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DOE/PC/91301-4

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

Technical Progress Report for the Period

June 1992-August 1992

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September 1992

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY-Pittsburgh Energy Technology Center

Under Contract No. DE-FG22-91PC91301

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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, high pressure (up to 100 atm = 10.3 MPa), high temperature (up to 350°C) catalyst testing was carried out with the 20 wt% Cs/MoS₂ catalyst that was prepared. It was verified that this is an active catalyst for the synthesis of linear C₁-C₄ alcohols and that the yield increases with increasing temperature. However, the product selectivity is shifted toward enhanced hydrocarbon production, principally of methane.

Temperature, pressure, and flow rate dependences of the synthesis reactions were also investigated in the presence and absence of H₂S in the H₂/CO = 1/1 synthesis gas during short term testing experiments. The temperature seemed to produce the largest effect on alcohol yield and on the hydrocarbon selectivity, with both increasing with increasing temperature. The presence of 45.5 ppm H₂S in the synthesis gas did increase the C₂⁺ alcohol/methanol molar ratio at 285°C, but this effect was not noticeable at higher temperatures under the reaction conditions that were employed. On the other hand, the presence of H₂S decreased the yield of methane at high temperatures (340-350°C), but this effect was not noticeable at the lower temperatures that were utilized. At high temperature and pressure (350°C and 10.3 MPa) with 45.5 ppm H₂S in the synthesis gas, it was shown that increasing the gas hourly space velocity of the synthesis gas reactant significantly decreased the yield of methane, while affecting the yield of alcohols to a much lesser extent.

ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

TECHNICAL PROGRESS

Cesium doped molybdenum disulfide, A/MoS₂, has been prepared and studied for the catalytic production of C₁-C₄ alcohols from H₂/CO synthesis gas. The MoS₂ catalyst was prepared by reacting ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄•4H₂O) with ammonium sulfide ((NH₄)₂S) in aqueous solution to give ammonium thiomolybdate ((NH₄)₂MoS₄). The ammonium thiomolybdate was then acidified to obtain MoS₃. The trisulfide was thermally decomposed to MoS₂. The disulfide was then doped with cesium using a methanolic solution of 0.1993 M cesium formate. The cesium formate solution was added in 10 ml aliquots and evaporated to dryness in air. The volume of solution utilized yielded a nominally 20 wt% cesium doped molybdenum disulfide.

1. Testing with H₂/CO = 1/1 Synthesis Gas

After the catalyst was prepared, a 1.5365 g portion was mixed with approximately 10 ml of 3 mm Pyrex beads. This mixture was then centered in a 316 stainless steel fixed bed reactor using additional quantities of the Pyrex beads. No effort was made to keep the catalyst from contacting air. After the reactor was in place, pretreatment of the catalyst was carried out by passing a 2.04/97.96 H₂/N₂ mixture over the catalyst at a rate of 60 ml/min at 1 atm. After the flow rate was attained, the catalyst was heated to 410°C and this temperature was maintained for one hr. The reactor was then allowed to cool to room temperature overnight under the hydrogen/nitrogen flow. The gas flow was then changed to the H₂/CO = 1/1 reactant mixture and the reactor was then pressurized and sequentially heated. With the 50/50 mixture of CO/H₂ synthesis gas at 8.3 MPa and with a gas hourly

space velocity (GHSV) of 7810 ℓ /kg cat/hr, catalytic testing was carried out at the temperatures of 245, 265, 285, and 310°C.

As shown in Table 1 and Figure 1, the catalyst was more active at higher temperatures and was more selective to alcohols than to hydrocarbons over the entire temperature range. However, as shown in Figure 2, as the temperature was increased the selectivity toward alcohols decreased, while the selectivity toward hydrocarbons increased, where the selectivities are expressed on a CO₂-free basis. This agrees with observations obtained in earlier work [1-3]. At the same time, the methanol/ethanol molar ratio decreased with increasing temperature, indicating that higher reaction temperatures enhance higher alcohol formation.

TABLE 1. Product yields obtained over the 20 wt% Cs/MoS₂ catalyst with H₂/CO = 1/1 synthesis gas at 8.3 MPa and with GHSV = 7810 ℓ /kg cat/hr.

