DOE-PC-90054

30/92

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

Technical Progress Report
July - September 1992

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E. Boakye, M. Vittal, K. Osseo-Asare and L. R. Radovic

Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802

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



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## DISCLAIMER

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## 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.

## INTRODUCTION

In our previous work we reported the effect of the occupancy number (i.e., the number of tetrathiomolybdate ions solubilized per water core) on particle size for the synthesis of molybdenum sulfide in the 0.15 M NP-5/cyclohexane microemulsion (1). In this quarter we report the effect of the water-to-surfactant molar ratio (R) on the particle size of molybdenum sulfide synthesized in the 0.4 M NP-5/tetralin/benzyl alcohol microemulsion system. The concentration of the reactant species, ammonium tetrathiomolybdate and sulfuric acid, was kept constant. From the results of the previous study, it was concluded that careful control of the occupancy numbers is critical in designing the optimum conditions needed to make particles of desired size. Thus it was necessary to extend the previous work to the 0.4 M NP-5/tetralin/benzyl alcohol microemulsion system. As the water content of the microemulsion increases, the surfactant aggregation number (i.e., the number of surfactant molecules in an inverse micelle) increases (2). This corresponds to a decrease in micellar concentration and an increase in the occupancy number. Therefore, the occupancy numbers can be changed by varying the water-to-surfactant molar ratio.

Also reported in this quarter is the characterization of molybdenum sulfide particles extracted from the 0.15 M NP-5/cyclohexane microemulsion system. The following methods were used: (i) X-ray diffraction, (ii) thermal gravimetric analysis (TGA), and (iii) differential thermal analysis (DTA).

Finally, some difficulties encountered in catalyst testing are described and discussed.

## EXPERIMENTAL SECTION

*Materials*. The following chemicals obtained from Aldrich were used as received: the non-ionic surfactant polyoxyethylene(5)nonylphenyl ether (NP-5), ammonium tetrathiomolybdate (99.97%), cyclohexane and 1,2,3,4-tetrahydronaphthalene (tetralin).

*Particle characterization.* Molybdenum sulfide was synthesized in the 0.15 M NP-5/cyclohexane microemulsion for the purpose of characterization. The synthesis protocol consisted of preparing 200 mL of 0.15 M solution of NP-5/cyclohexane and adding 1000 μL of 1.1 M aqueous sulfuric acid. The resulting microemulsion was deoxygenated with a high purity nitrogen gas. Then, 1500 μL of 0.1 M ammonium tetrathiomolybdate was added and molybdenum sulfide precipitated at room temperature according to Equation 1.

$$MoS_4^{2-} + 2H^+ = MoS_3 + H_2S \qquad (1)$$

The X-ray diffraction patterns were recorded on powdered samples, extracted from the microemulsions, using a Rigaku Geigerflex X-ray diffractometer. All patterns were taken employing CuKα radiation with a scan rate of 5 °C per minute. Differential thermal analysis measurements were done with a Dupont differential scanning calorimeter . Alumina was used as a standard. For the gravimetric analysis measurements, a Dupont 910 thermogravimetric analyzer was used.

*Particle synthesis.* The synthesis experiments were conducted at 50 °C. A solution of 0.4 M NP-5/tetralin/benzyl alcohol was first made at room temperature. A number of samples containing a fixed oil-to-surfactant and cosurfactant molar ratio with variable amounts of water were prepared. This was followed by adding 36.2 μL of 1.1 M aqueous sulfuric acid to a 10 mL solution of 0.4 M NP-5/tetralin/benzyl alcohol microemulsion. The acid solubilized microemulsion was deoxygenated by bubbling a high purity nitrogen gas through it. This procedure was followed by adding 36.2 mL of $1.25 \times 10^{-2}$ M ammonium tetrathiomolybdate to the 0.4 M NP-5/tetralin/benzyl alcohol/aqueous sulfuric acid microemulsion. Nitrogen gas was further bubbled while molybdenum sulfide was being precipitated according to Equation 1. The concentrations of the reactant species were as follows: $4 \times 10^{-3}$ M sulfuric acid and $4.5 \times 10^{-5}$ M ammonium tetrathiomolybdate.

