**ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL
SULFIDE CATALYSTS**

**Technical Progress Report for the Period
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ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

SUMMARY OF TECHNICAL PROGRESS

During this quarter, various preparation methods of synthesizing molybdenum disulfide and various alkali doping procedures were used. These studies were carried out to determine if various preparation parameters affected the activity of the catalyst. As of this time, only part of the catalysts that have been synthesized have been tested. Testing was performed on an undoped molybdenum disulfide sample with $H_2/CO = 1$ synthesis gas at 8.1 MPa and at temperatures of 245, 255, 265, 275, 280, 300, 320, and 295°C, and as expected only hydrocarbons were formed. A methanol injection experiment was also carried out with the undoped catalyst to determine whether homologation of methanol to ethanol would readily occur. It was found that homologation did not occur over the undoped MoS_2 sample. Catalytic testing was also performed on a cesium formate doped molybdenum disulfide catalyst corresponding to 9 wt% Cs/ MoS_2 . The catalyst was tested at a pressure of 8.1 MPa and at the temperatures of 245, 255, 265, 275, 285, and 295°C, and it was observed that the predominant products were linear alcohols. The Cs/ MoS_2 sample was protected from air exposure during preparation and testing. As with the other recently tested alkali-promoted MoS_2 catalysts, this catalyst was not as active as previous Cs/ MoS_2 catalysts [1], and some deactivation during these systematic studies was observed. X-Ray powder diffraction and BET surface area measurements are being used to characterize the catalysts, and electron microscopy analyses are being carried out.

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TECHNICAL PROGRESS

Catalyst Preparation and Doping Procedure:

Two batches of MoS_3 were synthesized. In a hood, 108 ml portions of 20% aqueous $(\text{NH}_4)_2\text{S}$ were added to 15.1520 g (Batch 1) and 15.0887 g (Batch 2) of $(\text{NH}_4)_2\text{Mo}_7\text{O}_{24}\cdot\text{H}_2\text{O}$ in an 800 ml beaker. The solution was stirred using a magnetic stirring bar and heated to 60°C . The solution turned a very deep red color as the $(\text{NH}_4)_2\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ dissolved.

An acid solution consisting of 100 ml of glacial acetic acid diluted to 400 ml using distilled water was prepared. This acetic acid solution was then added to the $(\text{NH}_4)_2\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{S}$ solution, and the heat was turned off but stirring was maintained for 3.5 hr. The very dark brown precipitate was filtered in a Buchner funnel and washed well with distilled water. The product was dried in an oven at 110°C overnight.

The MoS_3 was calcined to MoS_2 under the flow of various gases. The first sample was calcined under helium. For this treatment, 2-3 g of MoS_3 were mixed with 3 mm Pyrex beads. In a quartz tube about 24 inches long, glass wool was placed four inches from one end. The Pyrex beads/ MoS_3 mixture was then added to the tube, and another layer of glass wool was put on top of the mixture. More clean Pyrex beads were added with another layer of glass wool near the end of the tube. The quartz tube was then placed in a horizontal split-tube furnace and connected to a helium tank. The flow rate of the helium was set at 60 ml/min and checked periodically with a bubble meter. The temperature was turned up to 200°C quickly using a differential heating device and held for 10 min. Then the temperature was increased to 450°C for 1.5 hr. The clean Pyrex beads near the outlet end

of the tube were cool and collected the released sulfur by condensation as the MoS_3 was decomposed into black MoS_2 . The MoS_2 product was then separated from the Pyrex glass beads using a sieve in ambient air and placed in sample bottles. This same procedure was followed for two other samples, but different gases were used during the calcination process. In one sample, nitrogen was used. In the third case, a gas mixture of 204 ppm H_2S in hydrogen was used.

For the cesium-promoted catalyst prepared for catalytic testing, the MoS_3 was calcined under nitrogen using the same experimental conditions as described above. However, after calcination in flowing nitrogen, the MoS_2 was not allowed to come in contact with air, but rather the closed tube was moved into an adjacent nitrogen-filled glovebox. The MoS_2 was placed in a small beaker, and to this was added 0.2339 M CsOOCH aqueous solution. The sample was allowed to evaporate to dryness under nitrogen, and the resultant catalyst corresponded to 9 wt% Cs/ MoS_2 .

Catalytic Testing:

Undoped Molybdenum Disulfide. In a nitrogen-filled glove bag, 1.6567 g of undoped MoS_2 was mixed with clean Pyrex beads. A stainless steel reactor tube with a length of ≈ 76 cm, with an internal thermocouple, was filled with twelve inches of Pyrex beads, and then a layer of glass wool was put on top of the Pyrex beads. The Pyrex bead/catalyst mixture was added, the volume of which corresponded to a bed height of 10 cm. Glass wool was added, and the tube was filled to the top with more clean Pyrex beads. Another layer of glass wool was added and the top was closed except for a small hole at the top and bottom Swagelok fittings, which were covered with parafilm. The tube was taken out of the glove bag, and wrapped in brass sheaths, which were used to distribute heat evenly around the

reactor tube during catalytic testing. There was another thermocouple connected to the center outside wall so that one could monitor the temperature of the outside reactor wall, as well as the internal bed temperature. The reactor tube was centered in the vertical furnace and connected to the H₂/CO reactant synthesis gas system.