<u>Temperature (°C)</u>	<u>Product Yield (g/kg cat/hr)</u>			
	<u>CH₄</u>	<u>CO₂</u>	<u>Methanol</u>	<u>Ethanol</u>
245	3.09	14.15	38.91	0.00
265	18.57	52.61	107.88	31.83
285	30.95	87.54	120.70	52.17
310	45.98	122.47	137.95	71.63

2. Initial Testing with Synthesis Gas Containing 45.4 ppm H₂S

The purpose of this experiment was to investigate the report by Dow Chemical Co. that hydrogen sulfide in the synthesis gas makes alkali promoted molybdenum disulfide alcohol synthesis catalysts more selective to higher alcohols [4], although the Cs-doped MoS₂ catalyst was not studied by the researchers at Dow Chemical Co. The present experiment was carried out using the same catalyst as employed in the previous experiment; it was not

unloaded from the reactor and was not pretreated again. A GHSV of 7810 $\ell/\text{kg cat/hr}$ again was used with a CO/H_2 ratio of 1.0. A 91 ppm hydrogen sulfide in hydrogen mixture was used for the experiments in which the H_2S was introduced into the reactant synthesis gas stream. Therefore, there was 45.5 ppm of H_2S passing over the catalyst. Several temperatures and pressures were investigated in this initial screening of the catalyst, as described below.

To monitor if the presence of hydrogen sulfide was having an effect on the selectivity of higher alcohols, the ratio of methanol/ C_2^+ alcohols was used as an indicator. If the hydrogen sulfide had an effect as reported, the ratio would decrease. It was observed that at lower temperatures, the presence of H_2S in the reactant did have an effect. For example, at 8.3 MPa and 285°C the methanol/ C_2^+ alcohol molar ratio dropped from 6.76 for no H_2S added to 3.76 when H_2S was added, as indicated in Table 2. The effect occurred immediately upon addition of the hydrogen sulfide, and it was accompanied by a small

TABLE 2. Alcohol Yields and Product Molar Ratios over the Cs/MoS_2 Catalyst from H_2/CO Synthesis Gas at GHSV = 7810 $\ell/\text{kg cat/hr}$.

Pressure (MPa)	Temp (°C)	H_2S (Y/N)	Methanol/ C_2^+ Alcohols	Hydrocarbon/ Alcohol	Alcohol Yield (g/kg cat/hr)
8.3	285	N	6.76	0.15	166.9
8.3	285	Y	3.76	0.23	151.0
8.3	300	Y	2.49	0.25	200.1
8.9	325	Y	2.35	0.45	213.4
8.9	340	Y	1.47	0.78	227.8
8.9	350	Y	1.43	0.73	236.2
10.3	285	N	2.46	0.39	82.0
10.3	325	N	1.50	0.38	119.6
10.3	325	Y	1.85	0.52	180.6
10.3	350	N	1.44	0.75	228.0
10.3	350	Y	1.53	0.63	236.2

decrease in the total alcohol yield and a small increase in the hydrocarbon/alcohol ratio. These changes were not systematic at higher temperatures and higher pressures, and should be investigated in better designed experiments in the future.

To probe the effect of residence time on the product yields and selectivities, different reactant flow rates were investigated at 10.3 MPa and 350°C with hydrogen sulfide in the gas stream. At the lowest flow rate with GHSV of 6500 ℓ /kg cat/hr at this high temperature and pressure, a high yield of methane relative to the alcohols was observed, Figure 3. However, as the flow rate was increased, an appreciate drop in methane yield occurred, and this resulted in an increased selectivity to alcohols.

Alcohols higher than ethanol were only observed at the highest temperature utilized. This might have been due to poor sensitivity of the gas chromatographic column used during this study, and a new column will be employed in the experiments to be carried out during the next quarter.

3. Temperature Dependence of the H₂S Effect

A series of additional experiments was carried out in which the effect of temperature on the product yields and selectivities in the presence or absence of H₂S in the synthesis gas reactant was investigated. Utilizing H₂/CO = 1/1 synthesis gas at 8.9 MPa and with a GHSV of 7810 ℓ /kg cat/hr, the reaction temperature was varied in the sequence 285, 300, 310, 340, and 350°C using the same catalyst from the previous experiments. Steady state testing at each temperature was generally maintained for 3-4 hr before changing the reaction conditions.

