DOE/PC/90054--T11 Q3-3

20|93

DOE-PC-90054

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

Technical Progress Report
April - June 1993

by

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

RECEIVED
USDOE/PETC
95 MAR -8 AM 10:22
ACQUISITION & ASSISTANCE DIV.

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

July 1993

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

Technical Progress Report
April - June 1993

by

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

July 1993

DISCLAIMER

TABLE OF CONTENTS

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 is being carried out. It is based on the molecular design of inverse 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 is on molybdenum- and iron-based catalysts, but the techniques being 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 matrix are characterized using a battery of techniques, including dynamic light scattering, x-ray diffraction and transmission electron microscopy. Catalytic activity tests are conducted under standardized coal liquefaction conditions. The effects of particle size of these unsupported catalysts on the product yield and distribution during conversion of a bituminous and a subbituminous coal are being determined.

EXPERIMENTAL

Materials. The following chemicals were obtained from Aldrich: the non-ionic surfactant polyoxyethylene(5)nonylphenyl ether (NP-5, molecular weight, 440.63), sodium polyphosphate (96%), ammonium tetrathiomolybdate (99.97%), cyclohexane (99%), tetralin (99%), heptane (99%) and methanol (99.9%). Sodium bis (2-ethylhexyl) sulfosuccinate (AOT) was obtained from Sigma. (The molecular weight calculation for sodium polyphosphate was based on the assumption that the polymeric species is made up of six monomers, i.e., hexametaphosphate.) Before use cyclohexane was dried with molecular sieves.

Particle Synthesis. Particles were synthesized in the 0.15 M NP-5/cyclohexane microemulsion as previously reported (1), but in the presence of sodium polyphosphate. The concentrations of the reactant species with respect to the total microemulsion were as follows: 3.2×10^{-6} M ammonium tetrathiomolybdate and 1.3×10^{-3} M sulfuric acid. Particles were also made in water in the presence and absence of sodium polyphosphate. The concentrations of ammonium tetrathiomolybdate and sulfuric acid were maintained constant at 1×10^{-4} and 2×10^{-3} M, respectively.

Particle aggregation in the inverse micelles was reduced by adding sodium polyphosphate. The concentration of polyphosphate with respect to the total microemulsion was 3.2×10^{-6} M. The experiments were done for $R<2$. Phase separation occurred at $R>2$ due to the shift in the solubilization curve toward lower temperatures in the presence of polyphosphate.

Particle Characterization. For particles synthesized in microemulsions, the size was 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 size. For particles made in water, the size was measured by photon correlation spectroscopy.

Microemulsion Characterization. The microemulsion droplet size was determined by photon correlation spectroscopy. The fluctuations in scattered intensity due to Brownian motion of the inverse micelles was measured over small time intervals. In these experiments, the magnitudes of a signal and its delayed version are compared. The measured intensity autocorrelation function $G(\tau)$ is related to the autocorrelation function $g(\tau)$ by the equation

$$G(\tau) = A(1 + B\,|\,g(\tau)\,|^2), \qquad (1)$$

where A and B are instrumental constants. For monodispersed colloidal particles, the autocorrelation function $g(\tau)$ is represented by the equation

$$g(\tau) = \exp(-\Gamma\tau), \qquad (2)$$

where Γ (the decay constant) is related to the diffusion coefficient D of the particle by

$$\Gamma = Dq^2, \qquad (3)$$

and where

$$q = [4\pi n/\lambda]\,\sin(\theta/2). \qquad (4)$$

Here n is the refractive index of the solvent, λ is the wavelength of the incident light and θ is the scattering angle. A least-squares fit permits the determination of B and Γ, from which the diffusion coefficient is obtained. Finally, the diffusion coefficient is related to the micellar diameter via the Stokes-Einstein relation, which assumes that the inverse micelles are spherical in shape:

$$D = kT/6R\pi\eta. \tag{5}$$

Catalyst Testing. Catalyst screening tests are being performed with two coals - a Wyodak subbituminous coal (PSOC 1401) and a Blind Canyon bituminous coal (DECS-6) - both obtained from the Penn State Coal Sample Bank. The coal is ground to -200 mesh and dried under vacuum at 110 °C for 2 h prior to reaction. All tests - unless otherwise indicated - are performed at 350 °C, 1000 psi H_2 (cold) for 30 min (including heat-up time) in 25 cc stainless-steel microautoclave reactors. The reactors are subsequently quenched in water. After depressurizing, the contents of the reactor are washed using THF into tared ceramic thimbles. Overnight extraction with THF is performed in a soxhlet apparatus under N_2 flow. The THF-insoluble residue in the thimble is then washed with acetone and pentane to remove THF, dried in a vacuum oven for over 6 h at 110 °C, and weighed. The THF-soluble portion is further separated into oils and asphaltenes by adding approximately 50 volumes of hexane after removing the THF in a rotary evaporator. Following agitation, the asphaltenes are allowed to settle overnight and are separated from the hexane-solubles by filtration. The asphaltenes are dried in a similar fashion as the residue and weighed. The total conversion is based on the THF-insoluble residue. The yield of oils is calculated by difference. All conversions are reported on a dry, ash-free basis.

RESULTS AND DISCUSSION

Microemulsion Characterization. Summarized in Table 1 are the results of micellar size measurements for the following systems: (a) AOT/heptane/water, (b) AOT/tetralin/water, (c) NP-5/cyclohexane/water and (d) NP-5/tetralin/methanol/water. From the presented data, the following observations are made. The microemulsion droplet size increases as the water-to-surfactant molar ratio (R) is increased. Also, the size of the inverse micelle depends on the nature of oil used. For example, at R=3 the average size of the micelles is 4.6 nm for the AOT/heptane/water system, whereas it is 2.0 nm for the AOT/tetralin/water system. The difference in size may be due to the nature of interaction of tetralin and heptane molecules at the oil/surfactant interface (2). Tetralin may be penetrating the interfacial film to a greater extent, thus diluting the AOT molecules and reducing the number of surfactant aggregates.

The microemulsion droplet size also depends on the ionic strength of the aqueous domain of the microemulsion fluid phase. Figure 1 presents a plot of the average micellar diameter vs. R for the system 0.4 M NP-5/tetralin/methanol. The experiments were done as follows: For various R values, water and 0.034 M ammonium tetrathiomolybdate were solubilized in the microemulsion. The inverse micelle size was then measured for each R value. As shown in Figure 1, the size of the micelles increases as R increases. Furthermore, for the same R value the microemulsion droplet size decreases when ammonium tetrathiomolybdate is solubilized in the microemulsion. For a microemulsion system with a fixed cosurfactant-to-surfactant molar ratio, the effective size of the polar head group decreases (i.e., double layer contraction occurs) as the ionic strength of the aqueous domain of the microemulsion is increased. This causes the interface to become more rigid, reduces the inter-micellar interactions, decreases the agglomeration

Table 1

Summary of Inverse Micelle Diameters (nm) Obtained from Photon Correlation Spectroscopy

R	AOT/ heptane	AOT/ tetralin	NP-5/ cyclohexane	NP-5/tetralin/ methanol
1	3.5	1.6	2.2	1.3
2	-	1.9	2.6	1.7
3	4.6	2.0	2.9	2.4
4	-	2.6	3.3	3.1
5	6.5	2.9	3.7	5.2
6	-	-	4.1	7.3
7	6.9	-	-	16.3
8	-	3.5	5.1	-
9	-	-	5.5	-
10	-	4.3	-	-
11	7.3	-	6.5	-
12	-	4.8	-	-
13	7.9	-	-	-

number (3-5) and reduces the micellar size. On the other hand, the reduction in micellar size may be attributed to complexation or ion/dipole interaction between NH_4^+ and the poly(oxyethylene) chains (6), which reduces the effective concentration of surfactant molecules available for aggregation. This corresponds to a reduction in aggregation number and micellar size.

