was achieved. A suitable method for the preparation of molybdenum sulfide catalysts was identified.

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

In addition to the preparation of the Project Work Plan (in progress), the following are the task activities of 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 H_2S 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., naphthalene) 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

This reporting period emphasized Task 1, as indicated in the Project Work Plan. A major effort was put into organizing the laboratory facilities required to initiate this task.

Task 1: Catalyst Preparation

A dynamic light scattering system was ordered from Malvern Instruments (Photon Correlation Spectroscopy System, 4700PS/MW). This system will be used in the measurement of both static (time-averaged) and dynamic (time-dependent) light scattering intensities. These measurements will then be computer-processed to obtain particle size characteristics of the microemulsion droplets as well as the synthesized particles. The main components of the system are: (a) variable-angle spectrometer goniometer, (b) multi-bit correlator, (c) dedicated computer, (d) operating and size-analysis software, (e) laser light source and laser table.

Since it is generally believed that molybdenum sulfide is the active catalytic species in molybdenum-catalyzed coal liquefaction, it was decided to choose this material as the model catalyst in our preliminary experiments. (In subsequent work, iron sulfide will also be used.) Considerable effort was expended in identifying a suitable microemulsion formulation which would be compatible with the molybdenum/sulfur aqueous system. A

nonionic microemulsion system was chosen in order to avoid possible complications due to counterions associated with ionic surfactants. Figure 1 presents a ternary phase diagram for the nonionic microemulsion system that was investigated. It can be seen that the microemulsion region based on pure water as the solubilize is larger than that of ammonia as the solubilize. However, there is a sufficiently large microemulsion domain in the ammoniacal system to permit its exploitation in particle synthesis. It must be noted, nonetheless, that the fact that the presence of electrolyte shifts the microemulsion domains means that an important aspect of this work will have to involve the identification of the phase stability regions of the various microemulsion systems of interest in this research.

Based on a review of the catalyst preparation literature, a suitable preparation method for molybdenum sulfide was identified (Haruta et al., 1984). In this method the starting aqueous phase consists of an ammoniacal ammonium molybdate solution of pH=10. Thioacetamide is added and then the resulting solution is aged at 50-90 °C for about an hour. Hydrazine acetate solution is added and then acidified to a pH of 5.2 with nitric acid. In a modified procedure, the pH is fixed at 4.75 with NaAc-HAc buffer. Figure 2 presents a potential-pH diagram for the Mo-S-H₂O system at 25 °C. It can be seen that in the acidification of a molybdate solution, the reaction path may lead to MoO₂, MoS₂ or MoS₃, depending on oxidation conditions. It is clear from this observation that the effect of oxidation conditions in controlling the nature of the solid precipitate must become an important consideration in the synthesis experiments. It must be noted that the stability diagram presented in Figure 2 does not consider aqueous soluble thiomolybdate species. The solution chemistry of the Mo-S-H₂O system is currently under investigation and it is hoped to modify Figure 2 to incorporate the stability domains of the thio species. In addition, it is planned in future work to extend the stability diagram to higher temperatures (i.e., 50-90 °C), which are more consistent with the synthesis conditions.

Figure 1. Ternary phase diagram for the NP-5 (i.e., polyoxyethylene(5)nonylphenyl ether)/cyclohexane/H₂O-NH₄OH systems at 22 °C.

Figure 2. Eh(potential)-pH diagram for the Mo-S-H₂O system at 25 °C. Total dissolved molybdenum activity, {Mo} = 10⁻³; total dissolved sulfur activity, {S} = 1.0.

The molybdenum sulfide preparation method discussed above is based on precipitation in bulk aqueous solution. In order to adapt this method to nanoparticle synthesis in microemulsions, the microemulsion-plus-trigger and the microemulsion-plus-second-reactant methods (Osseo-Asare and Arriagada, 1990) will be used.

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 and designing the selective chemisorption addition to an existing adsorption apparatus.

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. We are in the process of setting up the laboratory procedures for performing the coal liquefaction tests to be used throughout the project.

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