Upon initiating this series of experiments, it appeared that the catalyst has deactivated because the yields of the total alcohols, indeed for all the product components,

were substantially lower than in the initial experiments, e.g. compare Figure 4 with Figure 1. This apparent deactivation might be due to the higher temperature testing, i.e. 350°C, that had been carried out. During testing under lower temperature conditions, it had previously been shown that a 10 wt% K_2CO_3 doped Co-MoS₂ catalyst did not exhibit any deactivation during a 400 hr test at 8.3 MPa and 305°C with $H_2/CO = 0.96$ synthesis gas with GHSV = 3600 $\ell/kg\ cat/hr$, which involved intermittent testing to 325°C [5].

At each reaction temperature, steady state product analyses by gas chromatography were collected and averaged before, during, and after hydrogen sulfide addition to the synthesis gas. The effect of temperature on the total alcohol yield seemed to be more pronounced than the effect of the presence or absence of H_2S , as shown in Figure 4. However, as the total alcohol yield was increasing with increasing temperature, the selectivity toward methanol was decreasing, see Figure 5. At the same time, the overall selectivity to C_2^+ alcohols increased from 285°C to 300°C, but it then remained rather constant, as shown in Figure 6. The reason for this is the increasing yields of hydrocarbons with increasing temperature, and this is shown as the molar ratio of hydrocarbons to alcohols in Figure 7.

As was found in a previous experiment, the hydrogen sulfide had the strongest effect at lower temperatures, e.g. on the methanol/ C_2^+ alcohol ratio. The significant H_2S effect on increasing the yield of the C_2^+ alcohols relative to methanol at 285°C is shown in Figure 8. At higher temperatures, it appeared that the presence or absence of H_2S had less of an effect on the methanol/ C_2^+ alcohols molar ratio than did the temperature.

The H_2S hardly affected the carbon dioxide yield, while at higher temperatures the hydrogen sulfide tended to lower the total alcohol yield (Figure 4). Of note is that at the higher temperatures, the H_2S also tended to lower the methane production (Figure 9). This

causes a lowering of the hydrocarbon/alcohol molar ratio even though the total alcohol yield was also lowered. This effect would warrant further study if these high reaction temperatures were to be employed to achieve the higher C_2^+ alcohol/methanol ratio product composition. Without the presence of H_2S , the higher temperatures increase the yield of methane in a more pronounced manner.

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FIGURE 1. Product Yield vs Temperature
at 8.3 MPa with $H_2/CO = 1/1$ Synthesis
Gas with GHSV = 7810 l/kg cat/hr

**FIGURE 2. Product Selectivity as a
Function of Temperature at 8.3 MPa with
 $H_2/CO = 1/1$ with GHSV = 7810 l/kg cat/hr**

**FIGURE 3. Product Yields vs Reactant
Flow Rate at 350°C and 10.3 MPa in the
Presence of 45.5 ppm H₂S**

**FIGURE 4. Total Alcohol Yield vs
Temperature at 8.9 MPa and GHSV =
7810 l/kg cat/hr with H₂/CO = 1**

FIGURE 5. Dependence of the Methanol Selectivity on Reaction Temperature at 8.9 MPa and GHSV = 7810 l/kg cat/hr

**FIGURE 6. Selectivity of C_2^+ Alcohols
vs Temperature at 8.9 MPa and GHSV =
7810 l/kg cat/hr with $H_2/CO = 1$**

FIGURE 7. Hydrocarbon/Alcohol Molar Ratio from $H_2/CO = 1$ Synthesis Gas at 8.9 MPa and 7810 l/kg cat/hr

FIGURE 8. Methanol/C₂⁺ Alcohol Molar Ratio vs Temperature from H₂/CO = 1 at 8.9 MPa and 7810 l/kg cat/hr

FIGURE 9. Methane Yield vs Reaction Temperature with $H_2/CO = 1$ at 8.9 MPa and GHSV = 7810 l/kg cat/hr

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