## RESULTS AND DISCUSSION

### Task 2: Catalyst Characterization

*Particle Characterization.* A sample of molybdenum sulfide extracted from the NP-5/cyclohexane microemulsion was sent to Galbraith laboratories for quantitative microanalysis. The results gave a molybdenum-to-sulfur molar ratio of 2.7242. Figure 1 presents the integral and differential gravimetric thermograms of molybdenum sulfide particles extracted from the 0.15 M NP-5/cyclohexane microemulsion system. A loss in weight is observed between 200 and 400 °C. This corresponds to the removal of the surfactant polyoxyethylene(5)nonylphenyl ether (NP-5). The results of the differential thermal analysis are summarized in Figure 2. The broad peak at 295 °C is due to the loss of NP-5, in agreement with the differential gravimetric curve in Figure 1. The sharp exothermic peak at 375 °C is due to the formation of hexagonal $MoS_2$ from $MoS_3$ (3). This observation suggests that the initial product formed, when ammonium tetrathiomolybdate reacts with sulfuric acid in the water core of the inverse micelle, is molybdenum trisulfide, and that it is converted to molybdenum disulfide when heated above 375 °C. The exothermic peak at 500 °C is attributed to the transformation $MoS_2$ (hexagonal) -> $MoS_2$ (rhombohedral). Similar observations have been made by other research groups (3-5).

Figure 3 summarizes the X-ray diffraction studies of molybdenum sulfide particles extracted from the NP-5/cyclohexane microemulsion. S1 and S3, respectively, represent X-ray patterns of the particles exposed to 150 and 900 °C; the former is amorphous to X-rays, while the latter is crystalline. The peak at $2\theta$ = 33°, 39°, 53° and 58° for S3 correspond to crystalline molybdenum disulfide. The peaks centered at $2\theta$ = 26.6 may be due to carbon while the peaks at $2\theta$ = 23.3° and 27.3° are attributed to molybdenum oxide.

*Effect of R on particle size.* Figure 4 presents a plot of the average particle diameter versus the water-to-surfactant molar ratio (R) for molybdenum sulfide particles synthesized in the 0.4 M NP-

