Catalytic Testing of Cs/MoS_2 Catalysts

Air-Doped $CsOOCH/MoS_2$ = 20/80 wt% Catalyst. This testing program utilized the 20 wt% $CsOOCH/MoS_2$ catalyst that was doped in air as described in the Experimental Section. Three catalytic tests were carried out with this catalyst, and they consisted of the following:

1. Testing with $H_2/CO = 1/1$ synthesis gas,
2. Initial testing with synthesis gas containing 45.4 ppm H_2S, and
3. Temperature dependence of the H_2S effect.

A 1.5365 g portion of the calcined $CsOOCH/MoS_2$ = 20/80 wt% catalyst that was prepared in air 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. Pretreatment of the catalyst was carried out at 0.1 MPa by passing a 2.04/97.96 mol% H_2/N_2 mixture. After the flow rate of 60 ml/min 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 $H_2/CO = 1/1$ synthesis gas mixture and the reactor was then pressurized to 8.3 MPa. With the CO/H_2 synthesis gas at 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 9 and Figure 22, the catalyst was more active at higher temperatures and was more selective to alcohols than to hydrocarbons over the entire temperature range. As expected, as the temperature was increased the selectivity toward alcohols decreased, while the selectivity toward hydorcarbons increased, as shown in Figure 23, where the selectivities are expressed on a CO_2-free basis. This agrees with observations

FIGURE 22. Product Yield vs Temperature at 8.3 MPa with H_2/CO = 1/1 Synthesis Gas with GHSV = 7810 l/kg cat/hr

