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

Technical Progress Report
October - December 1991

by

K. Osseo-Asare, E. Boakye, N. Vaidyanathan and L. R. Radovic

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

Date Published, April 1992

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

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

PA

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

Technical Progress Report

October - December 1991

by

K. Osseo-Asare, E. Boakye, N. Vaidyanathan and L. R. Radovic

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

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

April 1992

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

TABLE OF CONTENTS

ABSTRACT	iv
PROJECT OBJECTIVES	1
DESCRIPTION OF TECHNICAL PROGRESS	2
PART I: MICROEMULSION-MEDIATED SYNTHESIS OF NANOSIZE	
MOLYBDENUM SULFIDE COAL LIQUEFACTION CATALYSTS	2
REFERENCES (PART I).....	11
PART II: LIQUEFACTION OF A SUBBITUMINOUS COAL IN THE	
PRESENCE OF NOVEL MICROEMULSION-BASED	
MOLYBDENUM CATALYSTS	13
REFERENCES (PART II).....	20

ABSTRACT

A summary of the progress to date is provided, as presented at the recent meeting of the American Chemical Society (Division of Fuel Chemistry, Symposia on Novel Approaches in Coal Liquefaction and Design of Catalysts for Fuel Processing). The first phase of the project has thus been successfully completed. We have shown that nanosize molybdenum sulfide particles can be prepared in microemulsions and that they seem to be quite effective in catalyzing coal liquefaction.

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.

PART I: MICROEMULSION-MEDIATED SYNTHESIS OF NANOSIZE MOLYBDENUM SULFIDE COAL LIQUEFACTION CATALYSTS*

INTRODUCTION

In heterogeneous catalysis, the size of the catalyst is of considerable importance in that the extent of reaction is often inversely proportional to the particle size of the catalyst. As a consequence, various methods have been used to synthesize particles of large specific surface area for catalysis applications (1-3). Most of these methods are based on hydrocolloids (1) and aerosols (2). Recently microemulsion-based synthesis is also attracting attention (3). Haruta et al. (1) prepared molybdenum sulfide particles in the micrometer size range by reacting ammonium molybdate and thioacetamide. Different particle sizes were obtained by varying the pH. In the preparation of iron sulfide catalysts for coal liquefaction, Andres et al. (2) used an aerosol-based method to synthesize iron oxide particles which were used *in situ* with carbon disulfide to liquefy coal. The liquefaction yield was found to be inversely proportional to the particle size. The synthesis of nanosize particles using inverse microemulsions has been reported for a variety of materials (4,5), among which are the hydrogenation catalysts nickel and cobalt borides (3), and platinum-group metals (6,7). Others worth noting are cadmium sulfide (4,8-10), copper, lead, and indium sulfides (9,11), cadmium selenide (12), silica (5), and silver halide (13,14). In this communication a microemulsion-based method for the synthesis of molybdenum sulfide nanosize particles is reported for the first time. This material is currently under active investigation as a potential coal liquefaction catalyst (15).

An inverse microemulsion is a thermodynamically stable, optically isotropic dispersion of microdrops of water in an external oil phase stabilized by a surfactant (16-18). The microemulsion systems used in this study are: polyoxyethylene(5)nonylphenylether (NP-5)/cyclohexane/water and NP-5/tetralin/benzyl alcohol/water. The latter system was used previously in this laboratory as

*presented at the 203rd National Meeting of the American Chemical Society, San Francisco, 1992

a medium for the synthesis of silica nanoparticles (5). In these systems the water molecules interact with the hydrophilic portion of the surfactant molecules via hydrogen bonding to form inverse micelles. The addition of more water molecules results in the formation of swollen inverse micelles, often referred to as inverse microemulsions. The water pools inside the inverse micelles vary in size depending on the water-to-surfactant molar ratio (R) and are in the size range of 3-30 nm (16-18). Due to the cage-like nature of the water pools, particle growth is limited when particle precipitation is effected in them. Advantage has been taken of this unique property of inverse microemulsions to synthesize nanosize molybdenum sulfide particles in the size range 10-150 nm. The large surface area available on these nanoparticles results in a high yield of hexane-soluble oils when coal is liquefied (15).