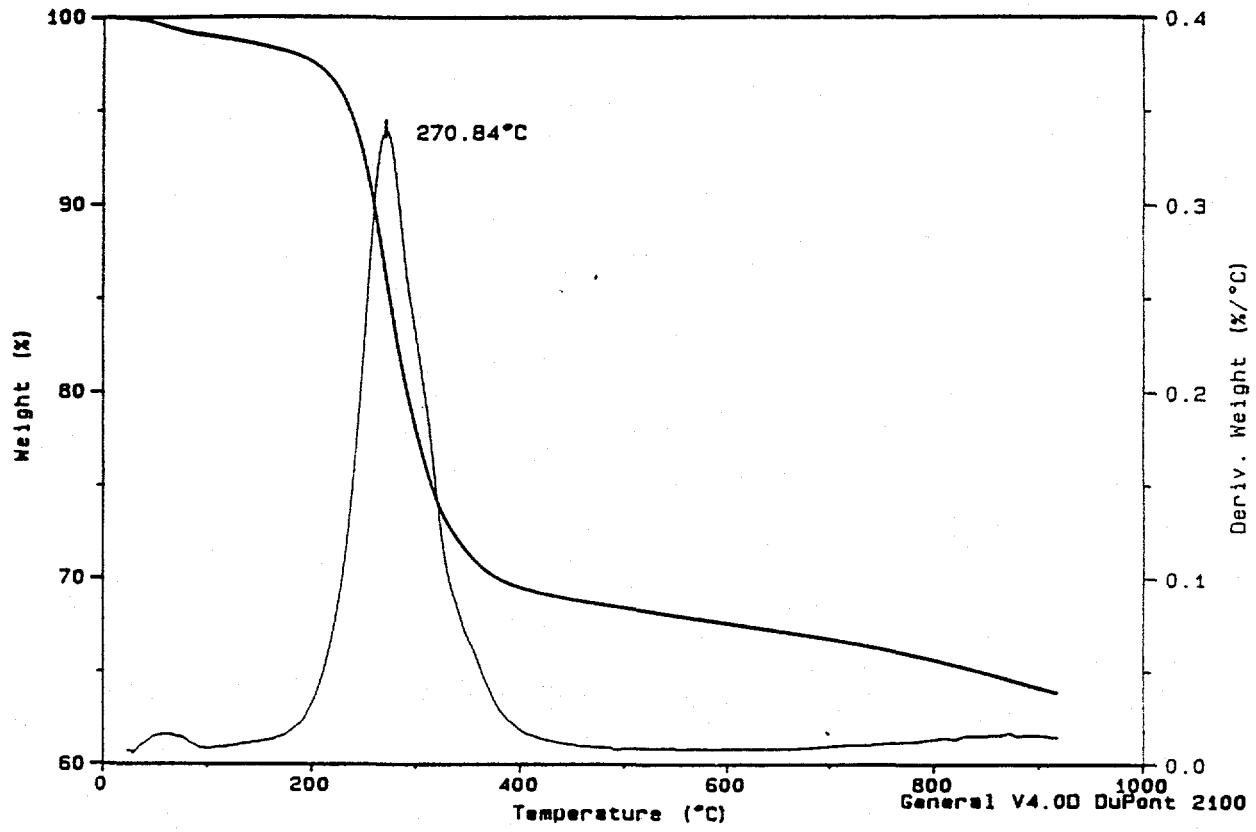


**Figure 1.** TGA curves of molybdenum sulfide particles extracted from the 0.15 M NP-5/cyclohexane microemulsion system.