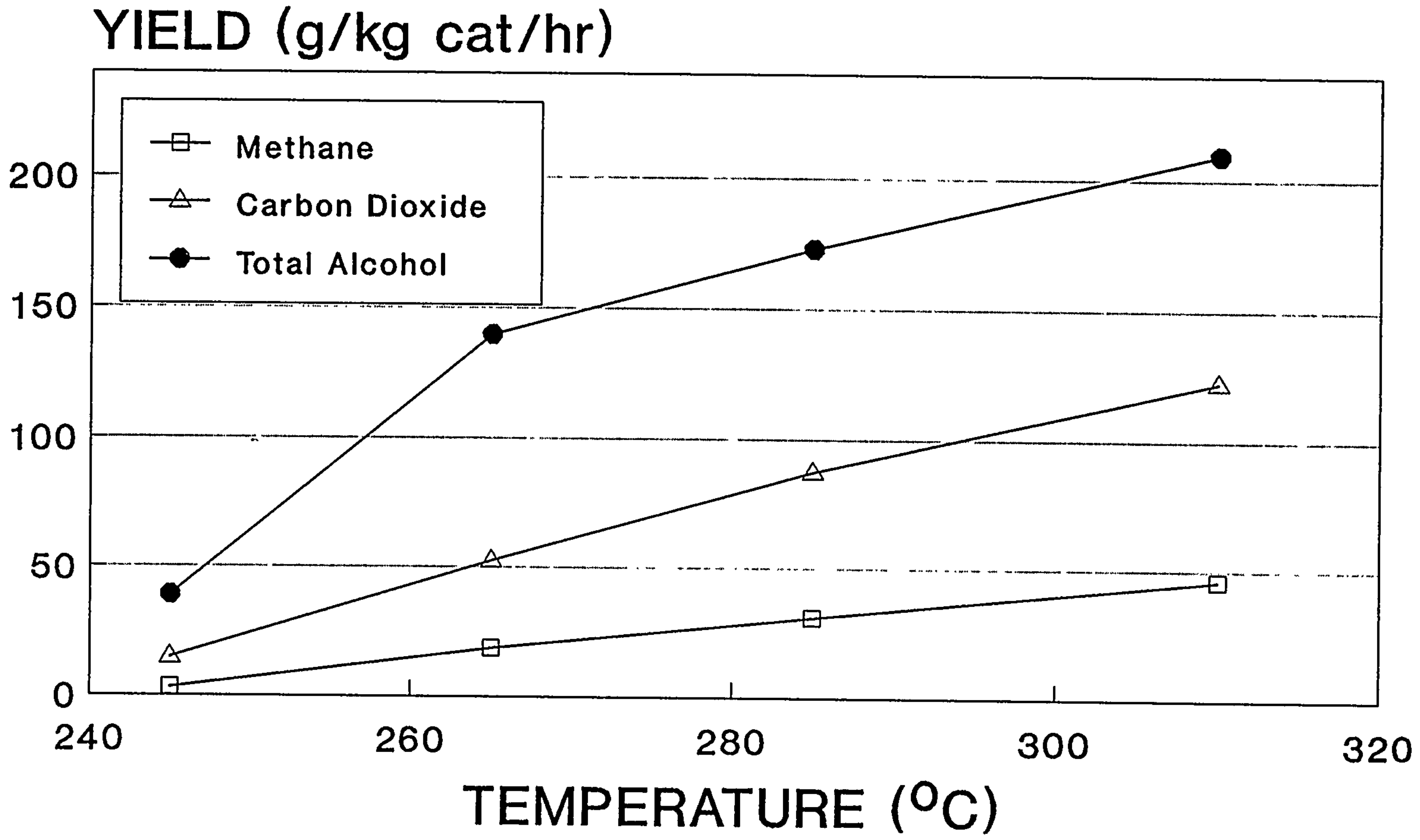
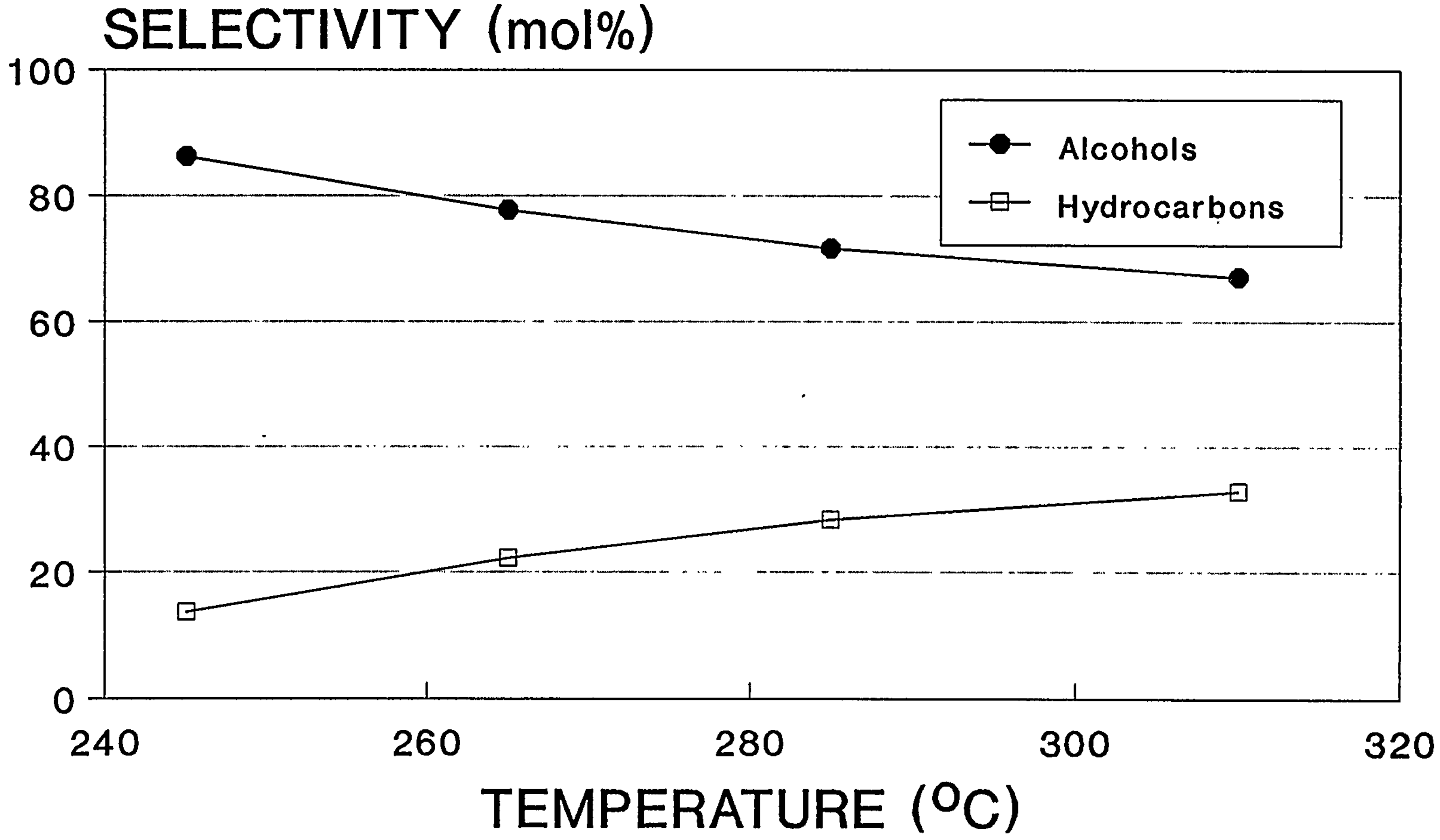


FIGURE 23. Product Selectivity as a Function of Temperature at 8.3 MPa with H_2/CO = 1/1 with GHSV = 7810 l/kg cat/hr



obtained in earlier work [11,65,87]. At the same time, the methanol/ethanol molar ratio decreased with increasing temperature, indicating that higher reaction temperatures enhance higher alcohol formation.