Particle Synthesis. Figures 2a and 2b present the size distribution of molybdenum sulfide particles prepared in distilled water in the presence and absence of sodium polyphosphate. Table 2 is a summary of the data on particles synthesized in water with various concentrations of the dispersant sodium polyphosphate. (Particle size

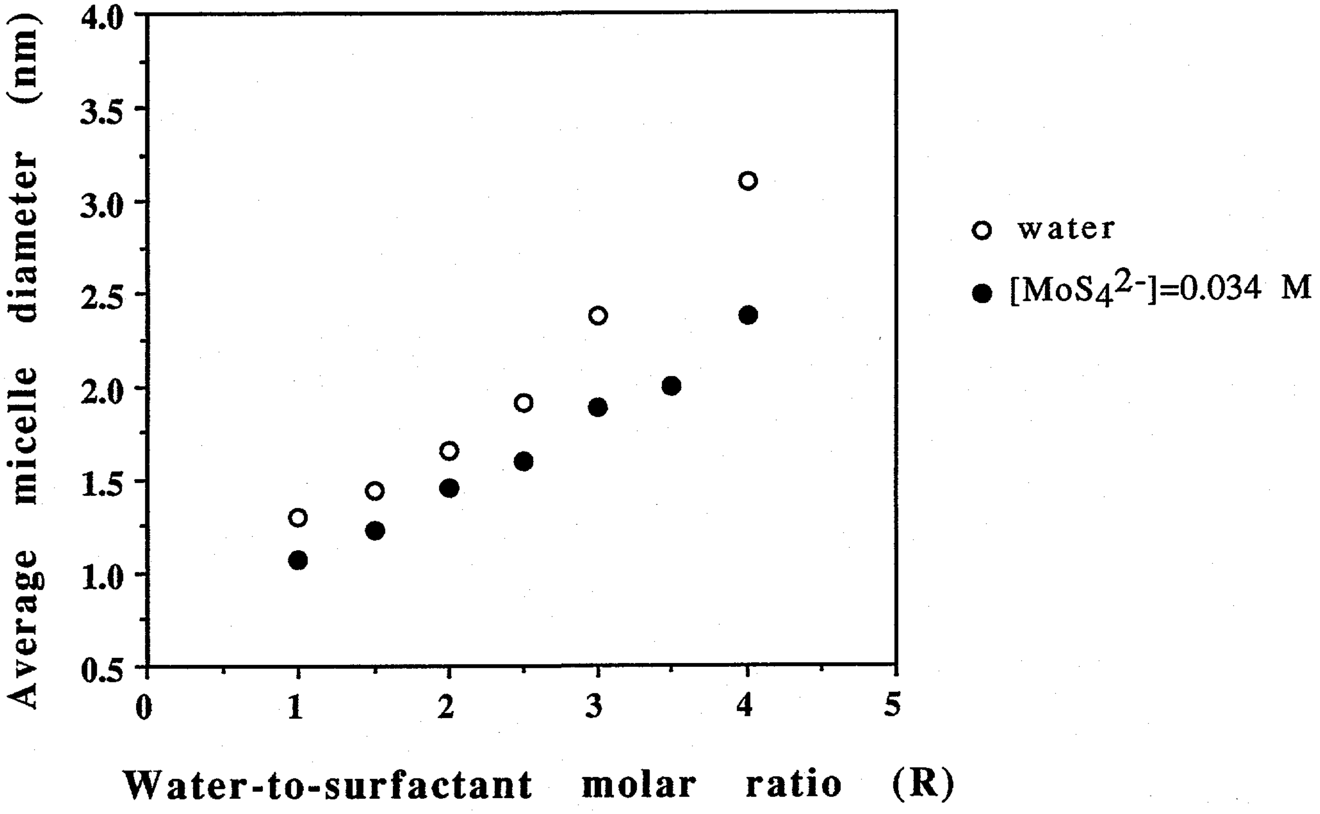

Figure 1. Photon correlation spectroscopic study of the variation of the hydrodynamic diameter with the water-to-surfactant molar ratio (R) for the 0.4 M NP-5/tetralin/methanol microemulsion system.

