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# CATALYSTS FOR ALCOHOLS FROM BIOMASS

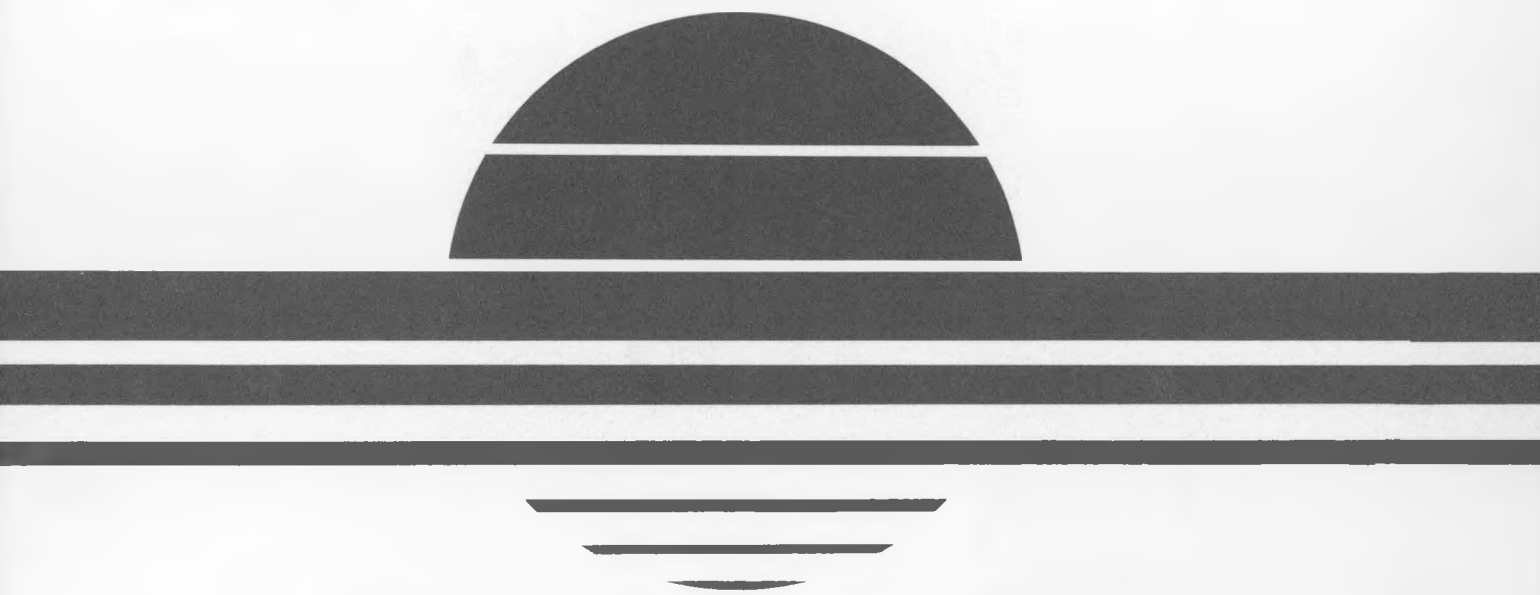
Final Technical Report for February 1980—January 1983

By
Kamil Klier
Richard G. Herman
Gary W. Simmons

March 1983

Work Performed Under Contract No. AC02-80CS83001

Lehigh University
Bethlehem, Pennsylvania





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# CATALYSTS FOR ALCOHOLS FROM BIOMASS


## ABSTRACT

Modification of the Cu/ZnO = 30/70 mol% methanol synthesis catalyst by incorporation of Mn, Fe, Co, Rh, and Pd by aqueous coprecipitation from nitrate solutions or by impregnation of the binary catalyst with metal carbonyls from organic media resulted in a lowering of the carbon conversion of synthesis gas to products. Of the coprecipitated ternary catalysts, the Fe/Cu/ZnO samples exhibited the largest change in selectivities, which was toward the formation of higher alcohols and hydrocarbons. It was demonstrated that the alcohols are formed as primary products and are produced at high rates over a Fe/Cu/ZnO catalyst containing 1 mol% iron than over Fischer-Tropsch catalysts. The catalysts that were prepared by impregnation of metal carbonyls onto the surface of reduced Cu/ZnO catalysts exhibited very low catalytic activities. However, it was shown that the activities of the Rh catalysts were increased by the utilization of elevated pressures.