TABLE 9. Product space time yields (g/kg catal/hr) obtained over the 20 wt% $CsOOCH/MoS_2$ catalyst with H_2/CO = 1/1 synthesis gas at 8.3 MPa and with GHSV = 7810 ℓ/kg cat/hr.

Temp. (°C)	CH_4	CO_2	Methanol	Ethanol
245	3.1	14.2	38.9	0.0
265	18.6	52.6	107.9	31.8
285	31.0	87.5	120.7	52.2
310	46.0	122.5	138.0	71.6

The second part of the testing program with the 20 wt% $CsOOCH/MoS_2$ catalyst involved testing with synthesis gas containing 45.4 ppm H_2S. The purpose of this experiment was to investigate the report by Dow Chemical Co. [88] that hydrogen sulfide in the synthesis gas makes alkali promoted molybdenum disulfide alcohol synthesis catalysts more selective to higher alcohols, although the Cs-doped MoS_2 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 ℓ/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 10. The effect occurred immediately upon addition of the hydrogen sulfide, and it was accompanied by a small decrease in the total alcohol yield and a small increase in the hydrocarbon (HC)/alcohol ratio. These changes were not systematic at higher temperatures and higher pressures, and should be investigated in better designed experiments in the future.

TABLE 10. Alcohol Yields and Product Molar Ratios over the Cs/MoS_2 = 20/80 wt% Catalyst from H_2/CO = 1 Synthesis Gas at GHSV = 7810 ℓ/kg cat/hr.

Pressure (MPa)	Temp. (°C)	H_2S (Y/N)	Methanol/ C_{2+} Alcohols Ratio	HC/ Alcohol Ratio	Alcohol Yield (g/kg/hr)
8.3	285	N	6.76	0.15	167
8.3	285	Y	3.76	0.23	151
8.3	300	Y	2.49	0.25	200
8.9	325	Y	2.35	0.45	213
8.9	340	Y	1.47	0.78	227
8.9	350	Y	1.43	0.73	236
10.3	285	N	2.46	0.39	82
10.3	325	N	1.50	0.38	120
10.3	325	Y	1.85	0.52	181
10.3	350	N	1.44	0.75	228
10.3	350	Y	1.53	0.63	236

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 24. However, as the flow rate was increased, an appreciable drop in methane yield occurred, and this resulted in an increased selectivity to alcohols.

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 H_2S in the synthesis gas reactant was investigated. Utilizing $H_2/CO = 1/1$ 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 25 with Figure 22. 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-MoS_2 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 ℓ/kg cat/hr, which involved intermittent testing to 325°C [89].

At each reaction temperature, steady state product analyses by gas chromatography were collected and averaged before, during, and after hydrogen sulfide addition to the

FIGURE 24. Product Yields vs Reactant Flow Rate at 350°C and 10.3 MPa in the Presence of 45.5 ppm H_2S