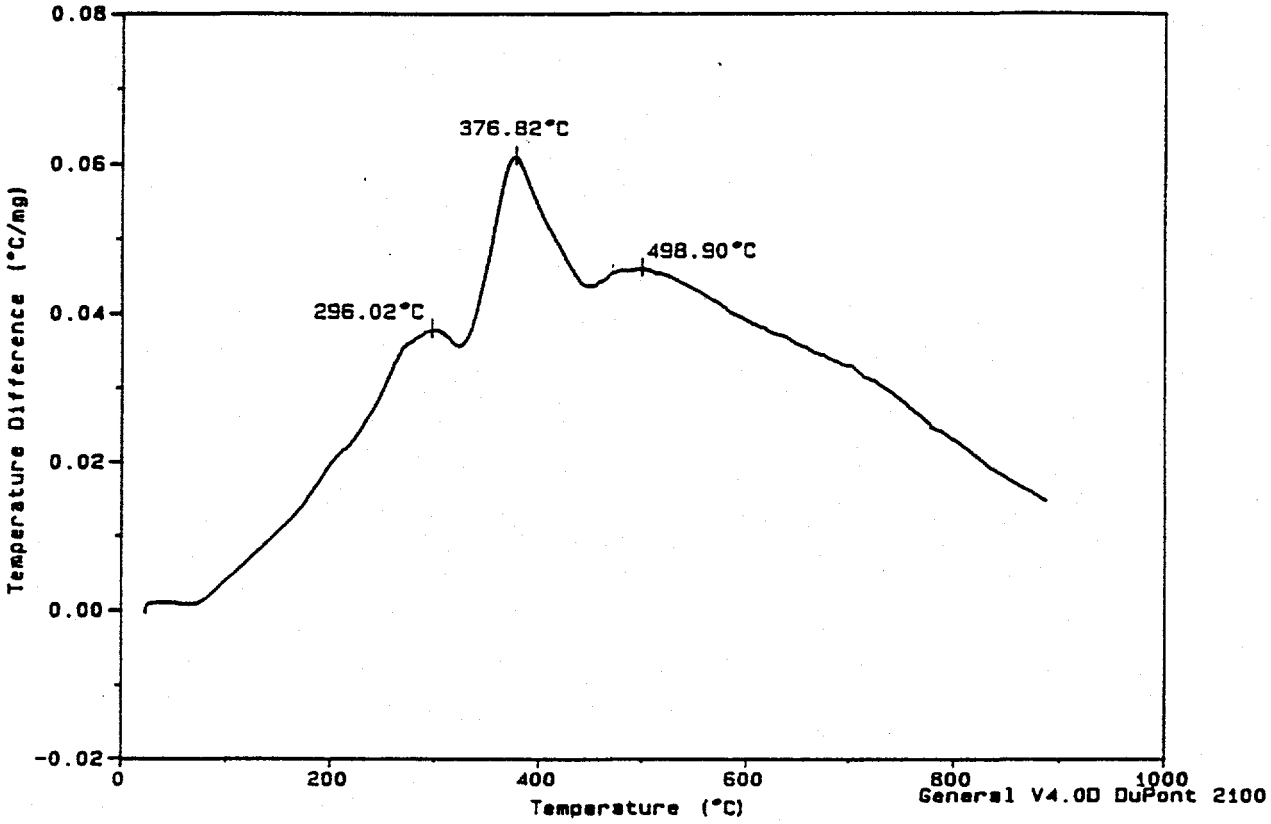


**Figure 2.** DTA curve of molybdenum sulfide particles extracted from the 0.15 M NP-5/cyclohexane microemulsion system.

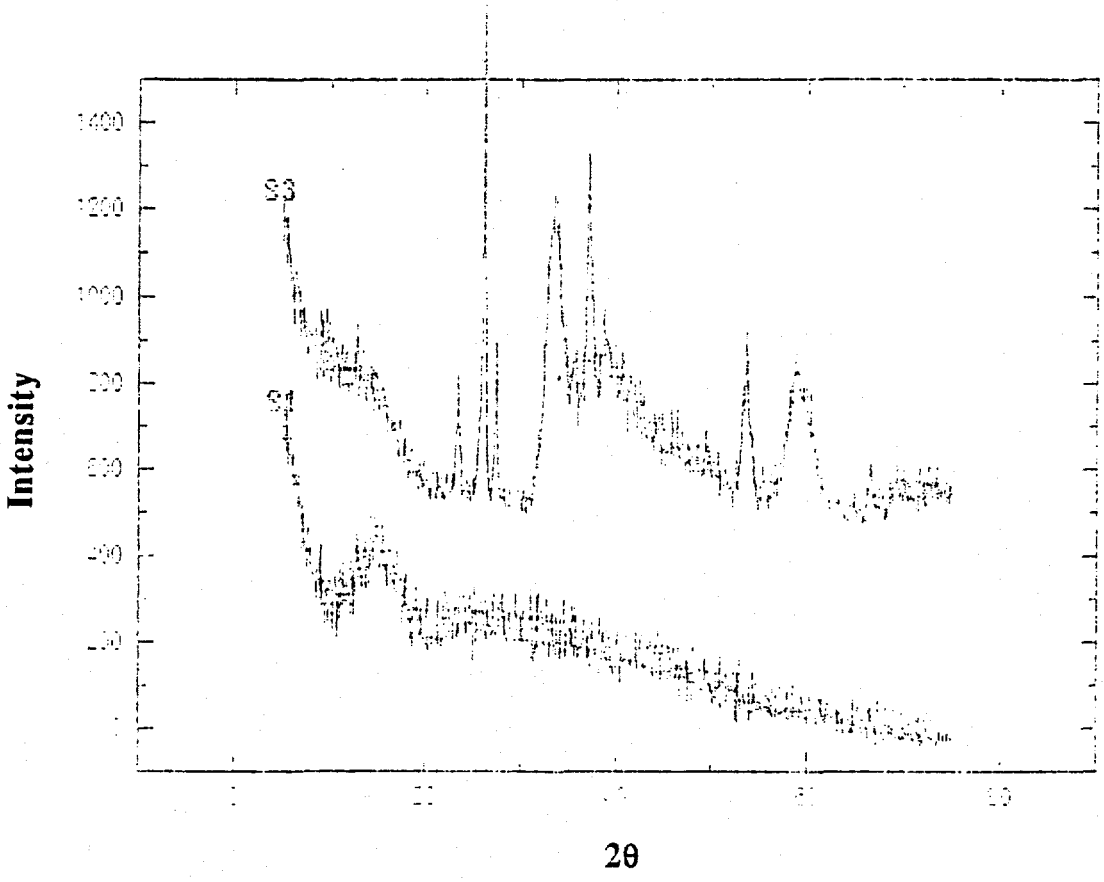


**Figure 3.** X-ray diffraction patterns of molybdenum sulfide particles extracted from the NP-5/cyclohexane microemulsion system. (Samples S1 