The effects of $CO_2$ and $H_2O$ in the $H_2/CO$ synthesis gas on the methanol yield over the binary Cu/ZnO catalyst were investigated. A pronounced maximum in % carbon conversion to methanol was observed at low concentrations of both additives, and at higher concentrations the methanol synthesis activity was severely inhibited. A comparison of the two experiments clearly demonstrates that water behaved as a more effective promoter at low concentrations and a more severe retardant at high concentrations that did

carbon dioxide under the same experimental conditions. This indicates that $H_2O$ is directly influencing the methanol synthesis reaction rather than the $CO_2$ formed from it by the water gas shift reaction.

# CATALYSTS FOR ALCOHOLS FROM BIOMASS

## Final Technical Report

## OBJECTIVES

This research aimed at the investigation of catalysts for direct synthesis of light alcohols from synthesis gas produced by gasification of biomass. Such a synthesis gas often contains significant amounts of $CO_2$. While methanol synthesis is an established process, the direct catalytic synthesis of other light alcohols ($C_1$-$C_4$) poses a challenging task for catalyst development. The specific goals of this research are (A) to determine the factors influencing the varying performance of copper-based catalysts for methanol in feedstocks with varying concentrations of carbon dioxide, and (B) to develop catalysts for the synthesis of $C_2$-$C_4$ alcohols by such modifications of the methanol synthesis catalysts that promote carbon-carbon bond formation among the mono-carbon intermediates.

To achieve these goals, the research was divided into four tasks with the following objectives: (1) to determine whether the Ichikawa-type cluster rhodium supported catalysts would perform in methanol and ethanol synthesis with the desired activity and selectivity in the pressure range of 1-75 atm, and whether these catalysts could be further improved by the choice of a suitable support; (2) to develop a ternary Cu/ZnO-based catalyst that would produce alcohols with economically feasible rates at pressures of 10-50 atm; (3) to prepare fine dispersions of iron group metal catalysts with 2-100 atoms in the metal particles, and to determine the activity and selectivity of these catalysts in the synthesis gas reactions; and (4) to

characterize the state of dispersion of the catalysts and the metal-to-support interactions by scanning transmission electron microscopy, optical and X-ray photoelectron spectroscopy, and adsorption methods.

## TECHNICAL REPORT

To test the catalysts prepared during this research project, a new testing system was constructed. This system, shown schematically in Figure 1, is similar to our other existing catalyst testing unit that has been described elsewhere [1]. However, the new system contains a larger reactor that has a 0.75 inch i.d. diameter and a 150 mℓ volume. In addition, the gas flow control system consists of Linde electronic mass flow controllers rather than the pneumatic flow controllers that were utilized on our older unit. Chemical analyses of the products are carried out by means of an on-line Hewlett-Packard 5730A gas chromatograph equipped with an automated heated sampling valve, which is coupled with and controlled by a Model 5880A GC Integrator terminal. A cold trap sampling system is also provided, and the trapped products can be analyzed by means of a Finnegan GC/MS/Nova system. Late in the project, a Gibson high pressure pump was added to the synthesis gas inlet line near the reactor preheater zone so that water could be injected directly into the gas stream at 75 atm pressure.