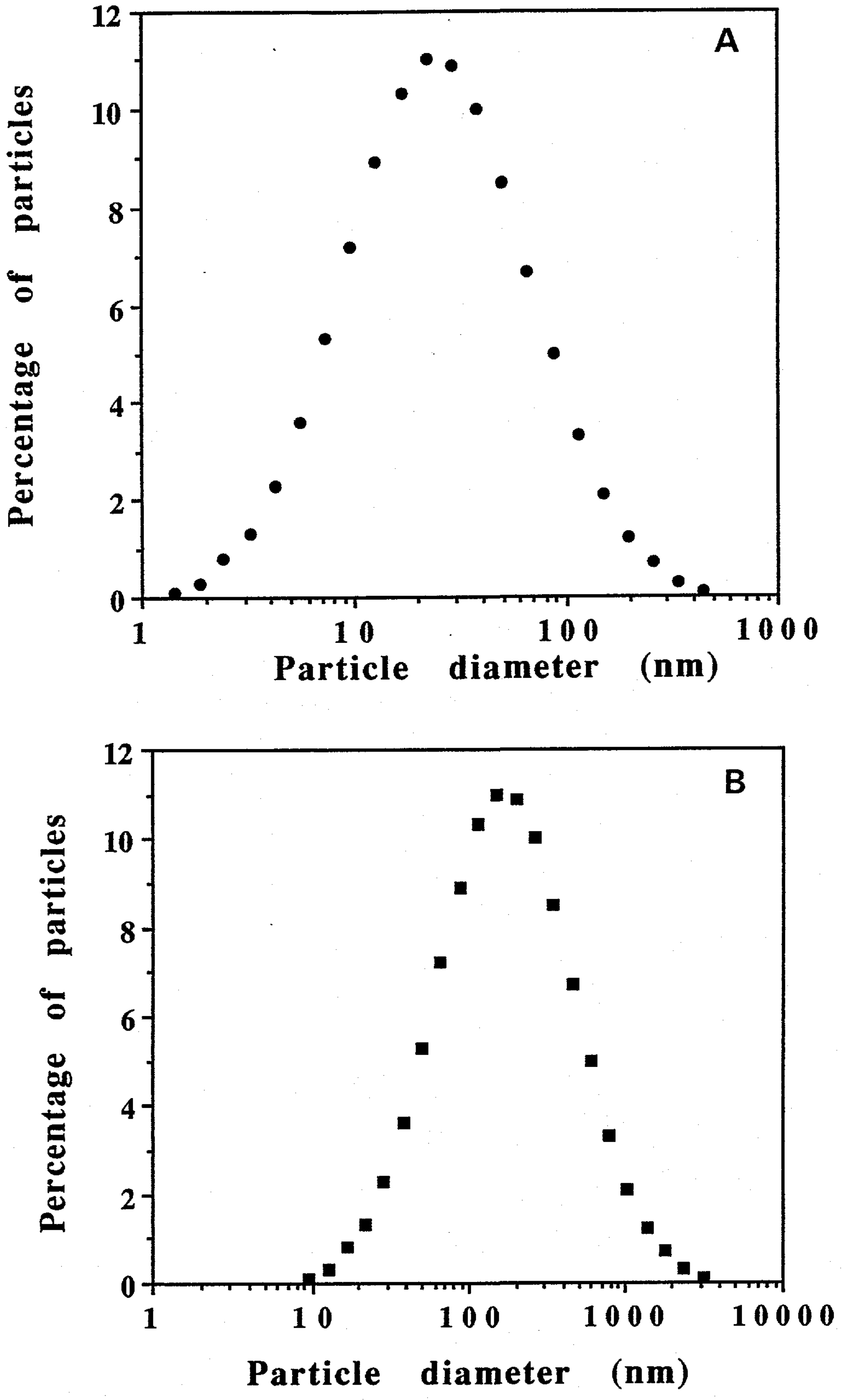

Figure 2. Size distribution of molybdenum sulfide particles synthesized in aqueous solution $[MoS_4^{2-}] = 1x10^{-4}$ M, $[H_2SO_4]=2x10^{-3}$ M: Top, (in the presence of hexametaphoshate) $[HMP]=2x10^{-4}$ M; bottom, in the absence of hexametaphoshate

measurements were done using photon correlation spectroscopy.) TEM pictures show that the particles are spherical in shape. However, the contrast of the TEM pictures was not good enough to allow one to obtain the average particle diameter. From these size distribution diagrams, the following inferences are made: (a) particles made with or without the dispersant are polydispersed; (b) the average particle diameter is relatively small for the particles synthesized in the presence of the dispersant; (c) doubling the concentration of the dispersant reduces the average particle diameter from 75.2 to 24.0 nm.

