DISPERSED-PHASE CATALYSIS IN COAL LIQUEFACTION

Bruce R. Utz, Anthony V. Cugini, and Elizabeth A. Frommell

Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236

ABSTRACT

The specific reaction ("preactivation") conditions for the conversion of catalyst precursors to unsupported catalysts have a direct effect on the catalytic activity and dispersion. The importance of reaction intermediates in decomposition of ammonium heptamolybdate and ammonium tetrathiomolybdate, and the sensitivity of these intermediates to reaction conditions, were studied in coal liquefaction systems. Recent results indicate that optimization of preactivation conditions facilitates the formation of a highly dispersed and active form of molybdenum disulfide for coal liquefaction. The use of the catalyst precursors ammonium heptamolybdate, ammonium tetrathiomolybdate, and molybdenum trisulfide for the conversion of coal to soluble products will be discussed.

INTRODUCTION

The use of an unsupported dispersed-phase catalyst for direct coal liquefaction is not a novel concept and has been employed with varying success. Dispersed-phase catalysts have been introduced via impregnation techniques (1-4), as water-soluble (5-8) and oil-soluble (9-12) salts, and as finely divided powders (1,2). While some methods of catalyst introduction result in greater dispersion of the catalyst and greater activity for the liquefaction of coal, all of the techniques allow the formation of a finely dispersed inorganic phase. The use of dispersed-phase catalysts in direct coal liquefaction offers several advantages. Since they could be considered "once-through" catalysts, deactivation problems are reduced when compared to supported catalysts, and catalytic activity remains high. Diffusion limitations are minimized because of the high surface area of small catalyst particles. Maximum interaction of coal, vehicle, and gaseous hydrogen can occur on the catalyst surface with a highly dispersed catalyst.

One of the more popular techniques for producing dispersed -phase catalysts involves the use of water- or oil-soluble catalyst precursors. Small amounts of the water-soluble catalyst precursor are added to the coal-vehicle feed and are subsequently converted to a highly dispersed insoluble catalytic phase. The reaction conditions that convert the soluble catalyst precursor to a highly active and dispersed-phase catalyst are critical. The objective of this paper is to identify techniques that will convert a molybdenum catalyst precursor to a highly dispersed MoS_2 phase that has greater activity for coal liquefaction than previously identified dispersed-phase MoS_2 catalysts.

EXPERIMENTAL

Catalyst screening tests were conducted in 40-mL microautoclave reactors. The liquefaction conditions were the following: temperature, 425°C; reaction pressure, 1000 psig H_2 (pressure at room temperature); residence time, 1 hour; and solvent/coal, 2/1. The coal used was Illinois No. 6, Burning Star Mine (ultimate analysis: C,71.02 wt%; H,4.95 wt%; O(diff.),9.26 wt%; N,1.41 wt%; S,3.23 wt%; and ash, 10.12 wt%, on a moisture-free basis), and the vehicle used was tetrahydronaphthalene (tetralin). Rapid heat-up rates were obtained by immersing the microautoclave in a preheated fluidized sand bath at 425°C. The microautoclave reached reaction temperature in 1-2 minutes. Slow heat-up rates were obtained by immersing the microautoclave in the fluidized sand bath at room temperature and gradually heating the sand bath to reaction temperature in 3/4 hour to 1 hour. Catalyst loadings were 1000 ppm, based on the weight of coal. Coal conversion was measured by the solubility of coal-derived products in methylene chloride and heptane using a pressure filtration technique(13).

Molybdenum trisulfide (MoS_3) was prepared by acidifying a solution of ammonium tetrathiomolybdate with 24 wt% formic acid (14). All other reagents were ACS grade.

X-ray diffraction studies were conducted with a Rigaku computer-controlled diffractometer equipped with a long fine-focus Cu X-ray tube, a receiving graphite monochromator to provide monochromatic Cu-K_α radiation, and a scintillation detector.

RESULTS AND DISCUSSION

Conversion of an aqueous solution of ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] to an active and high-surface-area catalyst is dependent on a number of factors. Gaseous hydrogen sulfide (H_2S) is required to convert ammonium heptamolybdate (AHM), which is essentially an oxide salt, to a series of oxysulfide salts (15) and ultimately to molybdenum disulfide (MoS_2), as shown in Figure 1. The ratio of ammonium ion to molybdenum may also be important, since studies have shown that increased NH_3/Mo ratios result in higher hydrogen consumption for the conversion of petroleum to upgraded products when AHM is used as a dispersed-phase catalyst (7,15). Petroleum upgrading studies demonstrated that the heat-up rate for the conversion of AHM to MoS_2 is extremely important (15). Slower heat-up rates resulted in a gradual transition of AHM to MoS_2 and significantly higher conversions of petroleum to distillate products.