### 1. Supported Rhodium Carbonyls for Alcohol Synthesis.

In 1978 it was reported that rhodium clusters supported on certain catalyst carriers selectively catalyze the synthesis of ethanol from CO + $H_2$ at subatmospheric pressures [2,3]. In an attempt to determine if the activity of these catalysts can be increased by

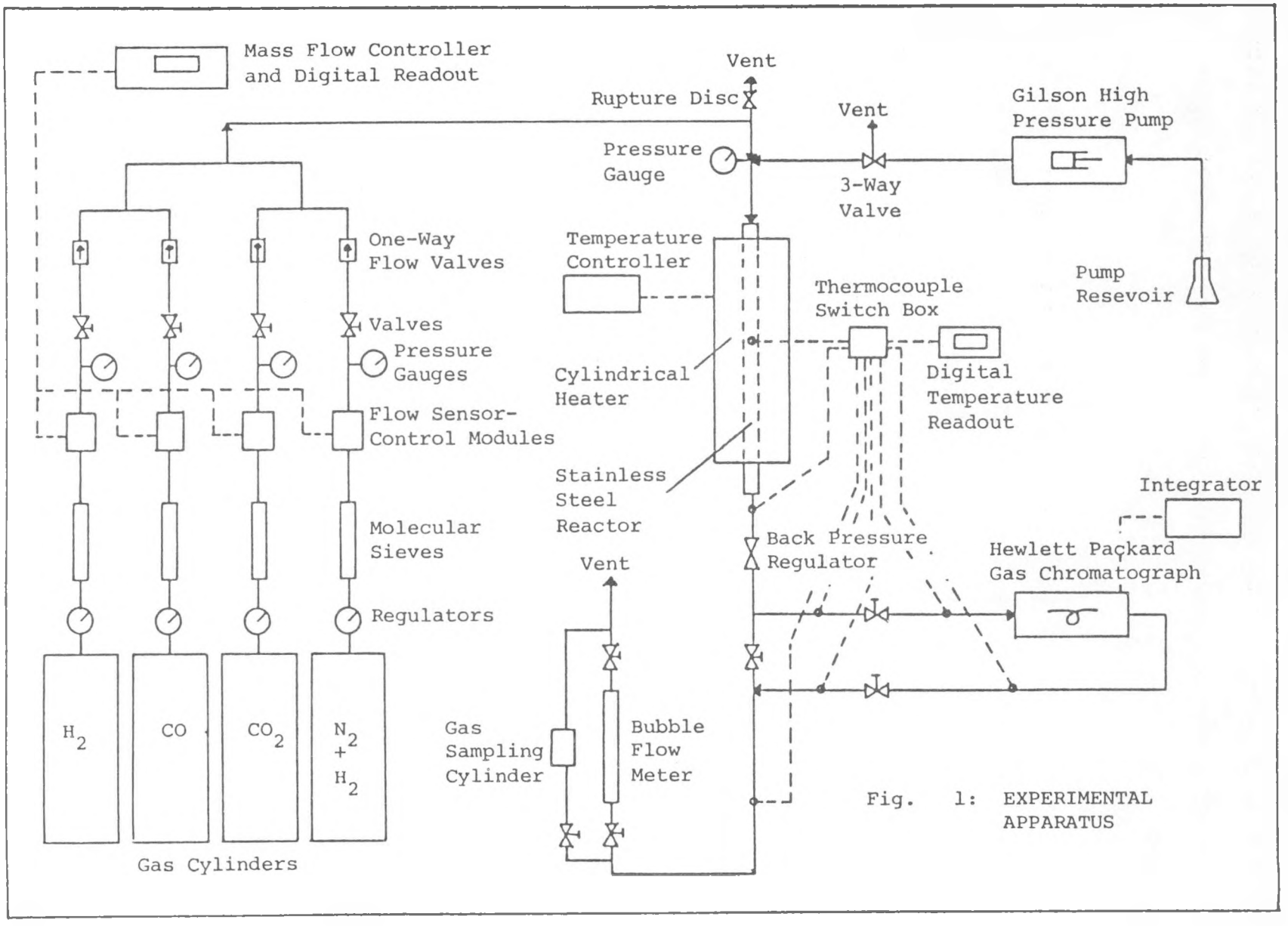



Fig. 1: EXPERIMENTAL APPARATUS

utilizing higher pressures, cobalt and rhodium carbonyl clusters have been placed on various catalyst supports by impregnation from tetrahydrofuran or n-hexane solution. Some of these experiments have been described previously [4,5].