Table 2

Summary of Results of Particle Synthesis in Water

System	Average particle diameter (nm)
water (no HMP)	166
1×10^{-4} M HMP	75.2
2×10^{-4} M HMP	24.0

HMP = hexametaphosphate

A systematic investigation of the effect of the concentration of sodium polyphosphate and pH on the average particle size is in progress.

To check the possibility of decreasing primary particle aggregation in the microemulsion fluid phase, molybdenum sulfide particles were synthesized in the 0.15 M NP-5/cyclohexane/water microemulsion system in the presence of sodium polyphosphate. This reagent has been reported to decrease particle aggregation (7). In a previous report (1), it was shown that for $[MoS_4^{2-}] = 3.2\times10^{-6}$ M, $[H_2SO_4] = 1.3\times10^{-3}$ M and R=1.5, molybdenum sulfide particles of an average diameter of ~43 nm could be made in the 0.15 M NP-5/cyclohexane/water microemulsion system. Furthermore, since sodium polyphosphate reduces the average particle size of the molybdenum sulfide particles prepared in aqueous medium, the dispersant was solubilized in the inverse micelles with the hope that it will decrease particle aggregation. The results of this experiment are presented in Figures 3a and 3b. As shown in Figure 3a, few particles with an average diameter of ~10 nm were formed. This suggests that particle aggregation was decreased in the presence of the polyphosphate but, apparently, only to a limited extent, as a greater number of larger particles (having an average diameter of 42 nm) was also found on many sections of the TEM grid (see Figure 3b).

Catalyst Testing. Table 3a shows the results obtained with the bituminous coal (DECS-6). Comparing runs #41 and #46, it is evident that, as expected, the presence of tetralin has a marked effect on both fractions of the dissolved coal. When benzyl alcohol is used as a solvent, the total conversion to soluble products increases dramatically. If runs #46 and #36 are compared, for example, the increase is seen to be nearly 30%. However, the hexane-soluble fraction decreases sharply from 15.4 to 2.2%. (It was also observed that the oils produced in runs #41 and #46 were free-flowing and light-colored, relative to those of run #36, which were dark and more viscous.) This seems to indicate that benzyl alcohol is an excellent solvent for the thermally derived coal fragments, but a poor hydrogen donor. Furthermore, if runs #36 and #41 are compared, it can be seen that not even the yield of oils (+gas) obtained under solvent-free conditions was achieved when coal was liquefied in the presence of benzyl alcohol. It appears, therefore, that the dissolution of thermally derived coal fragments precludes their conversion to low-molecular-weight, hydrogen-rich products that are soluble in hexane. Such phenomena have also been observed during investigations of the beneficial effect of phenolic compounds in coal liquefaction (8).