Information on the dispersion of MoS_2 was obtained from X-ray diffraction measurements, which are sensitive to the degree of stacking and dispersion of the MoS_2 layers (Figure 2). The diffraction pattern of single layers of MoS_2 shows the (100) and (110) bands, but no (002) band, as in the middle curve of Figure 2. These crystallites are considered two-dimensional, since there is no growth in the third dimension. When only a very small number of MoS_2 layers are in multilayer stacks, a weak (002) band is present, as in the top curve with the catalyst precursor, MoS_3. When many multilayer stacks of MoS_2 are present, a strong (002) band can be seen, as in the lower curve. The pattern is that obtained for three-dimensional crystallites. The widths-at-half-maximum can be used to estimate the size of the MoS_2 crystallites. The MoS_2 crystallites formed during a gradual heat-up of AHM, in the absence of coal, are three-dimensional, as shown in the bottom curve of Figure 2. Coal added to AHM under the same reaction conditions prevents the MoS_2 layers from growing in the third dimension. Since the crystallite size in the plane of the MoS_2 layers is about the same in both cases (150-200 angstroms), the addition of the coal produces a more highly dispersed, minimally stacked MoS_2. All of these results suggest that many factors can affect the extent of dispersion of MoS_2. The factors that have been identified include heat-up rate of the catalyst precursor during the conversion to MoS_2; the NH_3/Mo ratio; the H_2S pressure; and other reagents, such as coal, that might affect the transition of AHM to MoS_2.

Previous studies by Lopez et al. (16) show that small amounts of ammonium tetrathiomolybdate [$(NH_4)_2MoS_4$] are produced during the decomposition of AHM, which represents an intermediate of a minor decomposition pathway. One advantage of using ammonium tetrathiomolybdate (ATTM) as a dispersed-phase catalyst in coal liquefaction is that an external source of H_2S is not required because the catalyst precursor already exists as a water-soluble sulfide salt. It is known that ATTM thermally decomposes to MoS_3 and subsequently to MoS_2 (17). Eggertsen et al. (14) examined the reaction conditions for the thermal decomposition of MoS_3 to MoS_2 and determined that rapid heat-up (direct introduction of MoS_3 into a stream of hydrogen at 450°C) gave MoS_2 having a surface area of 85-158 m^2/gm, while gradual heat-up (25 min to 450°C) resulted in MoS_2 surface areas of less than 5m^2/gm. Naumann and coworkers(17) applied the results of Eggertsen to the catalyst precursor ATTM, since MoS_3 was considered to be an intermediate in the decomposition of ATTM (Figure 3). The results show that high-surface area MoS_2 is formed (88 m^2/gm) if the thermal transition of ATTM to MoS_2 is rapid, and the surface area is low if the thermal transition is gradual.

Studies at PETC examined the conversion of coal to methylene chloride- and heptane-soluble products using ATTM as a catalyst precursor. Experiments were performed using both rapid and gradual heat-up rates for the preparation of the dispersed-phase catalyst and were compared with results using AHM as a catalyst(Figure 4). The results demonstrate that rapid heat-up of ATTM resulted in coal conversions to methylene chloride- and heptane-soluble material that were higher than conversions from experiments done at a slower heat-up, consistent with expectations for surface area studies of pure compounds. Experiments were also performed with MoS_3, wherein MoS_3 was suspended in the same amount of water used for the water-soluble precursor, ATTM. Results show that conversion of coal to methylene chloride- and heptane-soluble products is greater for rapid heat-up experiments and is comparable to those using AHM (Figure 4). Experiments that verify the microautoclave studies were also performed in a 1-liter stirred autoclave, using both batch and continuous modes of operation.

Experiments were also performed with moisture-free solid MoS_3. Elimination of water has several advantages. The addition of water causes a decrease in hydrogen partial pressure within the reactor and is more energy intensive because water is being heated. Experimental results presented in Figure 4 demonstrate that the addition of the dry catalyst precursor, MoS_3, produced coal conversions comparable to those obtained with the water-soluble catalyst precursors. Therefore, MoS_3 may represent an ideal choice in the preparation of dispersed-phase catalysts. The X-ray diffraction pattern of MoS_2, from MoS_3, showed a very small (002) band, indicating minimal stacking. Minimal stacking infers a well-dispersed, high-surface-area material that provides comparable conversions to the water-soluble catalyst precursors. Scanning electron microscopy (SEM) was not able to detect the presence of MoS_2, suggesting that the particle size was less than 1000 angstroms. These results support the existence of highly dispersed MoS_2, which has resulted in the high conversion to solvent-soluble products.

