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

Technical Progress Report
January - March 1992

by

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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

Our previous work has shown that liquefaction yields are strongly correlated with the particle size of the molybdenum sulfide catalyst (1). In this quarter we report the effect of sulfuric acid concentration on the synthesis of molybdenum sulfide in the 0.15 M NP-5/cyclohexane/water microemulsion system. The results of this study provide additional information on how to manipulate the microemulsion composition to control particle size. This study will be extended to the NP-5/tetralin/benzyl alcohol/water microemulsion system.

EXPERIMENTAL SECTION

The following chemicals were obtained from Aldrich: the non-ionic surfactant polyoxyethylene(5)nonylphenylether(NP-5), ammonium tetrathiomolybdate(99.97%), and cyclohexane(99%). Before use cyclohexane was dried with molecular sieves. The inverse microemulsion 0.15 M NP-5/cyclohexane/sulfuric acid was prepared at room temperature by adding 10-12.4 μL of 0.53-2.3 M sulfuric acid to 10 mL of 0.15 M NP-5/cyclohexane solution. The acid-solubilized microemulsion was deoxygenated by bubbling nitrogen gas through it for 5 min. This procedure was followed by adding 12.8 μL of 5×10^{-3} M ammonium tetrathiomolybdate to the 0.15 M NP-5/cyclohexane/sulfuric acid microemulsion. Nitrogen was further bubbled while the molybdenum sulfide was being precipitated according to the equation:

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

The concentrations of the reactant species with respect to the total microemulsion were as follows: 6.4×10^{-6} M ammonium tetrathiomolybdate and 6.5×10^{-4}, 1.3×10^{-3}, 2.6×10^{-3} M sulfuric acid.

Samples for transmission electron microscopy were prepared by directly dropping a very small amount of molybdenum sulfide dispersion on carbon-coated copper grids and drying at room temperature. Prior to sample extraction, each sample bottle was sonicated for 1 min. Particle sizes were determined with a Philips 420 transmission electron microscope operating at 120 kV with a resolution of about 0.6 nm. The diameters of at least 300 particles were measured for each sample to obtain an average particle diameter and standard deviation.

RESULTS AND DISCUSSION

Figures 1 and 2 respectively present plots of the average particle diameter versus sulfuric acid concentration in the microemulsion for R values of 2 and 3. Figure 3 shows the TEM micrographs of molybdenum sulfide particles in the 0.15 M NP-5/cyclohexane/water microemulsion system. For both Figures 1 and 2, the average particle diameter initially decreases slightly with increase in acid concentration to a value of 1.30×10^{-3} M and then increases. This trend is most probably the result of the combined effects of pH on the extent of formation of molybdenum sulfide as in Equation 1 (2), and of the microemulsion environment on the nucleation and growth of molybdenum sulfide (3,4).

Further interpretations of these trends must await the results of additional experiments currently in progress. However, it is noteworthy that in a study of the effect of sulfuric acid on the formation of molybdenum sulfide, Beckstead and co-workers (2) found that the extent of conversion of tetrathiomolybdate species to molybdenum sulfide depended on the final pH of the solution. The extent of conversion first incresed with pH before passing through a maximum at a pH of 2-3, then declined to a pH of 5.