The chemistry pertaining to the formation of molybdenum sulfide is summarized below:

The following thiomolybdate species are formed when ammonium molybdate is reacted with the sulfide ligand at a pH of 3-11: $\text{MoO}_3\text{S}^{2-}$, $\text{MoO}_2\text{S}_2^{2-}$, MoOS_3^{2-} and MoS_4^{2-} . Extensive formation of the tetrathiomolybdate ion depends on the sulfur-to-molybdenum ratio and on solution pH (19-22). As can be seen from Equation 2, molybdenum sulfide forms when an acid is added to tetrathiomolybdate species.

EXPERIMENTAL SECTION

The following chemicals were obtained from Aldrich: the non-ionic surfactant polyoxyethylene(5)nonylphenylether (NP-5), ammonium tetrathiomolybdate (99.97%), cyclohexane (99%) and 1,2,3,4-tetrahydronaphthalene (tetralin). Before use cyclohexane and tetralin were dried with molecular sieves. The inverse microemulsions NP-5/cyclohexane/water and NP-5/tetralin/benzyl alcohol/water were prepared at room temperature by adding 10% sulfuric acid to a solution of 0.134 M NP-5/cyclohexane and 0.4 M NP-5/tetralin/benzyl alcohol, respectively. The acid-solubilized microemulsion was deoxygenated by bubbling nitrogen gas

through it for 20 min. This procedure was followed by adding 1×10^{-3} M and 1×10^{-2} M ammonium tetrathiomolybdate to the 0.134 M NP-5/cyclohexane and 0.4 M NP-5/tetralin/benzyl alcohol, respectively. Nitrogen was further bubbled while the molybdenum sulfide was being precipitated according to Equation 2. For the NP-5/cyclohexane/water microemulsion the concentration of the reactant species was constant with respect to the total microemulsion. On the other hand, in the case of the NP-5/tetralin/benzyl alcohol/water microemulsion, the concentration of the reactant species was maintained at a constant value with respect to the water pools.

Ultraviolet/visible spectra were obtained with a Hewlett Packard 84151A diode array spectrophotometer. 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

Molybdenum sulfide nanoparticles have been synthesized successfully in the following microemulsion systems: NP-5/cyclohexane/water and NP-5/tetralin/benzyl alcohol/water. Figures 1 and 2, respectively, refer to the ultraviolet/visible absorption spectra of ammonium tetrathiomolybdate and molybdenum sulfide particles in a 0.1 M NP-5/cyclohexane microemulsion system. The microemulsions represented in these two figures contained equal amounts of 1.0×10^{-3} M ammonium tetrathiomolybdate, except that the microemulsion in Figure 2 contained 10% sulfuric acid. These two figures are different in that the absorption peaks for MoS_4^{2-} and $\text{MoO}_2\text{S}_2^{2-}$ (23) are absent in Figure 2 while a peak with an onset wavelength of about 350 nm appears. The disappearance of the peaks for the thiomolybdate species suggests that conversion (i.e., Equations 2 and 3) took place in the inverse microemulsion when the thiomolybdate species found themselves in the same inverse micelle with protons:

Figure 1. Absorption spectrum of 1×10^{-3} M thiomolybdate species in 0.1 M NP-5/cyclohexane/water microemulsion, $R=3$. (The concentration of the thiomolybdate species is with respect to the water pool volume.)

Figure 2. Absorption spectrum of molybdenum sulfide in 0.1 M NP-5/cyclohexane/water microemulsion, $R=6$, $[\text{MoS}_4^{2-}] = 1 \times 10^{-3}$ M. (The concentration of thiomolybdate species is with respect to the water pool volume.)