CONCLUSIONS

Two catalyst precursors have been identified that result in high conversions of coal to solvent-soluble products when heated rapidly to reaction temperature. The use of MoS_3 and ATTM as catalyst precursors, rather than AHM as a catalyst precursor, offers a number of advantages. Both catalyst precursors are in a sulfided form, and therefore additional H_2S is not required, while AHM requires the addition of H_2S in order to form the oxysulfide intermediates and the final product, MoS_2. Both of the sulfided precursors are activated and highly dispersed when heated rapidly to reaction temperature, while AHM requires a gradual heat-up, and therefore activation of AHM is much more energy intensive. The ultimate goal is to identify a dry, highly dispersed, catalyst precursor or catalyst that can be added to a coal-vehicle feed without the addition of water and that results in yields of coal-derived products comparable to those produced using water- or oil-soluble catalyst precursors. Possibly MoS_3 is the catalyst precursor that satisfies those requirements.

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DISCLAIMER

REFERENCES

1. Schlesinger, M.D.; Frank, L.V.; Hiteshue, R.W. Bureau of Mines Report No. 6021 (1961).

2. Weller, S.W.; Pelipetz, M.G. Ind. Eng. Chem. 43(5), 1243 (1951).

3. Clark, E.L.; Hiteshue, R.W.; Kandiner, H.J. Chem. Eng. Prog. 48, 14 (1952).

4. Derbyshire, F.J.; Davis, A.; Lin, R.; Stansberry, P.G.; Terrer, M.T. Fuel Proc. Tech. 12, 127 (1986).

5. Moll, N.G.; Quarderer, G.J. Chem. Eng. Prog. 75(10), 46 (1979).

6. Moll, N.G.; Quarderer, G.J. U.S. Patent 4,090,943, May 23, 1978.

7. Lopez, J.; McKinney, J.D.; Pasek, E.A. U.S. Patent 4,557,821, December 10, 1985.

8. Cugini, A.V.; Ruether, J.A.; Cillo, D.L.; Krastman, D.; Smith, D.N.; Balsone, V. Preprints, Div. Fuel Chem., Am. Chem. Soc. 33(1), 6 (1988).

9. Hawk, C.O.; Hiteshue, R.W. Bureau of Mines Bulletin No. 622, 42 (1965).

10. Gatsis, J.G.; Gleim, W.K.T. U.S. Patent 3,252,894, May 1966.

11. Anderson, R.R.; Bockrath, B.C. Fuel, 64, 329 (1984).

12. Aldridge, C.L.; Bearden, R., Jr. U.S. Patent 4,298,454, September 5, 1978.

13. Utz, B.R.; Narain, N.K.; Appell, H.R.; Blaustein, B.D. in "Coal and Coal Products: Analytical Characterization Techniques" (Ed. E.L. Fuller, Jr.), Am. Chem. Soc. Symp. Ser. 205, 225 (1982).

14. Eggertsen, F.T.; Roberts, R.M. J. Phys. Chem. 63, 1981 (1959).

15. Lopez, J.; Pasek, E.A.; Cugini, A.V. U.S. Patent 4,762,812, August 9, 1988.

16. Lopez, J.; Pasek, E.A.; Cugini, A.V. Unpublished results.

17. Naumann, A.W.; Behan, A.S.; Thorsteinson, E.M. Proc. Fourth Int. Conf. Chemistry and Uses of Molybdenum (H.E. Barry and C.N. Mitchell Eds.) 313 (1982).

$$(NH_4)_6Mo_7O_{24}\cdot 4H_2O \quad + \quad H_2S \text{ ------> } (NH_4)_xMoO_yS_z$$

$$(NH_4)_xMoO_yS_z \; + \quad H_2S \qquad \text{------> } MoO_xS_y \; + \quad NH_3$$

$$MoO_xS_y \; + \quad H_2 \quad + \quad H_2S \qquad \text{------> } \text{"}MoS_2\text{"} \; + \quad H_20$$

Figure 1. Conversion of Ammonium Heptamolybdate to Molybdenum Disulfide.