and S3 were exposed to temperatures of 150 and 900 °C, respectively.)

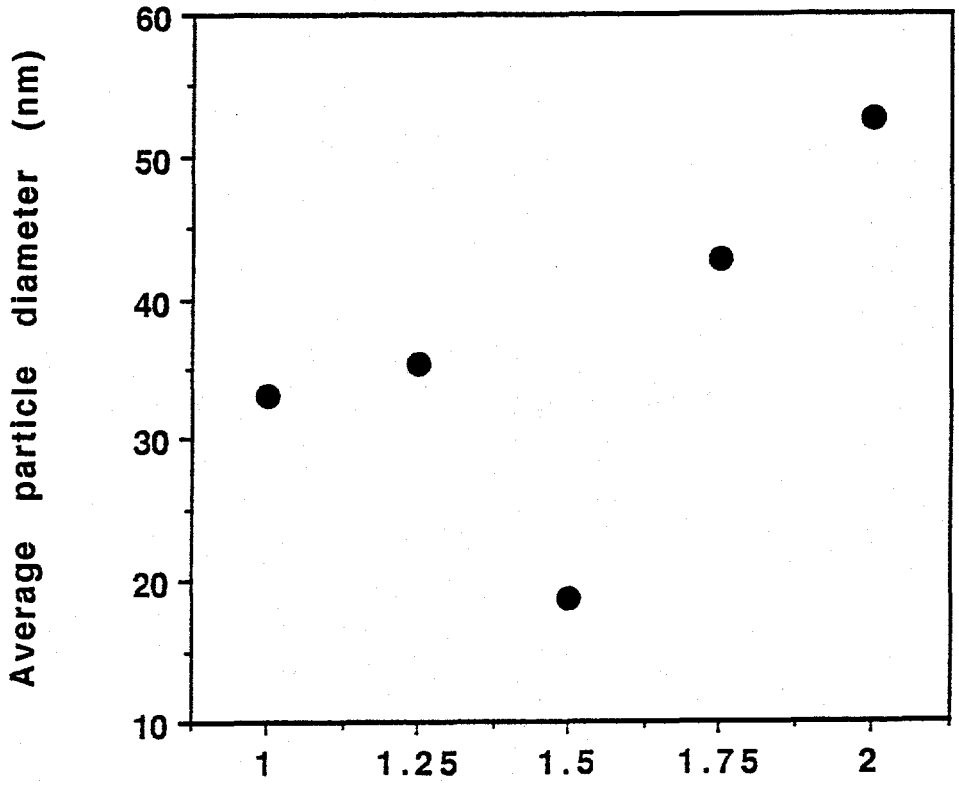


**Figure 4.** Effect of water-to-surfactant molar ratio (R) on the average molybdenum sulfide particle size for the 0.4 M NP-5/tetralin/benzyl alcohol microemulsion system. ($[MoS_4^{2-}]$ = $4.5x10^{-5}$ M; $[H_2SO_4]$ = $4.0x10^{-3}$ M).