NP-5/Cyclohexane/Water. Figures 3 and 4, respectively, present TEM micrographs of molybdenum sulfide particles in the 0.134 M NP-5/cyclohexane/water microemulsion system and a plot of water-to-surfactant molar ratio (R) versus the average particle diameter. The average particle diameter decreases with R to a value of 2 and then increases with R. This trend may be rationalized in terms of nucleation and growth phenomena (3,4,14). The process of particle formation from dissolved ions can be represented in the following order: Ions $\rightarrow$ Monomer $\rightarrow$ Nuclei $\rightarrow$ Particles (24). After a stable nucleus is formed, it can grow by the following growth processes: (a) Incorporation of ions and monomers in solution into already formed nuclei (3), and (b) aggregation of primary particles or nuclei to form bigger particles (4,14).

The nucleation and initial growth of particles takes place in the inverse micelles through collision, fusion and splitting of inverse micelles. The nucleation process is slower than the growth process. In order to form a stable nucleus, a cluster containing a critical number of monomers (N_c) must form. A useful parameter in this connection is that of the ion occupancy number, i.e., the number of reactant species in an inverse micelle. A nucleus is formed if the ion occupancy number is greater than N_c . As the water-to-surfactant molar ratio is decreased, the surfactant aggregation number decreases (25,26) and the micellar concentration increases. This corresponds to a decrease in the ion occupancy number because the concentrations of the reactant species (MoS_4^{2-} and H^+) in the microemulsion are constant. For low R values, relatively fewer water cores will therefore contain the minimum number of ions required to form a nucleus. As a result, the ions left over after the nucleation process are relatively large. These ions will be incorporated into the already formed nuclei via inter- and intramicellar communication and will contribute to growth leading to large particles, as demonstrated by the top left side of Figure 4.

As R increases, the aggregation number increases, the micellar concentration decreases, and therefore the ion occupancy number increases. The observed decrease in particle size with increase in R below $R=2$ can be attributed to the increase in ion occupancy number with R. From

Figure 3. TEM micrographs of molybdenum sulfide particles prepared in 0.134 M NP-5/cyclohexane/water microemulsions: (A) $R=1$; (B) $R=1.5$; (C) $R=2$; (D) $R=3$.

Figure 4. Effect of water-to-surfactant molar ratio (R) on average particle size for the 0.134 M NP-5/cyclohexane/water microemulsion. (The concentration of reactant species is constant with respect to the microemulsion.)

Figure 5. TEM micrograph of molybdenum sulfide prepared in 0.4 M NP-5/tetralin/benzyl alcohol microemulsion.

nucleation theory, the greater the number of nuclei in the inverse microemulsion, the smaller the particle size. This is because there will be relatively few ions left over after the nucleation process, i.e., almost all the ions are used up in the nucleation process.

At $R > 2$ the proportion of water in the microemulsion is relatively large, hence the aggregation number is large and the concentration of swollen inverse micelles (water pools) is significantly reduced. As a first approximation, if only one nucleus forms in a water pool then the decrease in the number of water pools corresponds to a decrease in the number of nuclei that transform into primary particles; hence, an increase in the concentration of excess ions which are not utilized in the nuclei formation results. This approximation is justified by the fact that the nucleation process is relatively slow compared to the growth process and that, once a nucleus is formed, it grows by incorporating the excess ions in the microemulsion through inter- and intramicellar communication.

NP-5/Tetralin/Benzyl Alcohol/Water. The microemulsion system consisting of NP-5/tetralin/benzyl alcohol has an inherent advantage for coal liquefaction in that tetralin is an excellent process solvent and hence the need to harvest the particles from the synthetic medium can be avoided. Figures 5 and 6 represent the TEM micrograph and a plot of the average particle size versus the water-to-surfactant molar ratio (R) in the 0.4 M NP-5/tetralin/benzyl alcohol/water microemulsion. The particle size decreases with increasing R to a value of 2, and then increases with R . The trend in Figure 6 can be explained in an analogous manner to that observed in Figure 4. In this system two factors, i.e., the water-to-surfactant molar ratio (R) and reactant concentration, increased the ion occupancy number simultaneously.