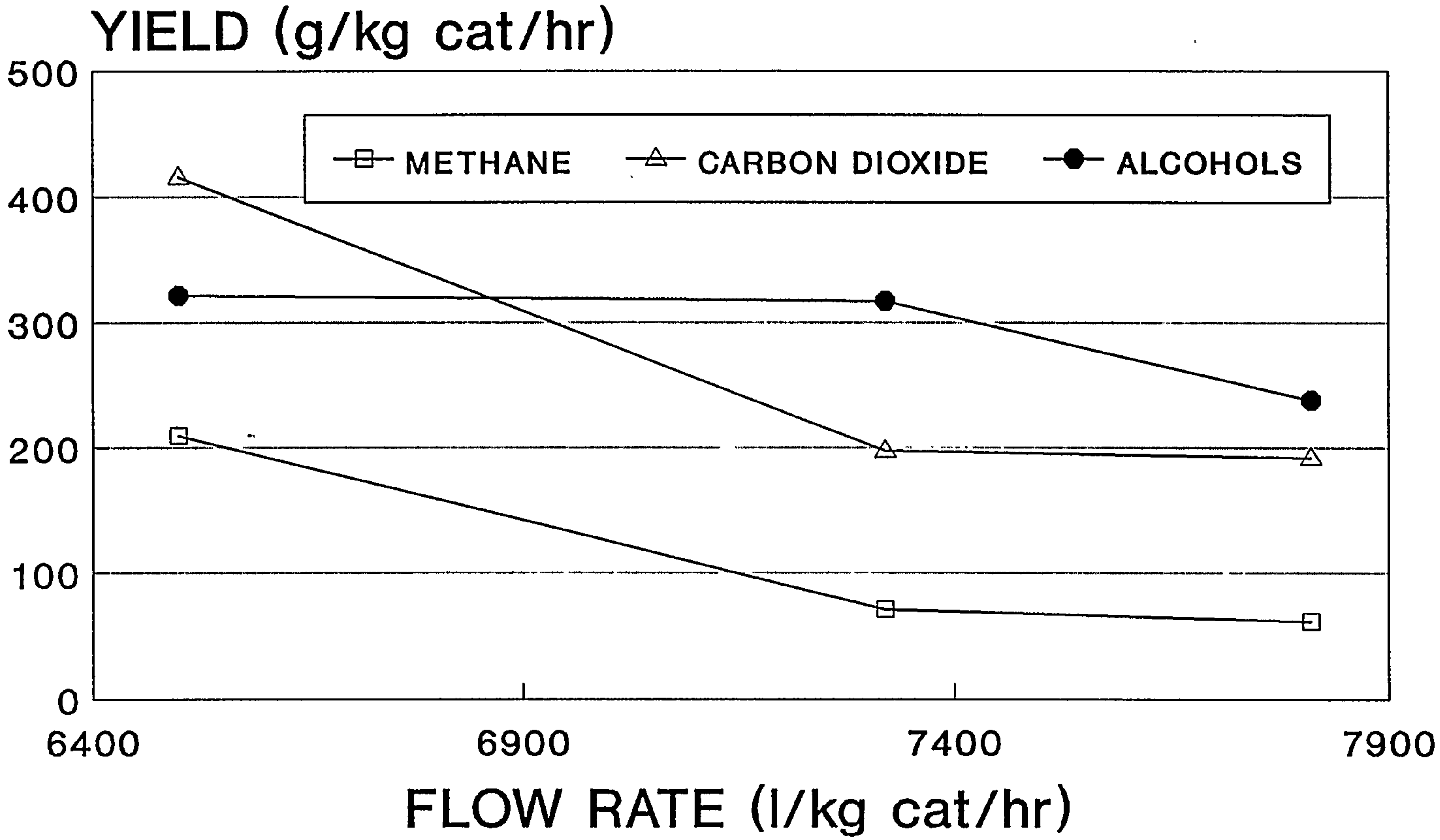
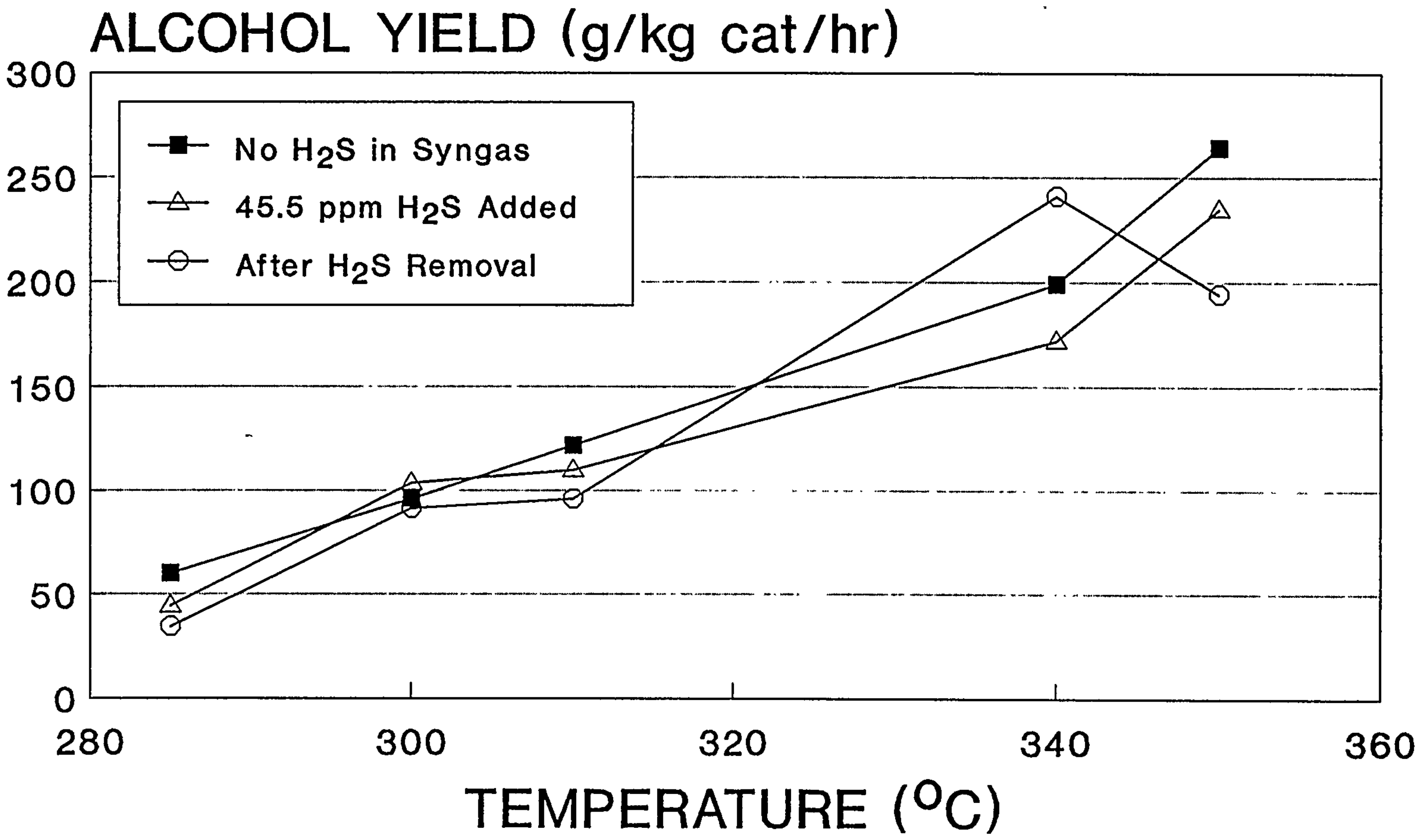