The catalyst testing reactor system has high pressure and high temperature capabilities. The entire apparatus is made of stainless steel. The inlet gas manifold has four tanks of gas connected to it. These consisted of H₂, CO, N₂, and 2 vol% H₂/98 vol% N₂, each with its own flow regulator and in-line pressure gauges. All of the gas lines converge into a reactor inlet tube before the pressure gauge that measures the pressure at the top of the reactor. There is also a high pressure Gilson pump connected to the gas inlet above the reactor for the injection of liquids if desired. The temperature of the electric furnace is controlled by a proportional controller interfaced with the thermocouple on the reactor wall. At the bottom of the reactor, an outlet tube wrapped in heating tape carries the products to a back pressure regulator, which controls the pressure in the reactor. After the back pressure regulator, the outlet tube is directly connected to sampling valves on a Hewlett-Packard 5730A gas chromatograph, all of which are controlled by PC data station interfaced with a Hewlett-Packard 3396 Series II integrator. The products and excess gases are then sent to a bubble meter that monitors the gas flow rate.

After the catalyst was loaded into the reactor, it was reductively pretreated at ambient pressure before testing. The temperature was brought up to 400°C under a flow of 2.04 vol% H₂/97.96 vol% N₂ with a rate of 60 ml/min for 1 hr in order to get rid of any surface sulfates that might have formed. Then the reactor was allowed to cool overnight. With only H₂/CO synthesis gas flowing, preset to a H₂/CO molar ratio of 1/1, through the system, the reactor was pressurized and catalytic testing was begun. In general, the reaction

temperature was varied stepwise while keeping all other reaction conditions constant.

This catalytic testing was run at a pressure of 8.1 MPa with a gas hourly space velocity (GHSV) of 7750 ℓ /kg cat/hr at the following temperatures 245, 255, 265, 275, 280, 300, and 320°C. For each temperature change, the reaction was run until it reached steady state, and then testing was maintained under constant reaction conditions for 4 to 12 hr. As expected, the reaction over MoS₂ only produced hydrocarbons, water, and carbon dioxide. At lower temperatures, the major product was methane. As the reaction temperature was sequentially increased, higher molecular weight products were formed (up to C₆). Other trends that were seen included the observation that as the temperature was increased, the conversion of CO tended to increase, as can be seen in Figure 1. During this test, the CO₂/H₂O molar ratio also increased with increasing temperature, as shown in Figure 2. This increase in the CO₂/H₂O molar ratio occurred because the equilibrium of the water gas shift reaction, Equation 1, was shifted to the H₂ + CO₂ side as the temperature was increased.

Since C₁-C₆ hydrocarbon products were formed at the higher reaction temperatures, Schulz-Flory distribution plots were made for each of the higher temperatures used. These plots are shown in Figures 3-7. In constructing these graphs, Equation 2 was utilized and the log of the product concentration, given in terms of mol/hr, was plotted vs the carbon number (n) of that product. For normal carbon-carbon bond formation *via* addition of a C₁ unit to a growing C_n carbon chain according to polymerization kinetics, this should give a straight line with a negative slope. The slope of the line expresses the probability of carbon chain growth and is designated as being equal to the log of α , where α is expressed

as shown by Equation 3.

$$\log C_n = 2 \log (\ln \alpha) + n \log \alpha \quad (2)$$

$$\alpha = k_p/(k_p + k_t) \quad (3)$$

This expression relates the probability that any intermediate carbon chain will grow by propagation rather than terminating *via* hydrogenation and desorption. k_p is the rate for the propagation reaction and k_t is the rate of termination. The α value for each reaction was determined from the least squares best fit of the data at each reaction temperature from the Schulz-Flory distribution of products. An appreciable scatter in the value of α was obtained, but no large variation of α was noted, as shown in Table 1. Table 2 shows that higher temperatures higher molecular weight products were produced at higher temperatures, meaning that propagation was more likely at the higher temperatures. This can be seen in Figure 8, where the space time yields of all of the hydrocarbon products increased with increasing reaction temperature. However, there were appreciable variations in the C_2 - C_4 product space time yields at the temperatures of 265, 280, and 300°C.

After the above tests were conducted, the temperature was decreased to 295°C, and methanol was injected into the inlet synthesis gas at a rate of 18 μ l/min using the high pressure Gilson pump. This experiment was carried out to determine if the undoped MoS_2 catalyst would homologate the methanol into ethanol. No oxygenates were observed during the pumping of methanol. However, it was observed that the methanol was decomposed to carbon monoxide and hydrogen, and higher yields of hydrocarbons were obtained (Figure 7).