CONCLUSIONS

Nanosize molybdenum sulfide particles have been synthesized in 0.134 M NP-5/cyclohexane/water and 0.4 M NP-5/tetralin/benzyl alcohol/water microemulsions. The particle size varies with the water-to-surfactant molar ratio. The synthesis of molybdenum sulfide using

Figure 6. A plot of average particle diameter versus water-to-surfactant molar ratio (R) for the 0.4M NP-5/tetralin/benzyl alcohol microemulsion. The concentration of reactant species is constant with respect to the water pools.

tetralin as a solvent has potentially important technological applications since catalyst preparation does not involve particle harvesting. Advantage can be taken of the variation of particle size with the water-to-surfactant molar ratio (R) to make particles of desired sizes for coal liquefaction. It should be mentioned that liquefaction tests conducted so far have given high yields of hexane-soluble oils and the yield of oils has been found to be inversely proportional to particle size (15).

REFERENCES

1. M. Haruta, J. Lemaitre, F. Delannay and B. Delmon, *J. Coll. Interf. Sci.* **101**, 59 (1984).
2. M. Andres, H. Charcosset, P. Chiche, L. Davignon, G. Djega-Mariadassou, J.P. Joly and S. Pregermain, *Fuel* **62**, 69 (1983).
3. I. Ravet, J.B. Nagy and E.G. Derouane, in "Preparation of Catalysts IV," Elsevier (B. Delmon, P. Grange, P.A. Jacobs and G. Poncelet, Eds.), 1987, p. 505.
4. T.I. Towey, A. Khan-Lodhi and B.H. Robinson, *J. Chem Soc. Faraday Trans.* 3757 (1990).
5. K. Osseo-Asare and F.J. Arriagada, *Coll. Surf.* **50**, 321 (1990).
6. M Boutonnet, J. Kizling and P. Stenius, *Coll. Surf.* **5**, 209 (1982).
7. A. Claerbout and J.B. Nagy, in "Preparation of Catalysts V," Elsevier (G. Poncelet, P.A. Jacobs, P. Grange and B. Delmon, Eds.), 1991, p. 705.
8. S Petit and M.P. Pileni, *J. Phys. Chem.* **98**, 2282 (1988).
9. P. Lianos and J.K. Thomas, *Mater. Sci. Forum* **25-26**, 369 (1988).
10. S. Modes and P. Lianos, *J. Phys Chem.* **93**, 5854 (1989).
11. T. Danhausser, M. O'Neil, K. Johansson, D. Whitten and G. McLendon, *J. Phys. Chem.* **90**, 6074 (1986).

12. M.L. Steingerwald, A.P. Alivisatos, J.M. Gibson, T.D. Harris, R. Kortan, A.J. Muller, A.M. Thayer, T.M. Duncan, D.C. Douglas and L.E. Brus, *J. Am. Chem. Soc.* **110**, 3048 (1988).
13. M. Dvoslaitzky, R. Ober, C. Taupin, R. Anthore, X.C. Aurray, C. Petipas and C. Williams, *J. Dispers. Sci. Technol.* **4**, 29 (1988).
14. M.I. Hou and D.O. Shah, in "Interfacial Phenomena in Biotechnology and Materials Processing" (Y. Atia, Ed.), Elsevier, 1988, p. 443.
15. N. Vaidyanathan, E. Boakye, K. Osseo-Asare and L.R. Radovic, *ACS Preprints, Fuel Chem. Div.* (San Francisco, 1992), in press.
16. J.H. Fendler, *Chem. Rev.* **87**, 877 (1987).
17. B. Lindman, P. Stilbs and M.E. Moseley, *J. Coll. Interf. Sci.* **83**, 569 (1981).
18. S.E. Friberg and P. Bothorel (Eds.), *Microemulsions: Structure and Dynamics*, CRC Press (Boca Raton, FL), 1987.
19. J. Prasilova and J. Burclova, *Radiochem. Radioanal. Lett.* **11**, 351 (1972).
20. V. Yatirajam, U. Ahuja and L.R. Kakkar, *Talanta* **23**, 819 (1975).
21. N.J. Clarke and S.H. Laurie, *J. Inorg. Biochem.* **12**, 37 (1980).
22. M.A. Hammer and A.G. Sykes, *Inorg. Chem.* **19**, 2881 (1980).
23. P.J. Aymonino, A.C. Ranade, E. Diemann and A. Muller, *Z. Anorg. Allgem. Chem.* **371**, 300 (1969).
24. A.E. Nielson, *Kinetics of Precipitation*, MacMillan, New York, 1964.
25. A. Veerbek, E. Gelade and F.C. De Schryver, *Langmuir* **2**, 448 (1986).
26. J.C. Railey and M. Buzier, *J. Coll. Interf. Sci.* **116**, 30 (1987).
27. J.B. Nagy, A. Gourgue and E.G. Derouane, *Stud. Surf. Sci. Catal.* **16**, 93 (1983).

