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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

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ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

SUMMARY OF TECHNICAL PROGRESS

During this quarter, a 10wt% CsOOCH/MoS₂ catalyst was prepared for catalytic testing using slight modifications of previous attempted preparations. The MoS₂ was prepared from MoS₃ via thermal decomposition. The resultant product was then doped using an aqueous solution of cesium formate under vacuum. The doped catalyst was then loaded into a single pass fixed-bed tubular flow reactor under nitrogen to minimize exposure to air. The catalyst was pretreated with 2vol% H₂/98vol% N₂ at 400°C and then tested at 8.3 MPa at 245, 256, 265, 275, and 295°C for a total of 168 hours. The catalyst displayed the activity and selectivity similar to that of previous workers [1]. The surface areas of the doped and undoped catalysts were also determined.

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TECHNICAL PROGRESS

Catalyst Preparation and Doping Procedure:

The molybdenum disulfide was synthesized by thermally decomposing molybdenum trisulfide that had been previously prepared. Approximately 3 g of the trisulfide was centered in a quartz tube reactor 51 cm long with an inner diameter of 8 mm. The catalyst was not diluted with Pyrex beads as had been done in earlier work. The loaded quartz tube was placed in a tubular oven and nitrogen was flowed through at a rate of 60 mL/min. Using a differential heating device, the temperature was raised to 250°C and held there for 30 min. Then the sample was heated to 450°C as fast as possible (20°C/min) and held at 450°C for 2 hr. The sample was cooled to room temperature while still under the nitrogen flow. The MoS₂ was excluded from air as much as possible.

Immediately after cooling in nitrogen, 2.1189 g of the disulfide was weighed out and placed in the doping apparatus which was then attached to a rotary vacuum pump as shown in Figure 1 [2]. The sample was heated to 100°C for 2 hrs and then allowed to cool to room temperature. Three equivolume portions totalling 10.5 ml of a 0.1224M CsOOCH solution were added to the catalyst via a syringe. The high purity grade CsOOCH was supplied by Cabot Corporation. Each portion was enough to just cover the catalyst. The catalyst was allowed to dry under vacuum at 60°C before the next portion was added. After drying, the catalyst was placed under nitrogen overnight.

Catalytic Testing:

1.7313 g of the 10wt% CsOOCH/MoS₂ was weighed out, mixed with 6 cc of 3 mm Pyrex beads, and loaded in the center of a 66 cm stainless steel reactor under nitrogen. The bed height was approximately 12 cm. The reactor was then placed on the system and 2vol% H₂/98vol% N₂ was passed through the reactor at a rate of 60 mL/min. The catalyst was heated slowly up to 400°C while water and carbon dioxide were monitored with a gas chromatograph and hydrogen sulfide was monitored with lead acetate paper. Hydrogen sulfide was first detected at 191°C. A Small amount of hydrogen sulfide was still detected at 400°C, but no water or carbon dioxide was detected. The temperature of 400°C was held for 1 hr with H₂S being detected throughout this time period. The catalyst was left overnight to cool to room temperature in the hydrogen/nitrogen mixture.

The target Gas Hourly Space Velocity (GHSV) was 7750 L/kg cat/hr. The flows of CO and H₂ were set to give H₂/CO $\approx$ 1. A GHSV of 7758 was obtained. The reactor was then pressurized to 8.3 MPa. After the reactor was pressurized and no leaks were detected, the catalyst was heated to 245°C. The products were monitored approximately every 33 min using an on-line GC. Liquid products were also collected at each temperature for analysis by GC/MS. After reaching steady state conditions (Figures 2-5), the temperature was increased to the next desired point. The temperatures of 245, 256, 265, 275, and 295°C were used. The selectivities and yields are presented in Figures 6-9.