5/tetralin/benzyl alcohol microemulsion system. Figures 5 and 6, respectively, present TEM micrographs and the size histograms of molybdenum sulfide particles. The average particle diameter is about the same for R values of 1 and 1.25. The particle size decreases with the water-to-surfactant molar ratio (to R=1.5) and then increases with R. This trend is similar to that observed for the 0.15 M NP-5/cyclohexane microemulsion (6), except that the minimum occurs at a smaller R value (i.e., 1.5, compared to 2.5 for the NP-5/cyclohexane microemulsion system). The trend observed in this report is rationalized by considering the following particle formation and growth mechanism (7-9): (i) ammonium tetrathiomolybdate reacts with aqueous sulfuric acid to form molybdenum trisulfide monomer; (ii) before a stable nucleus is formed, a critical number of molybdenum trisulfide monomers must combine (7); (iii) after a stable nucleus is formed, it can grow by incorporating the molybdate ions in solution to the already formed nuclei (8); (iv) as a consequence of inter-micellar interactions, primary particles and/or nuclei may aggregate to form bigger particles (9). An important parameter in connection with the growth mechanism is the average molybdate occupancy number (i.e., the number of tetrathiomolybdate ions per inverse micelle).

The aggregation number decreases (2) as the water-to-surfactant molar ratio is decreased. For a fixed volume of microemulsion it follows that the number of inverted micelles will increase. Consequently the number of tetrathiomolybdate ions per inverted micelle will decrease. For very low R values, relatively few water cores will contain the minimum number of monomers needed to form a nucleus. As a result, the nucleation rate is slow and the remaining ions not utilized in nuclei formation are incorporated into the already formed primary particles and/or nuclei to form bigger particles.

As R increases the aggregation number increases, the micellar concentration decreases, the occupancy number increases and the nucleation rate increases. The observed decrease in particle size at $R < 1.5$ is due to the increasing occupancy number. At $R > 1.5$ the occupancy number is relatively high and hence smaller-sized particles are expected. Contrary to expectation, larger-sized particles are found. At $R > 1.5$ particle growth via fusion of nuclei or primary particles is more