PART II: LIQUEFACTION OF A SUBBITUMINOUS COAL IN THE PRESENCE OF NOVEL MICROEMULSION-BASED MOLYBDENUM CATALYSTS*

INTRODUCTION

The state of knowledge in catalysis of direct coal liquefaction has been reviewed recently by Derbyshire (1988). An efficient catalyst for coal solubilization and/or upgrading of coal liquids not only improves the yield and distribution of products but relaxes some of the stringent demands placed upon the (process-derived) solvent. An inexpensive, disposable catalyst, which does not have to be recycled or recovered, is of particular interest for improved process economics (and thus commercialization potential). Use of "dispersed" catalysts (i.e., catalysts which are "unsupported" or initially supported by the coal prior to its dissolution) has been of increasing interest in recent years (Utz et al., 1989; Cugini et al., 1991; Hirschon and Wilson, 1991; Miki et al., 1991; Bi et al., 1991), particularly for the dissolution stage of coal liquefaction, but also for liquid upgrading purposes. In most studies, the relatively expensive molybdenum-based catalysts have been found to provide greater rate enhancement (at comparable catalyst loadings) than the inexpensive iron-based catalysts. (Both are probably most active in their (at least partially) sulfided form.) Derbyshire (1988) correctly concludes, however, that "there is usually insufficient information available on catalyst dispersion and composition to provide a sound basis for direct comparison" and that "the available information on catalyst dispersion is totally inadequate."

The objective of our work is to use a novel approach to synthesize direct liquefaction catalysts of known particle size (and thus known dispersion). It is based on the molecular design of metal-loaded reverse micelles (microemulsions). In particular, the synthesis and catalytic testing of nanosize molybdenum sulfide particles is of interest. In this regard, the approach taken here differs from the early work at the Dow Chemical Company (Moll and Quarderer, 1979) in which micrometer-size particles were obtained by emulsifying a solution of AHM in a recycle oil. The

*presented at the 203rd National Meeting of the American Chemical Society, San Francisco, 1992

emphasis in this paper, which reports the results of our initial efforts, is on the synthesis and use of molybdenum-based catalyst particles but the techniques being developed should also be generally applicable.

EXPERIMENTAL SECTION

Microemulsion Catalyst Synthesis. Molybdenum sulfide particles were synthesized in three different microemulsion systems: (a) 0.1 M sodium bis (2-ethylhexyl) sulfosuccinate (AOT)/decane/water (b) 0.1 M polyoxyethylene nonylphenyl ether (NP-5)/cyclohexane/water, and (c) 0.4 M NP-5/tetralin/benzyl alcohol/water. The use of an anionic (AOT) and a nonionic (NP-5) surfactant was thus explored. The microemulsions were prepared at room temperature by first adding 10% sulfuric acid to the oil/surfactant solution. The acid-solubilized microemulsion was deoxygenated by bubbling nitrogen through it for 20 min. This procedure was followed by adding 10^{-3} , 10^{-3} and 10^{-2} M ammonium tetrathiomolybdate (ATTM) to the AOT/decane, NP-5/cyclohexane and NP-5/tetralin/benzyl alcohol systems, respectively. Additional information on the microemulsion synthesis procedures are given in a companion publication (Boakye et al., 1992). To investigate the effect of particle size on liquefaction kinetics, the water-to-surfactant molar ratio was varied during microemulsion formulation.