FIGURE 25. Total Alcohol Yield vs Temperature at 8.9 MPa and GHSV = 7810 l/kg cat/hr with $H_2/CO = 1$



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 25. However, as the total alcohol yield was increasing with increasing temperature, the selectivity toward methanol was decreasing, see Figure 26. 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 27. 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 28.

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 29. 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 25). Of note is that at the higher temperatures, the H_2S also tended to lower the methane production (Figure 30). This causes a lowering of the hydrocarbon/alcohol molar ratio even though the total alcohol yield was also lowered. This effect would warrent 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.

FIGURE 26. Dependence of the Methanol Selectivity on Reaction Temperature at 8.9 MPa and GHSV = 7810 l/kg cat/hr

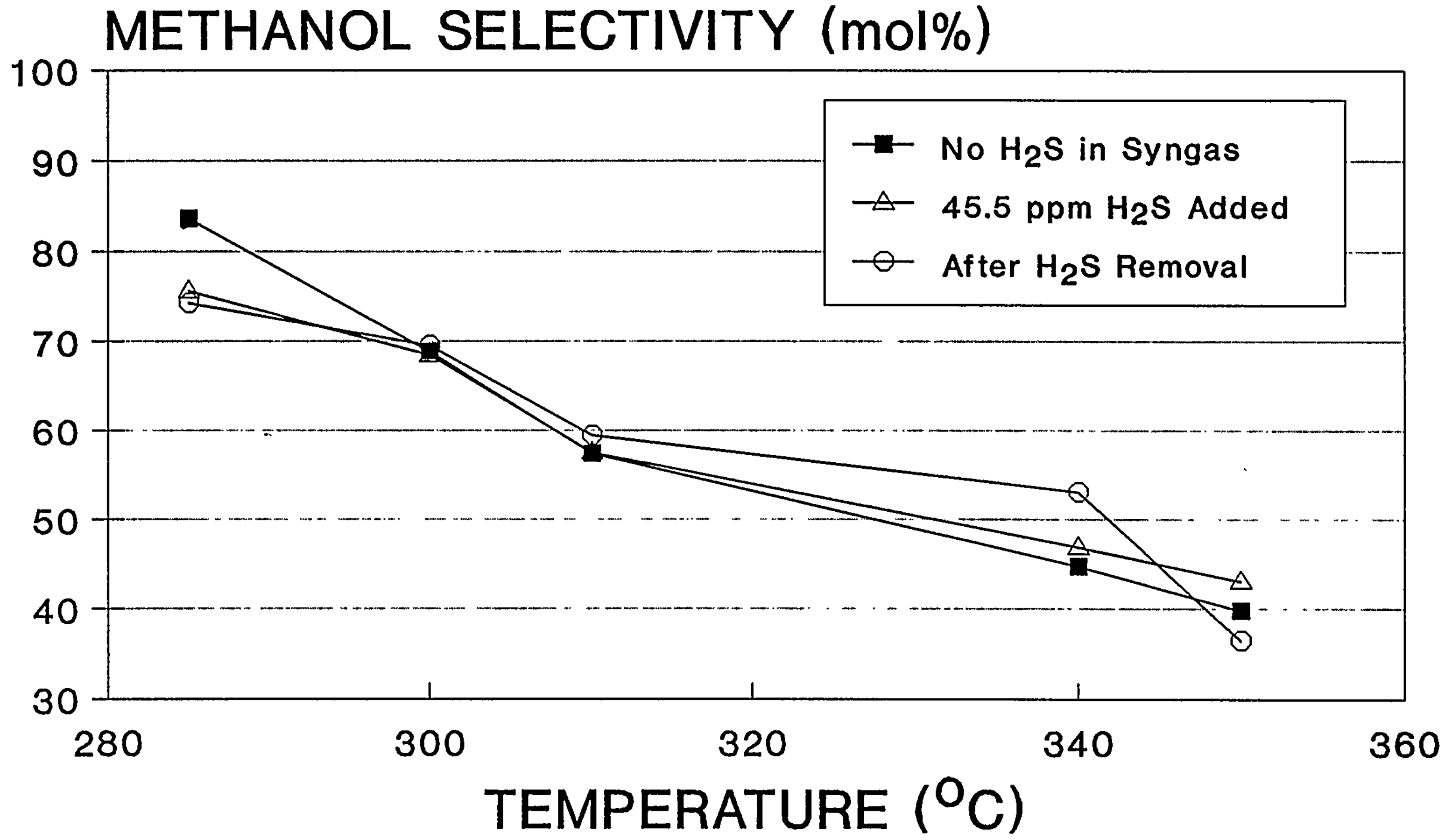


FIGURE 27. Selectivity of C_2^+ Alcohols vs Temperature at 8.9 MPa and GHSV = 7810 l/kg cat/hr with H_2/CO = 1