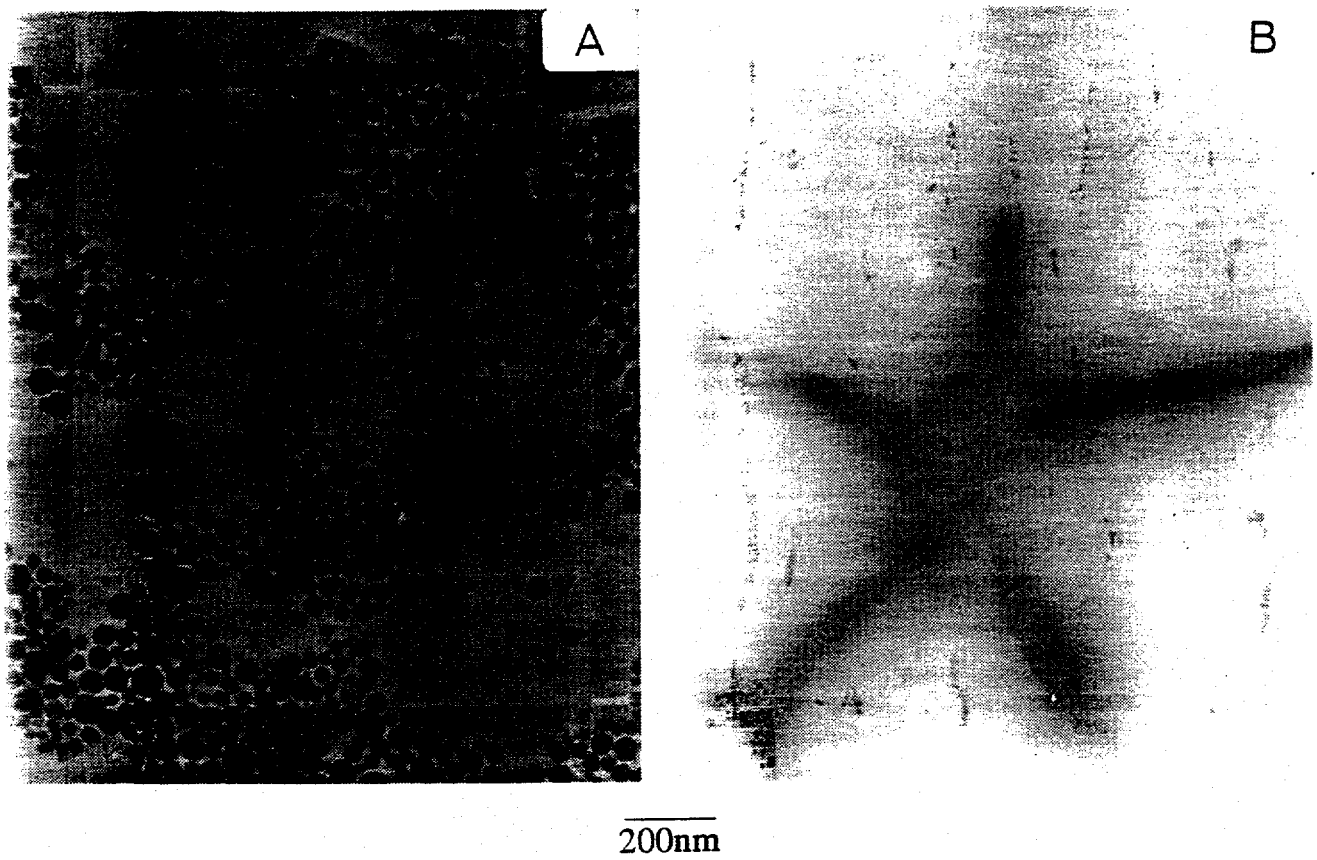


**Figure 5.** TEM micrographs of molybdenum sulfide particles prepared in the 0.4 M NP-5/tetralin/benzyl alcohol microemulsion system: (a) R = 1.25; (b) R = 1.5.

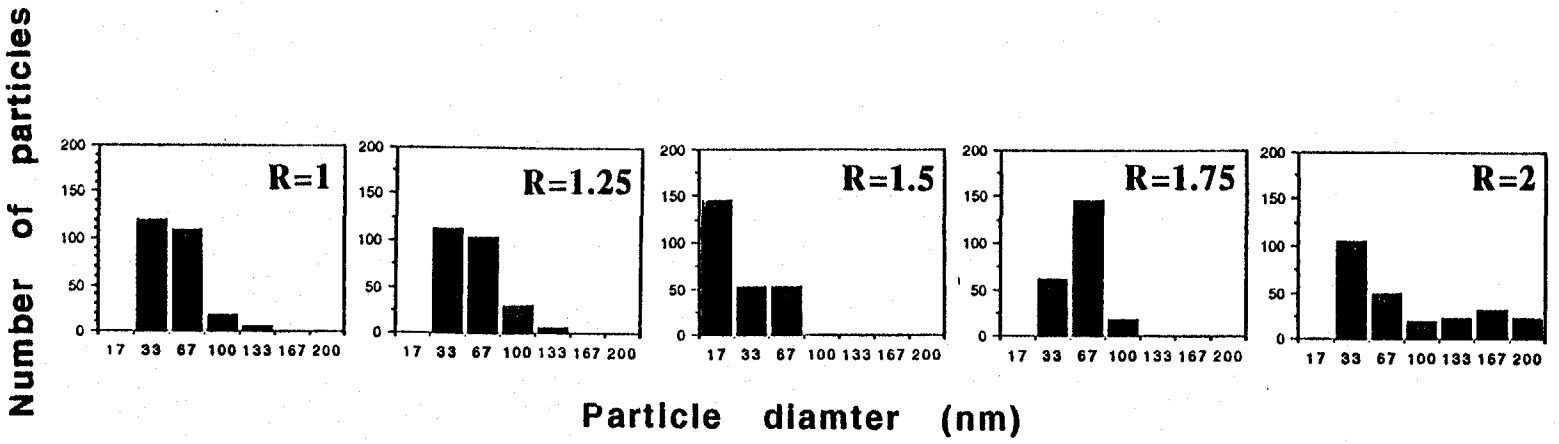


**Figure 6.** Size histograms of molybdenum sulfide particle prepared in the 0.4 M NP-5/tetralin/benzyl alcohol microemulsion system. ($[MoS_4^{2-}] = 4.5 \times 10^{-5}$ M; $[H_2SO_4] = 4.0 \times 10^{-3}$ M).