For comparative purposes, molybdenum catalysts were also prepared in a conventional manner, by excess-solution impregnation. The catalyst precursor was ammonium heptamolybdate (AHM). It was dissolved in deionized water, at 1 % (wt) Mo loading. Five grains of coal were added to this solution and stirred overnight at 60 °C. The impregnated coal was dried under vacuum for 48 h at room temperature. In selected experiments, the pH of the solution was adjusted to 2.5 using formic acid.

Coal Liquefaction. Conventional liquefaction experiments were conducted following the procedures used previously at Penn State (Derbyshire et al., 1986; Davis et al., 1991). The coal (2.5 g), tetralin (5 g) and carbon disulfide (0.12 g) were charged into a standard (25 cc) tubing

bomb reactor and agitated for 30 min in a preheated fluidized sand bath. The reaction conditions were: 350 ± 2 °C, 1000 psig H₂ (cold). In the case of microemulsion-based NP-5/cyclohexane catalysts, the microemulsion was added to 2.5 g of coal; no tetralin was used. Tetralin was added to the AOT/decane system. The NP-5/tetralin/benzyl alcohol catalyst system was also simply added to 2.5 g of coal in the tubing bomb reactor. "Blank" microemulsions, without the molybdenum catalyst, were also tested.

After reaction, the tubing bomb was rinsed with hexane into a weighed ceramic thimble. The reaction products were extracted with hexane in a conventional Soxhlet extractor assembly for 12-18 h, until 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 weighed. The thimble with the residue (referred to as residue) was dried and weighed. The reaction yields are thus reported as weight percent oils (hexane solubles) plus gases; gas production at the relatively low temperature of 350 °C was not very significant, however.

RESULTS AND DISCUSSION

A Wyodak subbituminous coal was used in this study. Its properties are summarized in Table 1. Figure 6 shows the plot of the average particle size vs. the water-to-surfactant molar ratio (R) for molybdenum sulfide in the 0.4 NP-5/tetralin/benzyl alcohol microemulsion. It is interesting to note that an optimum R value exists for which a minimum particle size of ca. 40 nm was obtained.

Tables 2 and 3 show the yield of oils (plus gas) in liquefaction tests using the AOT/decane and NP-5/cyclohexane microemulsions. At comparable Mo loadings, the yields are lower for the latter system, possibly due to the absence of a hydrogen donor solvent, whose role is crucial for low-rank coals when an efficient catalyst is not available to meet the relatively high hydrogen demand (Derbyshire and Stansberry, 1987).

Table 4 illustrates the use of NP-5/tetralin microemulsions for R values of 1-4. The oil (plus gas) yield is seen to be remarkably high at low Mo loadings. Furthermore, a comparison with the data in Figure 1, as well as those in Table 3, suggests that there is an optimum water-to-

Table 1
Characteristics of Low-Rank Coal Used in the Liquefaction Experiments

Penn State Sample Bank Number	PSOC 1401
Seam	Lower Wyodak
State	Wyoming
ASTM Rank	Subbituminous B
Mean Maximum Vitrinite Reflectance, %	0.42
Ultimate Analysis, % daf	
Carbon	72.23
Hydrogen	4.59
Nitrogen	1.06
Sulfur (total)	0.29
Oxygen (by difference)	21.83
Proximate Analysis	
Moisture	16.33
Volatile Matter	37.74
Fixed Carbon	41.14
Ash	4.79
Petrographic Composition (% vol, mf)	
Vitrinite	85.0
Liptinite	2.0
Inertinite	13.0

Table 2
Preliminary Results of Liquefaction Tests with the
AOT/Decane Microemulsion Catalyst

Run #	Sample	Mo Loading	Yield of Oils (+Gas), %	% Residue
4	Coal/Mo ME	1.2 ppm	33.8	66.2
8	Coal/Mo ME	2.6 ppm	47.9	52.1

Table 3

Results of Liquefaction Tests with the 0.1 M NP-5/Cyclohexane
Microemulsion (ME) Molybdenum Sulfide Catalyst

Run #	Sample	Mo Loading	Yield of Oils (+Gas), %	% Residue ^a
17	Coal/Mo ME (R=0.5)	1.9 ppm	14.1	85.9
18	Coal/Mo ME (R=1)	2.0 ppm	19.9	80.1
19	Coal/Mo ME (R=2)	2.0 ppm	20.5	79.5
20	Coal/Mo ME (R=3)	1.9 ppm	14.4	85.6
21	Coal/ME ^b	0.0 ppm	4.6	95.4