The following $Rh_6(CO)_{16}$ impregnated catalysts have been prepared: Rh/CuO/ZnO, Rh/$LaB_6$, Rh/$TiO_2$, Rh/$La_2O_3$. The Cu/ZnO catalyst (30 wt% CuO and 70 wt% ZnO) was coprecipitated in the usual way [1] from the nitrate salts by sodium carbonate, calcined at 350°C, and pelletized to a 10-20 mesh size from an aqueous slurry prior to the Rh impregnation step. The other supports were commercial samples that were used in powder form, and the surface areas of $LaB_6$ (Alfa) and $TiO_2$ (Fisher) were found to be 14.5 and 112 $m^2/g$, respectively. The impregnation procedure was to dissolve the $Rh_6(CO)_{16}$ in dry tetrahydrofuran, add the catalyst support, and evaporate to dryness under ambient conditions. The $Rh_6(CO)_{16}$-to-support ratios (0.1-0.15 g/20 g) were similar to those utilized by Ichikawa [2].

Of these catalysts, only the Rh/Cu/ZnO catalyst containing 0.0174 g $Rh_6(CO)_{16}$ on 2.453 g CuO/ZnO exhibited a fairly high alcohol synthesis activity. This catalyst was tested with a synthesis gas mixture of $H_2/CO/CO_2$ = 70/24/6 vol% at 75 atm pressure and 250°C, which are our usual methanol synthesis screening conditions. Prior reduction in 2% $H_2$/98% $N_2$ was carried out at 250°C. The two gas hourly space velocities used were 3000 and 1500 $l/l$ of catalyst/hr. The results of these tests are presented in Table I. Each test was run under steady-state conditions for a minimum of 24 hours. The final used rhodium catalysts, when removed from the reactor under nitrogen, was pitch black, which is the expected color for

a very reactive Cu/ZnO methanol synthesis catalyst. Characterization of this catalyst by X-ray powder diffraction showed that the ZnO and Cu crystallite sizes were of the expected dimensions [6,7] of 13 and 8 nm, respectively. However, the presence of crystalline Rh was not detected by this technique.

A portion of the Cu/ZnO catalyst without rhodium was tested under the same experimental conditions as listed for Test 1 in Table I. The observed carbon conversion was 58% with a 100% selectivity to methanol. Table I shows that the Rh impregnation reduced the activity of the catalyst, but some formation of ethanol occurred. This selectivity can be compared with that observed by Ichikawa at 250°C on a $Rh_6(CO)_{16}$-ZnO catalyst in a recirculating system at near ambient pressure [2], for which no production of ethanol was detected.

Three other rhodium catalysts were prepared and tested for catalytic activity in which the rhodium precursor in each case was $Rh_4(CO)_{12}$. This complex was dissolved in n-hexane prior to deposition on the catalyst supports. The first preparation involved 2.45 g (3.4 mℓ) of CuO/ZnO = 30/70 mol% (10-20 Mesh), which was reduced using the usual procedure [1] and tested for methanol synthesis activity at 250°C and 75 atm with $H_2/CO/CO_2$ = 70/24/6 vol% synthesis gas. A carbon conversion to methanol of 57% was observed. The reactor was cooled and then opened in a nitrogen-filled glove bag. The Cu/ZnO catalyst was added to a beaker containing 40 mℓ n-hexane, in which 0.1263 g $Rh_4(CO)_{12}$ had been previously dissolved. The n-hexane was evaporated with the aid of a stream of nitrogen, and during this procedure, the sample was periodically stirred. When the catalyst was dry (after approximately 2.5 hr), it was diluted with 7 mℓ Pyrex beads and centered in the reactor, which was then

TABLE I

CATALYST: Rh/Cu/ZnO ATOMIC FORMULA: $ZnCu_{0.43}Rh_{0.005}$

PREP. METHOD: Coprecipitation of Cu and Zn from nitrates $Na_2CO_3$
Calcined at 350°C and pelletized from slurry
Impregnated with $Rh_6(CO)_{16}$ from tetrahydrofuran
Evaporated to dryness and reduced in 2% $H_2$/98% $N_2$ at 1 atm and 250°C