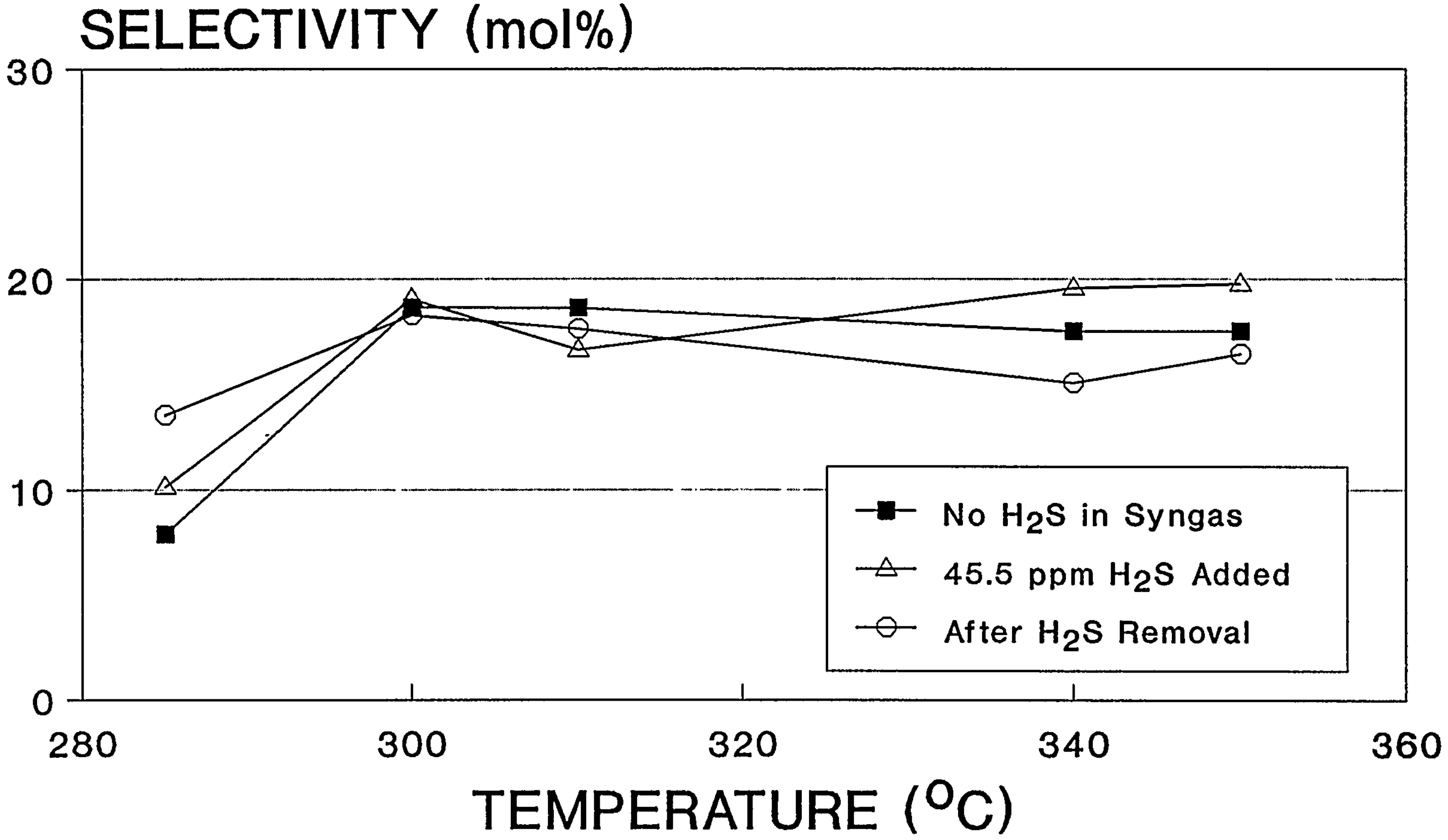


FIGURE 28. Hydrocarbon/Alcohol Molar Ratio from H_2/CO = 1 Synthesis Gas at 8.9 MPa and 7810 l/kg cat/hr