^a Includes preasphaltenes and asphaltenes

^b Surfactant plus cyclohexane alone

Table 4

Results of Liquefaction Tests Using 0.4 M NP-5/Tetralin/Benzyl Alcohol
Microemulsion (ME) Molybdenum Sulfide Catalyst ^a

Run #	Sample	Mo Loading	Yield of Oils (+Gas), %	% Residue ^b
23	Coal/Mo ME (R=1)	58 ppm	78.4	21.6
24	Coal/Mo ME (R=2)	118 ppm	83.2	16.8
26	Coal/Mo ME (R=3)	185 ppm	9.1	90.9
27	Coal/Mo ME (R=4)	243 ppm	9.9	90.1
29	Coal/ME (R=1)	0.0 ppm	7.3	92.7
30	Coal/ME (R=2)	0.0 ppm	5.2	94.8
31	Coal/ME (R=3)	0.0 ppm	2.9	97.1
32	Coal/ME (R=4)	0.0 ppm	6.2	93.8

^a Coal/tetralin = 1/2.5-2.6

^b Includes preasphaltenes and asphaltenes

surfactant ratio for which the average particle size is at a minimum and the yield of oils at a maximum. (The oils produced are relatively viscous, suggesting that they contain some higher-molecular-weight (hexane-soluble) components.)

Table 5 was compiled in an attempt to place our initial results into proper perspective. For a subbituminous coal, high oil yields were obtained by Weller and Pelipetz (1951), when the catalyst precursor was added to the coal in an acidic medium. This could be due either to the favorable interaction with the coal or to a more effective sulfidation of the catalyst. It should be noted, however, that our attempt to maximize the dispersion of the catalyst at pH=2.5 by favoring the electrostatic interaction between the positively charged coal surface and molybdate anions (Solar et al., 1990) was not successful.

Hirschon and Wilson (1991) have recently reported relatively high yields (~84%) of toluene-solubles (corresponding roughly to the sum of asphaltenes, oils and gases) for an Illinois No. 6 bituminous coal (425 °C, 500 psi H₂, 20 min) using an organometallic Mo complex, with 0.6 mmol Mo/g coal, i.e., 5.8% Mo. The use of an organometallic Fe complex resulted in yields of ~40% (in the absence of a hydrogen donor solvent), with ~3.4% Fe. Also using "dispersed-phase" Mo catalysts (1000 ppm of ATTM, MoS₃, AHM), Utz et al. (1989) obtained yields of ≤60% heptane-solubles for a bituminous coal (425 °C, 1000 psi H₂, 1 h). Similar results were reported more recently for "dispersed-phase" Fe catalysts by Cugini et al. (1991).

Under appropriately selected conditions, the microemulsion-based catalysts are seen to be able to produce comparable yields of oils at much lower Mo loadings.

CONCLUSIONS

Our initial results on the kinetics of coal liquefaction in the presence of microemulsion-mediated molybdenum sulfide particles are very encouraging. Yields of oils which are equal or superior to those obtained using conventional catalyst preparation techniques are achieved at molybdenum loadings that are lower by one order of magnitude. At a more fundamental level, the variation in the water-to-surfactant molar ratio, during the formulation of the microemulsion system, offers the

Table 5
Compilation of Results of Liquefaction Tests on Subbituminous Coals
Using Conventional Catalysts