FEED: $H_2/CO = 2.92$ $CO_2$: 6 vol. %

BULK DENSITY: 0.49 g/cc

| TEST: | 1 | 2 |
|---|---|---|
| Avg. temp. °C | 250 | 250 |
| Pressure, psig | 1100 | 1100 |
| GHSV, ℓ/hr/kg cat. | 6120 | 3060 |
| CONVERSION: | | |
| ($CO+CO_2$), vol.% | 29 | 52 |
| CO, mol/hr/kg cat. | 21.6 | 19.4 |
| CO, kg/kg cat/hr | 0.61 | .54 |
| SELECTIVITY: | | |
| $CH_4$ | 3.2 | 1.8 |
| $CH_3OH$ | 94.5 | 96.5 |
| $C_2H_5OH$ | 1.3 | 1.3 |
| Other[a] | 1.0 | 0.4 |

[a]Include dimethyl ether and diethyl ether

sealed under nitrogen.

The reactor was pressurized with $H_2/CO/CO_2$ = 70/24/6 vol% synthesis gas and the flow rate was adjusted to 5840 ℓ/kg catalyst/hr. Heating to 225°C was carried out at about 3.5 °C/min. A rather low activity was observed, as shown in Table II. The carbon conversions in each test were constant, and the set of tests was obtained during 7 days of continuous operation. It is evident from Table II that longer gas residence times enhanced the yield of ethanol. No methane or ethane was detected.

Since the carbon conversions were so low and might be caused by blockage of surface sites on the Cu/ZnO support by the rhodium clusters, another catalyst was prepared that contained approximate one-half as much rhodium. The Cu/ZnO was from the same batch as that used for the first $Rh_4$/Cu/ZnO preparation, and it was reduced and tested using the same procedure as previously described. The results are presented in Table III. After testing, the reactor was opened in a $N_2$-filled glove bag, and the catalyst was added to 25 ml n-hexane in which 0.0632 g $Rh_4(CO)_{12}$ was dissolved. The solvent was evaporated, the catalyst was returned to the reactor, and the reactor was purged with nitrogen after being placed in the testing unit. The reactor was heated from ambient temperature to 180°C at the rate of 2.7°C/min and maintained at the latter temperature for 30 min, during which it was expected that the carbonyl groups would be removed from the tetrarhodium clusters. After cooling, the reactor was pressurized to 75 atm with hydrogen, and then a flow of $H_2/CO$ = 70/30 vol% was established. The catalytic results obtained at 250°C are tabulated in Table III. Higher carbon conversions and higher selectivities to

TABLE II

CATALYST: $Rh_4/Cu/ZnO$ ATOMIC FORMULA: $ZnCu_{0.43}Rh_{0.03}$

PREP. METHOD: Coprecipitation from Cu, Zn Nitrates with $Na_2CO_3$ Calcined, reduced, and tested. Under nitrogen, $Rh_4(CO)_{12}$ was deposited on Cu/ZnO from n-hexane

BULK DENSITY: 0.72 g/cc

| TEST: | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Feed, $H_2/CO/CO_2$ | a | a | a | b | b | c | b |
| Temp., °C | 225 | 250 | 250 | 250 | 250 | 250 | 250 |
| Pressure, psig | 1100 | 1100 | 1100 | 1100 | 1100 | 1100 | 1100 |
| GHSV, l/hr/kg | 5840 | 5840 | 2920 | 2410 | 780 | 5840 | 5840 |
| CONVERSION: | | | | | | | |
| $(CO+CO_2)$, vol% | 1.49 | 2.78 | 5.77 | 8.59 | 12.38 | 1.16 | 2.49 |
| CO, mol/hr/kg | 1.07 | 1.99 | 2.07 | 2.54 | 1.18 | 0.83 | 1.78 |
| CO, kg/kg/hr | 0.030 | 0.056 | 0.058 | 0.071 | 0.033 | 0.023 | 0.050 |
| SELECTIVITY(%) | | | | | | | |
| $CH_3OH$ | 99.1 | 99.4 | 96.1 | 96.3 | 96.8 | 99.0 | 100 |
| $C_2H_5OH$ | 0.9 | 0.6 | 3.9 | 3.7 | 3.2 | 1.0 | d |