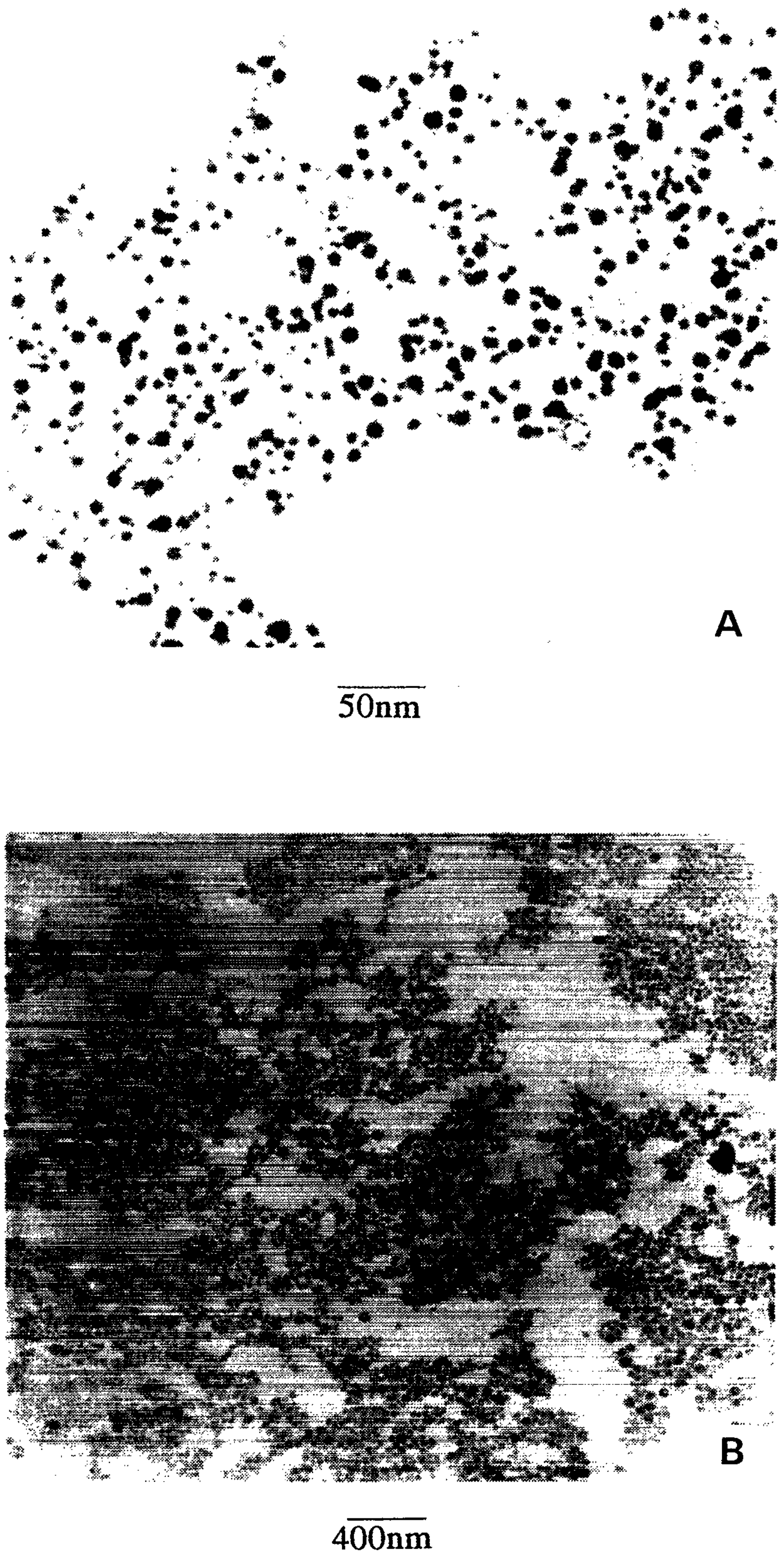

Figure 3. TEM micrographs of molybdenum sulfide particles prepared in the 0.15 M NP-5/cyclohexane/water microemulsion in the presence of hexametaphosphate. $[MoS_4{}^{2-}]=3.2\times10^{-6}$ M; R=1.5

Table 3a

Summary of Data for NonCatalytic (Thermal) Liquefaction Experiments with Bituminous Coal

Number	Experiment	Yield of oils (plus gas) (%)	Yield of asphaltenes (%)	Total conversion (%)	Remarks
41	Coal	11.1	6.1	17.2	No solvent
46	Coal + tetralin	15.4	24.8	40.2	Solvent/coal =2.8
36	Coal + benzyl alcohol	2.2	67.2	69.4	Solvent/coal = 3.2
28	Coal + (blank) benzyl-alcohol-based microemulsion	~0	61.3	61.3	Solvent/coal = 6.8
47	Coal + methanol	-12.3	28.6	16.3	Solvent/coal = 2.7
48	Coal + (blank) methanol-based microemulsion	-4.1	35.5	30.4	Solvent/coal = 2.5
64	coal + surfactant (NP-5)	-38.9	58.8	19.9	Solvent/coal = 1.3

In a recent publication on the liquefaction of a subbituminous coal at 400 °C in the presence of various solvents (9), it was reported that benzyl alcohol can induce extensive crosslinking reactions involving itself and coal, leading to extremely low or even negative conversions. These results differ from ours in that all yields were found to be adversely affected.