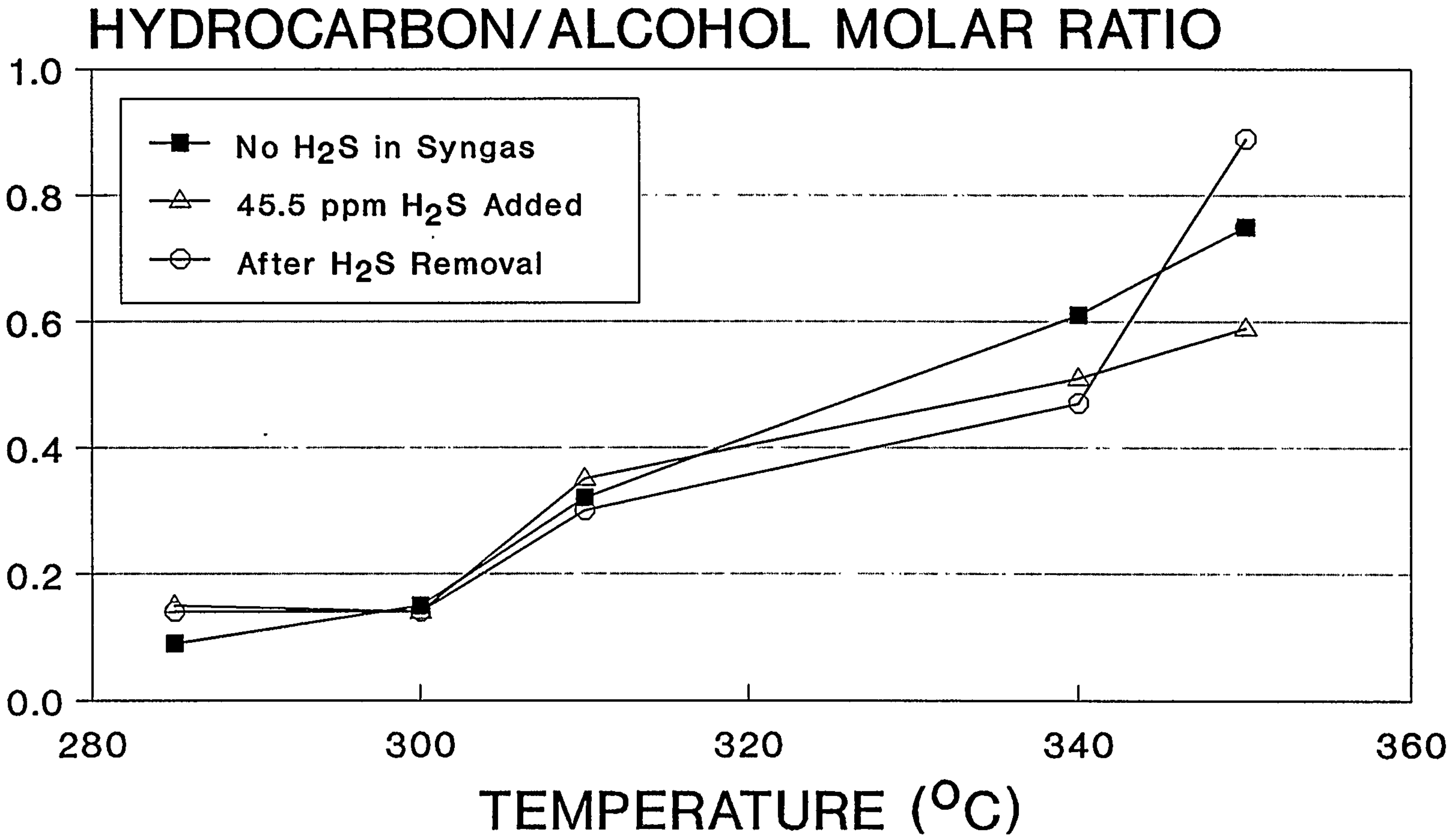


FIGURE 29. Methanol/C_2^+ Alcohol Molar Ratio vs Temperature from $H_2/CO = 1$ at 8.9 MPa and 7810 l/kg cat/hr