Author(s)	Coal	Conditions	Catalyst	Yield of Oils (+Gas), %
Weller and Pelipetz (1951)	Subbit. B	450 °C, 1 h 1000 psi H ₂	None	10.4
Weller and Pelipetz (1951)	Subbit. B	450 °C, 1 h 1000 psi H ₂	AHM ^a (1% Mo)	41.1
Weller and Pelipetz (1951)	Subbit. B	450 °C, 1 h 1000 psi H ₂	AHM ^b (1% Mo)	76.5
Epstein (1987) (see Burgess et al., 1991)	Subbit. B	425 °C, 10 min 1000 psi H ₂	None	37.8
Epstein (1987) (see Burgess et al., 1991)	Subbit. B	425 °C, 10 min 1000 psi H ₂	SAM ^c (1% Mo)	24.9
Epstein (1987) (see Burgess et al., 1991)	Subbit. B	Two-stage ^d	None	32.0
Epstein (1987) (see Burgess et al., 1991)	Subbit. B	Two-stage ^d	SAM (1% Mo)	44.0
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	350 °C, 1 h 1000 psi H ₂	None	11.2
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	350 °C, 1 h 1000 psi H ₂	SAM (1% Mo)	14.0
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	350 °C, 1 h 1000 psi H ₂	STM (1% Mo)	14.7
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	Two-stage ^d	None	16.9
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	Two-stage ^d	SAM (1% Mo)	21.7
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	Two-stage ^d	STM (1% Mo)	30.7
This study	Subbit. B	350 °C, 30 min 1000 psi H ₂	AHM/CS ₂ (1% Mo)	70.2
This study	Subbit. B	350 °C, 30 min 1000 psi H ₂	AHM/CS ₂ (1% Mo) ^g	71.1
This study	Subbit. B	350 °C, 30 min 1000 psi H ₂	None	29.1

^a AHM = ammonium heptamolybdate

^b AHM acidified with H₂SO₄

^c SAM = sulfided ammonium molybdate

^d 350 °C, 1 h; 425 °C, 10 min

^e STM = sulfided tetrahydroquinolinium molybdate

^f ATTM = ammonium tetrathiomolybdate

^g pH adjusted to 2.5 during catalyst impregnation

possibility to vary catalyst particle size and surface area over a wide range. This in turn allows the testing of correlations between liquefaction kinetics and catalyst dispersion.

REFERENCES

- Bi, X.-X., Derbyshire, F.J., Eklund, P.C., Hager, G.T. and Stencel, J.M., *Proc. Inter. Conf. Coal Sci.*, 1991, p. 683.
- Boakye, E., Vaidyanathan, N., Radovic, L.R. and Osseo-Asare, K., "Microemulsion-Mediated Synthesis of Nanosize Molybdenum Sulfide Coal Liquefaction Catalysts," *ACS Preprints (San Francisco)*, 1992.
- Burgess, C.E., Artok, L. and Schobert, H.H., *ACS Preprints (Div. Fuel Chem.)* **36** (2), 462 (1991).
- Cugini, A.V., Utz, B.R., Krastman, D., Hickey, R.F. and Balsone, V., *ACS Preprints (Div. Fuel Chem.)* **36** (1), 91 (1991).
- Davis, A., Mitchell, G.D., Derbyshire, F.J., Schobert, H.H. and Lin, R., *ACS Preprints (Div. Fuel Chem.)* **36** (2), 445 (1991).
- Derbyshire, F.J., "Catalysis in Coal Liquefaction," IEA CR/08, London, 1988.
- Derbyshire, F.J., Davis, A., Epstein, M.J. and Stansberry, P.G., *Fuel* **65**, 1233 (1986).
- Derbyshire, F.J. and Stansberry, P., *Fuel* **66**, 1741 (1987).
- Hirschon, A.S. and Wilson, Jr., R.B., *ACS Preprints (Div. Fuel Chem.)* **36** (1), 103 (1991).
- Miki, K., Yamamoto, Y., Inaba, A. and Sato, Y., *Proc. Inter. Conf. Coal Sci.*, 1991, p. 675.
- Moll, N.G. and Quarderer, G.J., U.S. Patent 4,136,013 (1979).
- Solar, J.M., Leon y Leon, C.A., Osseo-Asare, K. and Radovic, L.R., *Carbon* **28**, 369 (1990).
- Utz, B.R., Cugini, A.V. and Frommell, E.A., *ACS Preprints (Div. Fuel Chem.)* **34** (4), 1423 (1989).
- Weller, S. and Pelipetz, M.G., *Ind. Eng. Chem.* **43**, 1243 (1951).

**DATE
FILMED
8 107192**