Since the main purpose of this experiment is to reproduce previous results, Table I compares previous space time yields [2] with the present work. As can be seen, the present catalyst is slightly less active at lower temperatures, and slightly more active at higher temperatures. This catalyst experienced none of the deactivation of some of the more recently tested catalysts (Figure 2). Figures 10 and 11 show that the methanol/C₂+ alcohol

molar ratio decreases with increasing temperature and the alcohol/hydrocarbon molar ratio reaches a maximum at 256°C. Figure 12 shows that the CO conversion rate increased with increasing temperature.

BET surface areas were run on the doped and undoped catalysts. The undoped molybdenum disulfide was found to have a surface area of 90 m²/g and the doped catalyst had a surface area of 36 m²/g. The previous tested catalysts had a surface area of 63 m²/g for the undoped catalyst and 17 m²/g for the 10wt% CsOOCH/MoS₂ catalyst [2].

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).

TABLE I. COMPARISON OF PRODUCT YIELDS (g/kg cat/hr)

PRODUCT	245°C	256°C	265°C	275°C	295°C	Catalyst
Carbon Dioxide	55.48 52.47	75.48 79.74	113.69 136.83	159.06 166.66	273.71 317.10	New [2]
Water	-- tr	-- tr	-- tr	-- 0.49	1.59 3.66	New [2]
Methane	7.03 12.75	9.21 16.73	14.61 26.31	23.08 31.50	42.87 62.00	New [2]
Ethylene	0.79 0.28	0.96 0.76	1.06 0.68	0.98 0.63	1.07 0.92	New [2]
Ethane	2.55 0.92	2.80 2.01	4.35 4.18	5.87 5.71	11.72 13.52	New [2]
Propane	tr --	1.37 0.28	1.55 1.03	1.07 1.87	5.63 6.77	New [2]
Butane	-- --	-- --	-- --	tr --	tr 2.76	New [2]
Methanol	53.67 85.32	83.22 106.22	119.18 132.71	168.87 141.04	192.50 152.86	New [2]
Ethanol	20.16 24.12	28.55 32.96	43.47 48.87	56.83 52.75	70.06 62.70	New [2]
1-Propanol	6.17 5.06	7.78 7.54	13.11 12.71	15.74 14.93	25.04 22.23	New [2]
1-Butanol	-- --	-- tr	1.42 tr	3.62 tr	5.86 3.63	New [2]
Methyl Formate	tr 0.86	0.95 1.20	1.83 1.03	2.52 1.54	2.62 tr	New [2]
Methyl Acetate	5.20 1.30	5.09 1.96	7.97 2.63	9.06 2.88	9.23 1.33	New [2]
Acetaldehyde	2.19 --	2.54 --	3.83 --	4.90 --	5.77 --	New [2]
Propanal	-- --	-- --	2.34 --	3.05 --	3.93 --	New [2]
CO Conversion Rate (mol/kg cat/hr)	3.83 4.53	5.23 6.06	7.77 8.63	10.76 9.74	14.67 14.09	New [2]

FIGURE 1. Diagram of the Vacuum System

FIGURE 2. CO CONVERSION RATE VS TIME

FIGURE 3. TOTAL ALCOHOL AND HYDROCARBON SPACE TIME YIELDS VS TIME

FIGURE 4. CARBON DIOXIDE SPACE TIME YIELDS VS TIME

FIGURE 5. METHANOL SPACE TIME YIELDS VS TIME

FIGURE 6. SELECTIVITY (C MOLE%)
VS TEMPERATURE

FIGURE 7. CO₂ SPACE TIME YIELD
VS TEMPERATURE

FIGURE 8. TOTAL ALCOHOL AND HYDROCARBON
SPACE TIME YIELDS VS TEMPERATURE

FIGURE 9. ALCOHOL SPACE TIME YIELDS VS TEMPERATURE

FIGURE 10. METHANOL/C₂+ ALCOHOL
MOLAR RATIO VS TEMPERATURE

FIGURE 11. ALCOHOL/HYDROCARBON
MOLAR RATIO VS TEMPERATURE

FIGURE 12. CO CONVERSION RATE
(mol/kg cat/hr) VS TEMPERATURE

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