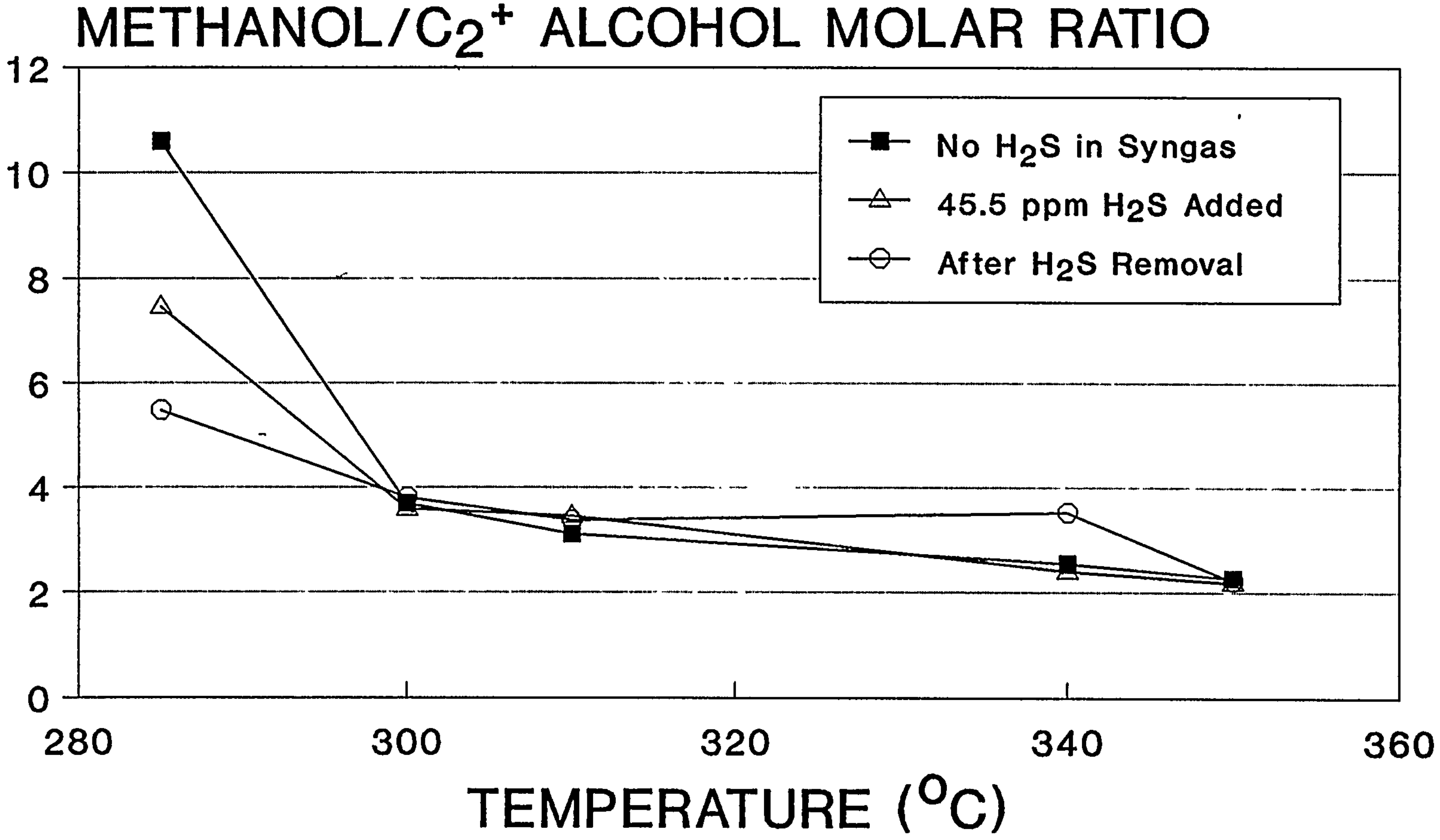


FIGURE 30. Methane Yield vs Reaction Temperature with $H_2/CO = 1$ at 8.9 MPa and GHSV = 7810 l/kg cat/hr