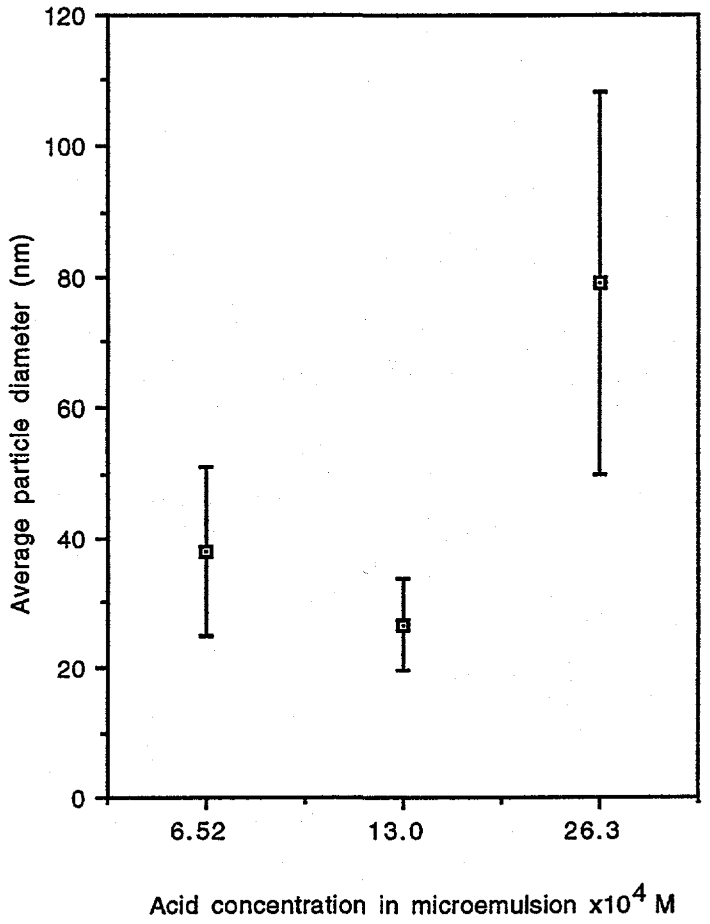

FIGURE 1

Effect of acid concentration on average particle size (R=2)

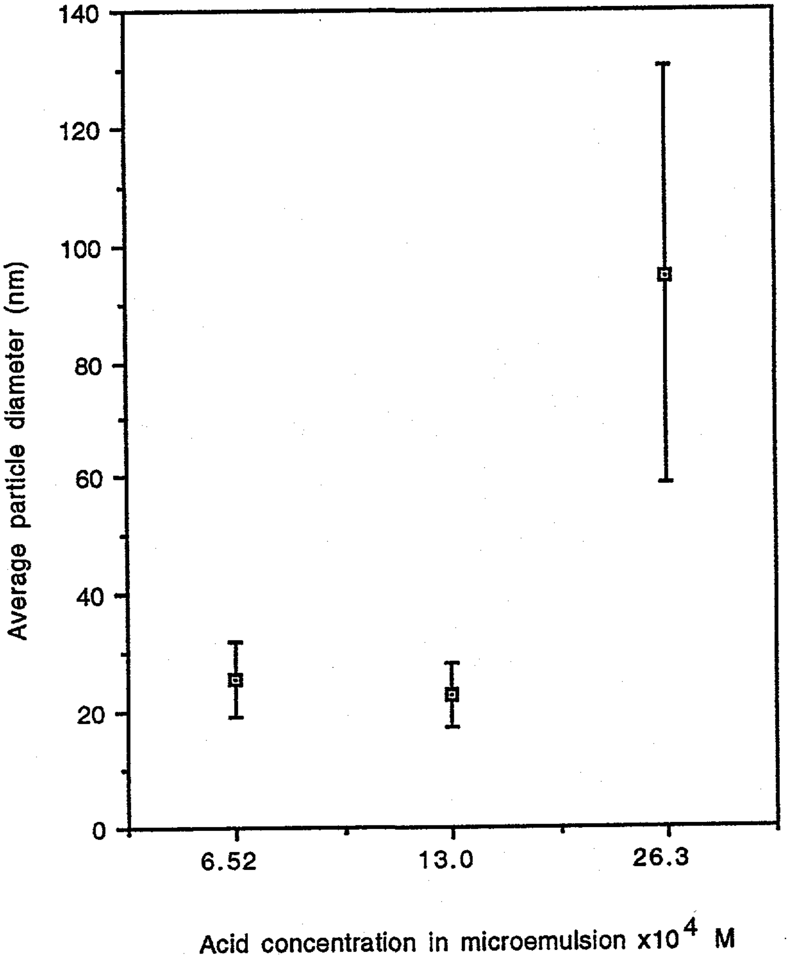

FIGURE 2

Effect of acid concentration on average particle size (R=3)