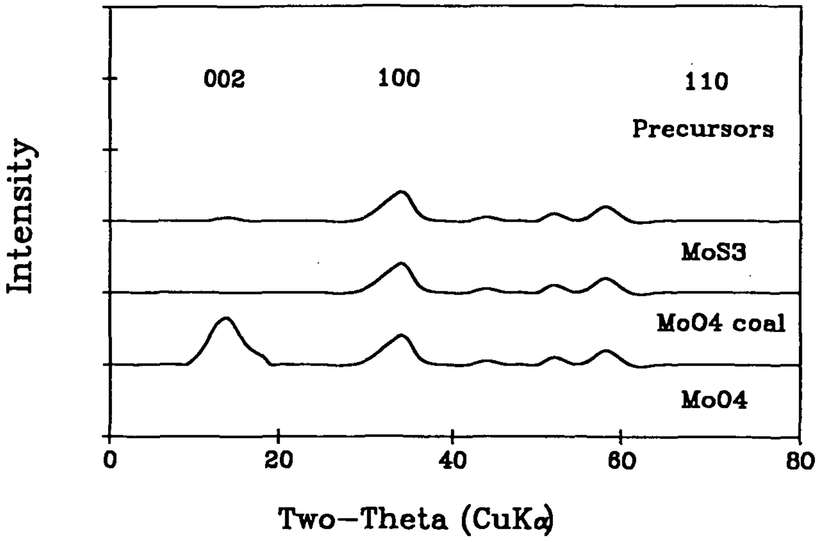

Figure 2. X–Ray Diffraction Patterns for Molybdenum Disulfide (h,k,l) Generated from Mo(VI) Precursors Reacted at Coal Liquefaction Conditions.

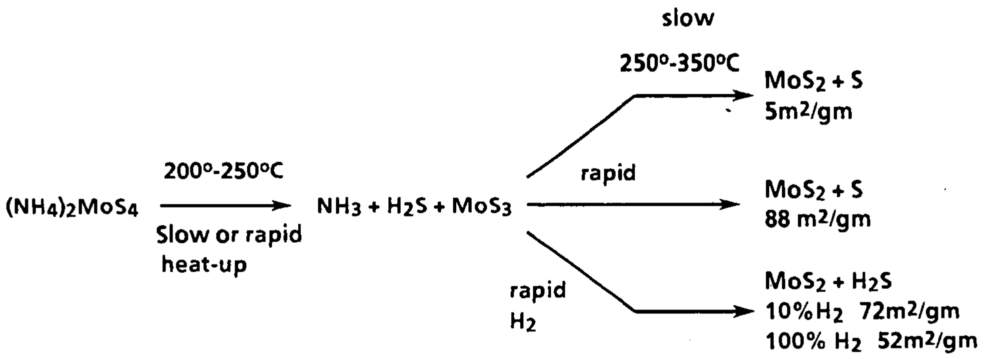

Figure 3. Decomposition of Ammonium Tetrathiomolybdate.

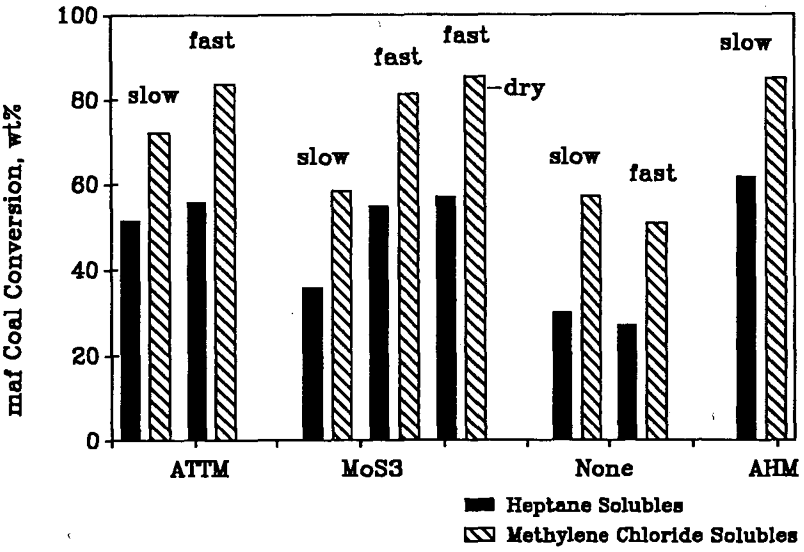

Figure 4. Effect of heat–up rate on coal conversion using presulfided catalyst precursors.