TABLE 1. ALPHA VALUES

TEMPERATURE	SLOPE	ALPHA
265°C	-0.621	0.239
280°C	-0.508	0.310
300°C	-0.540	0.288
320°C	-0.589	0.258

TABLE 2. PRODUCT SPACE TIME YIELDS (g/kg cat/hr)

TEMP	CH ₄	C ₂	C ₃	C ₄	C ₅	C ₆	CO ₂	WATER
245°C	23.16	0	0	0	0	0	3.65	45.15
255°C	15.34	0	0	0	0	0	5.78	40.54
265°C	12.00	2.25	3.36	0	0	0	8.82	23.29
280°C	20.71	72.43	20.53	2.60	0	0	16.14	92.37
300°C	57.90	62.63	8.79	7.29	0	0	44.64	91.81
320°C	303.89	75.62	30.40	19.77	5.18	1.21	87.01	65.29

Testing of 9 wt% Cs/MoS₂. This promoted catalyst was loaded into the reactor and pretreated in the same manner as described earlier for the undoped MoS₂. The testing was carried out at 8.1 MPa with H₂/CO = 1 synthesis gas at a GHSV of 7750 ℓ/kg cat/hr at 245, 255, 265, 275, 285, and 295°C. After this set of temperatures was run, the reaction was run at 245°C again to determine if there was any deactivation of the catalyst. As can be seen in Figure 9, which is a plot of the space time yield of methane versus time, there was apparent deactivation at each of the higher reaction temperatures, as well as by comparing the initial test and the final test at 245°C. A plot of the total space time yield of oxygenates (alcohols + esters) yielded very similar behavior, but there was more scatter in the experimental data at each temperature. The data in Figure 9 were collected during approximately 100 hr of continuous testing. Prior to Sample No. 94, the furnace was turned off and the reactor was allowed to cool to 245°C, at which point a rather constant reactor temperature of 245°C was maintained at the end of the experiment.

During this testing program at temperatures of 275°C and higher, apparent deactivation can be seen from the gradual decline in methane formation with time. The products that were formed in the reaction in appreciable yields were methane, methanol, ethanol, propanol, ethyl formate, water, and carbon dioxide. The general trends that were followed by the catalyst were increasing selectivity of hydrocarbons, principally methane, and decreasing selectivity to alcohols with increasing temperature (Figure 10), increasing hydrocarbon/alcohol molar ratio with increasing temperature (Figure 11), decreasing methanol/C₂⁺ oxygenated products molar ratio with increasing temperature (Figure 12), and increasing space time yield of the products with increasing temperature (Figure 13).

REFERENCES:

1. Klier, K., Herman, R. G., Simmons, G. W., Lyman, C. E., Santiesteban, J. G., Najbar, M., and Bastian, R., "Direct Synthesis of Alcohol Fuels Over Molybdenum-Based Catalysts," Final Technical Report DOE/PC/80014-F, 261 pp (December 1988).
2. Santiesteban, J. G., Ph.D. Dissertation, Department of Chemistry, Lehigh University (1989).

**FIGURE 1. CO Conversion (mol/kg cat/hr)
vs Temperature Over MoS₂ at
8.1 MPa and GHSV = 7750 l/kg cat/hr**

FIGURE 2. $\text{CO}_2/\text{H}_2\text{O}$ Molar Ratio
vs Temperature at 8.1 MPa and
GHSV = 7750 l/kg cat/hr with $\text{H}_2/\text{CO} = 1$

**FIGURE 3. Schulz-Flory Plot
for MoS₂ at 265°C, 8.1 MPa,
and GHSV = 7750 l/kg cat/hr**

**FIGURE 4. Schulz-Flory Plot
at 280°C, 8.1 MPa, and GHSV =
7750 l/kg cat/hr**

**FIGURE 5. Schulz-Flory Plot
at 300°C, 8.1 MPa, and GHSV =
7750 l/kg cat/hr**

**FIGURE 6. Schulz-Flory Plot
for MoS₂ at 320°C, 8.1 MPa,
and GHSV = 7750 l/kg cat/hr**

FIGURE 7. Schulz-Flory Plot
for MoS_2 at 295°C , 8.1 MPa ,
and $\text{GHSV} = 7750\text{ l/kg cat/hr}$

FIGURE 8. Space Time Yield vs Temperature at 8.1 MPa and GHSV = 7750 l/kg cat/hr Over MoS₂

FIGURE 9. Methane Productivity vs Time

FIGURE 10. Selectivity vs Temperature
Over the Cs/MoS₂ Catalyst

**FIGURE 11. Hydrocarbon/Alcohol
Molar Ratio Over Cs/MoS₂**

FIGURE 12. Methanol/ C_2^+
Oxygenated Products Molar Ratio

FIGURE 13. Space Time Yield of Products Over Cs/MoS₂ with H₂/CO = 1 vs Temperature at 8.1 MPa

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