likely. Similar observations have been made in this laboratory (6) in the synthesis of molybdenum sulfide particles in the NP-5/cyclohexane microemulsion system, where TEM micrographs showed 5-nm sized particles aggregating to form 80-100 nm sized particle. An interesting aspect of the particle aggregation in the NP-5/cyclohexane microemulsion and the NP-5/tetralin/benzyl alcohol microemulsion is that in the latter microemulsion system particle aggregation occurs at R = 1.5, which is smaller than that in the former microemulsion system. (That is, in the NP-5/cyclohexane microemulsion particle aggregation occurs at R = 2). In the NP-5/tetralin/benzyl alcohol microemulsion system, the particles form aggregates at a lower R value because, presumably, benzyl alcohol increases the fluidity of the interface and facilitates the exchange of the contents of the water pools, which favors particle aggregation and growth.

## Task 3: Catalyst Testing

As reported by Derbyshire (10), very little work has been done to characterize the dispersion of catalysts used in coal liquefaction. This is chiefly because of the difficulty in measuring catalyst particle sizes. Invariably, the superiority of one catalyst preparation technique over another must be inferred from liquefaction data. This is totally inadequate for both qualitative and quantitative optimization of liquefaction catalysts. In this respect, a big fundamental advantage offered by microemulsion-based catalysts is that their (initial) particle size is well known (1). Furthermore, the particle size may be controlled by changing certain parameters, e.g., the R value (see Task 2). Thus, it is possible to study the effect on the yield of (i) increasing the catalyst loading while maintaining the particle size constant, and (ii) varying the particle size while keeping the loading constant.

With the purpose of carrying out the first study mentioned above, a microemulsion with R=2 was chosen, since previous work has shown that it contains particles (or aggregates of particles) whose average size is 40 nm. An important question had to be resolved first, prior to performing more detailed liquefaction tests. It is related to our intention to vary the catalyst loading

by adding different amounts of microemulsion into the reactor. Now, the microemulsion has a particular composition, in that the weight ratios of its components are fixed. Therefore, by adding different amounts of microemulsion, the coal-to-tetralin ratio is not held constant, as it should be if its effect is to be distinguished from that of varying the catalyst loading. To see if changes in this ratio have a significant effect on the yield under our reaction conditions, the literature was surveyed first and a set of four preliminary tests, described below, was conducted.

Not surprisingly, it was found that liquefaction yields are indeed affected by the coal-to-solvent ratio. Consequently, it is not straightforward to separate the effect of increasing the amount of tetralin from that of increasing the catalyst loading. A series of "blank runs", the results of which will be discussed in the next quarterly report, is necessary to serve as a baseline for subsequent experiments.

## REFERENCES


1. K. Osseo-Asare, E. Boakye and L.R. Radovic, Quarterly Progress Report to DOE, April-June 1992.
2. A. Kitahara, *J. Phys. Chem.* **69**, 2788 (1965).
3. L. Ratnasamy, L. Rodrique and A.J. Leonard, *J. Phys. Chem.* **77**, 2242 (1978).
4. L. Busetto, A. Iannibello, F. Pincolini and F. Trifiro, *Bull. Soc. Chim. Belg.* **90,** 1233 (1981).
5. P. Ratnasamy and A.J. Leonard, *J. Catal.* **26,** 352 (1972).
6. E. Boakye, L R. Radovic and K. Osseo-Asare, "Microemulsion-Mediated Synthesis of Molybdenum Sulfide Particles," to be submitted (1992).
7. A.E. Nelson, "Kinetics of Precipitation", MacMillan, New York (1964).
8. J.B. Nagy, *Coll. Surf.* **35,** 201 (1989).
9. T.I. Towey, A. Khan-Lodhi and B.H. Robinson, *J. Chem. Soc. Faraday Trans.* **86,** 3757 (1990).
10. F.J. Derbyshire, "Catalysis in Coal Liquefaction," IEA CR/08, London, 1988.