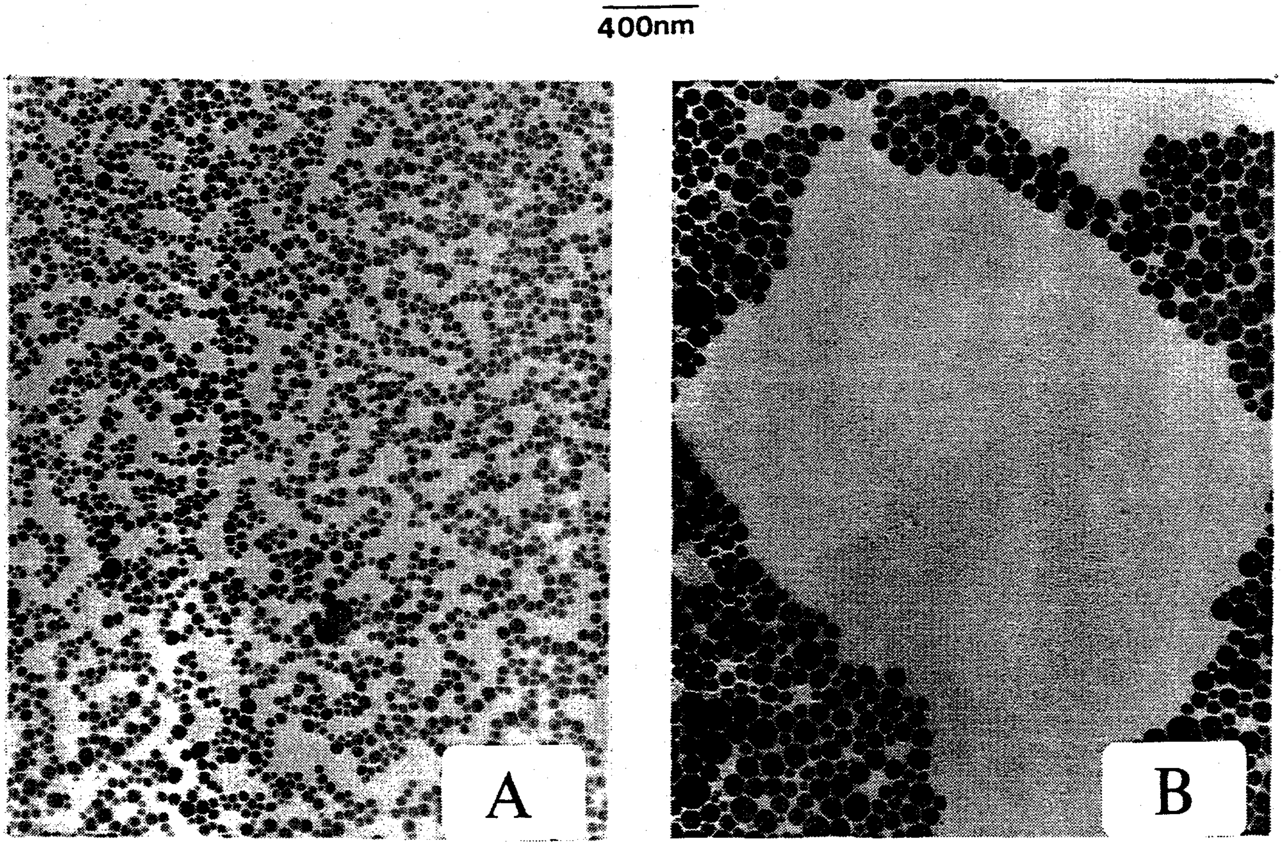

Figure 3. TEM micrographs of molybdenum sulfide in 0.15 M NP5/cyclohexane/water microemulsion: (A) R=2, [H_2SO_4] = 6.52x10^{-4} M; (B) R=3, [H_2SO_4] = 2.63x10^{-3} M.

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