Run #28, with the blank benzyl-alcohol-based microemulsion, appears to display a complex interplay between the effects of individual microemulsion components, i.e., surfactant (NP-5), cosurfactant (benzyl alcohol) and nonpolar phase (tetralin), on the liquefaction process. The total conversion is about 20% greater than when tetralin alone is used (#46). This seems to be due to the superior ability of benzyl alcohol to dissolve thermally derived coal fragments, as mentioned earlier. The fact that the oil (+gas) yield was found to be ~0% seems to indicate that the simultaneous presence of tetralin in the reactor had little or no effect on the hydrogenation process. Moreover, the total conversion is also ~8% less than that obtained with benzyl alcohol alone as the solvent (#36). This suggested the possibility that the surfactant could also have a retrogressive effect on the overall process.

With a view to gaining a better understanding of the possible effect of NP-5 (surfactant), it was examined more closely. It is a commercial product, Igepal CO-520, from GAF Chemicals Corp. The percentage of ethylene oxide in the molecule is 50 (10). It is highly viscous, but hexane-soluble. An experiment was conducted using NP-5 as the solvent (run #64). The total conversion is comparable to that obtained under solvent-free conditions (#41), perhaps indicating that NP-5 is neither a good hydrogen donor like tetralin, nor a good solvent for coal molecules like benzyl alcohol. However, the yield of oils (+gas) is -38.9%. Therefore, it appears that the initially hexane-soluble surfactant was transformed into hexane-insoluble substances.

Several phenomena might be responsible for this. Choi et al. (11) have studied the adsorption of surfactants by coals and macerals. They found that surfactants are adsorbed until the available surface area is saturated or the equilibrium concentration of the surfactant reaches the critical micelle concentration. It is possible, therefore, that pore blockage by surfactant molecules may limit access of hydrogen to the coal matrix - especially during the initial stages of reaction, when hydrogen supply is critical. Another factor could be the high chemical functionality of NP-5. It contains large amounts of oxygen; structures containing oxygen functional groups are believed to participate in retrogressive crosslinking reactions (8).

When methanol was used as the solvent (run #47), the total conversion (16.3%) was comparable to that obtained under solvent-free conditions (run #41, 17.2%). This could be due to its poor (or nonexistent) hydrogen-donor capability. When the soluble products were fractionated, there were indications of rather severe retrogressive reactions having occurred. The yield of oils (+gas) was -12.3%, while that of asphaltenes was 28.6%. This suggests that methanol reacted with, and bonded to, the thermally derived coal fragments and wound up amongst the high-molecular-weight hexane-insoluble species.

The run with the blank methanol-based microemulsion (#48) reflects the part played by tetralin in mitigating the above-described retrogressive reactions. The total conversion (30.4%) was between those obtained when methanol (#47, 16.3%) and tetralin (#46, 40.2%) were used (exclusively) as liquefaction media. Possible effects of surfactant (NP-5) were not immediately evident.

Table 3b summarizes the results of catalytic runs for the bituminous coal. (The results of the thermal runs - see Table 3a - are reproduced in parentheses, below the corresponding catalytic runs.)

Table 3b

Summary of Data for Catalytic Liquefaction Experiments with Bituminous Coal

Number	Experiment	Yield of oils (plus gas) (%)	Yield of asphaltenes (%)	Total conversion (%)	Remarks
42	Coal	12.4	8.9	21.3	No solvent;
	(impregnated with ATTM)	(11.1)	(6.1)	(17.2)	loading = 5000 ppm
39	Coal + tetralin	23.2	20.5	43.7	Solvent/coal =2.6;
	(impregnated with ATTM)	(15.4)	(24.8)	(40.2)	loading = 5000 ppm
32	Coal + (metal-loaded)	-5.0	67.0	62.0	Solvent/coal = 7.4;
	benzyl alcohol-based μE	~0	(61.3)	(61.3)	loading = 50 ppm
50	Coal +(metal-loaded)	1.6	44.0	45.6	Solvent/coal = 2.5;
	methanol-based μE	(-4.1)	(35.5)	(30.4)	loading = 100 ppm

μE = microemulsion

When no solvent is present (#42), the effect of catalyst is small and manifests itself as a slight increase in the total conversion. However, in the presence of a H-donor solvent (#39), while the total conversion does not change much relative to the thermal run, a marked improvement in the yield of oils (+gas) is observed. This is consistent with other reports in the literature (12); apparently, when the Mo catalyst is used to liquefy bituminous coals, it participates mainly in the hydrogenation of asphaltenes to oils, and not in the dissolution process itself.

In run #32, the results of using the metal-loaded, benzyl-alcohol-based microemulsions are shown. Surprisingly, they indicate no beneficial effect of the catalyst, as far as the total conversion is concerned. Furthermore, the yield of oils (+gas) is actually slightly negative. Evidently, some of the initially hexane-soluble material was converted to hexane-insoluble products.

In run #50 it is seen that when the metal-loaded, methanol-based microemulsion is used, the total conversion is comparable to that obtained with tetralin alone (#39). There is also ~15% increase in total conversion relative to the corresponding thermal run. The presence of catalyst has also contributed to the rise in the yield of oils (+gas), from a negative value (-4.1%) to a positive one (1.6%). It appears, therefore, that the catalyst is active under the conditions employed. However, the yield of oils is low compared to even the uncatalyzed, solvent-free run (#41).

An additional reason for the observed absence or low level of catalytic activity in the case of benzyl-alcohol- and methanol-based microemulsions may be the low catalyst loading. Also of importance may be the fact that particles synthesized in microemulsion media are coated with surfactant, thereby lowering the accessibility of reactants to their surface. Such a poisoning effect has also been observed by other investigators (13,14) who performed *in situ* catalyst screening tests on metal catalyst particles synthesized in microemulsions. In our future work, we shall thus emphasize more the *ex situ* catalyst preparation techniques.

REFERENCES

1. K. Osseo-Asare, E. Boakye and L. R. Radovic, DOE Technical Progress Report, April-June 1992.
2. J. Lang, A. Jada and A. Mallaris, *J. Phys. Chem.* **92**, 1946 (1988).
3. R. Leung, M. J. Hou and D. O. Shah, in "Surfactants in Chemical/Process Engineering" (D. T. Wasan, M. E. Ginn and D. O. Shah, Eds.), Surfactant Science Series, Vol. 28, Marcel Dekker, New York, 1988.
4. K. Shonoda and B. Lindman, *Langmuir* **3**, 135 (1987).
5. C. H. Chew, L. M. Gan and D. O. Shah, *J. Dispers. Sci. Technol.* **11**, 593 (1990).
6. D. M. Zhu, X. Wu and Z. A. Schelly, *Langmuir* **8**, 1538 (1992).
7. A. Henglein, *Chem. Rev.* **89**, 1861 (1989).
8. D. D. Whitehurst, T. O. Mitchell and M. Farcasiu, "Coal Liquefaction", Academic Press, New York, 1980, p. 274.
9. A. K. Saini, M. M. Coleman, C. Song and H. H. Schobert, *Energy Fuels* 7, 328 (1993).
10. E. W. Flick, in "Industrial Surfactants", Noyes Publications, Park Ridge, NJ, 1988, p. 255.
11. C.-Y. Choi, A. A. Bloomquist, G. R. Dyrkacz, *Energy Fuels* **3**, 38 (1989).
12. C. E. Burgess, L. Artok and H. H. Schobert, *Preprints, Amer. Chem. Soc., Div. Fuel Chem.* **36** (2), 462 (1991).
13. M. Boutonnet, J. Kizling, R. Touroude, G. Maire and P. Stenius, *Appl. Catal.* **20**, 163 (1986).

14. I. Ravet, A. Gourgue, Z. Gabelica, J. B. Nagy, in "Proceedings of the 8th International Congress on Catalysis" (Berlin, FR Germany, 1984), Verlag Chemie, Basel, Switzerland, Vol. 4, 1984, p. 871.