[a] 70/24/6 vol%

[b] 70/28/2 vol%

[c] 70/29.99/0.01 vol%

[d] trace present

TABLE III

CATALYST: $Rh_4/Cu/ZnO$ ATOMIC FORMULA: $ZnCu_{0.43}Rh_{0.016}$

PREP. METHOD: Coprecipitation from Cu, Zn Nitrates with $Na_2CO_3$ Calcined, reduced, and tested. Under nitrogen, $Rh_4(CO)_{12}$ was deposited on Cu/ZnO from n-hexane. Carbonyl was decomposed at 185°C in flowing nitrogen.

BULK DENSITY: 0.70 g/cc

| TEST: | 1 | 2* | 3* | 4* |
|---|---|---|---|---|
| Feed, $H_2/CO/CO_2$ | 70/24/6 | 70/29.75/0.25 | 70/24/6 | 70/24/6 |
| Temp., °C | 250 | 250 | 250 | 250 |
| Pressure, psig | 1100 | 1100 | 1100 | 1100 |
| GHSV, $l$/hr/kg cat | 5510 | 6000 | 6000 | 6680 |
| CONVERSION: | | | | |
| $(CO+CO_2)$, vol% | 59 | 4.61 | 12.70 | 7.92 |
| CO, mol/hr/kg cat | 39.9 | 3.39 | 9.35 | 6.49 |
| CO, kg/kg cat/hr | 1.12 | 0.10 | 0.26 | 0.18 |
| SELECTIVITY: (%) | | | | |
| $CH_3OH$ | 100 | 99.6 | 99.6 | 99.7 |
| $C_2H_5OH$ | trace | 0.4 | 0.4 | 0.3 |

* After deposition of $Rh_4(CO)_{12}$

methanol were observed with this catalyst than with the previous catalyst, which contained more rhodium on the Cu/ZnO catalyst surface. Test 3 was run for 1 day and the $H_2O$ and $CO_2$ content of the exit gas indicated that the reverse water gas shift reaction was converting about 6.6% of the $CO_2$ in the inlet stream into CO. Test 4 proceeded for 3 days, during which lower methanol synthesis activity and lower reverse water gas shift activity was observed.

Since the catalytic activities of the rhodium doped Cu/ZnO catalysts prepared by deposition from organic solvents were much lower than those observed for the undoped materials, a check was made to see if the organic solvents could act to inhibit the activity. A fresh Cu/ZnO = 30/70 mol% sample (2.45 g) was reduced as usual and tested with $H_2/CO/CO_2$ = 70/24/6 vol% synthesis gas at 250°C, 75 atm, and GHSV = 6120 $\ell$/kg/hr. A "normal" carbon conversion to methanol of 59% was observed. The catalyst was removed from the reactor in a nitrogen-filled glove bag and was added to 40 m$\ell$ tetrahydrofuran. The solvent was evaporated with the aid of a flow of nitrogen, and the catalyst was placed back into the reactor. With the same reaction conditions as those given above, again the "normal" 57% carbon conversion to methanol was observed. Therefore, the solvent treatment of the catalyst does not adversely affect the catalyst in terms of activity or selectivity.

A final rhodium catalyst that was tested consisted of $Rh_4/LaB_6$. This material was prepared by dissolving 0.162 g $Rh_4(CO)_{12}$ in 50 m$\ell$ of n-hexane and adding 25 g $LaB_6$ (with a surface area of 14.5 $m^2/g$) to the continuously stirred solution. This procedure was carried out in a glove bag and nitrogen was bubled through the solution. The

n-hexane evaporated in 2 hr and the resultant powder was dried for an additional 45 min in the nitrogen atmosphere. The powder was divided into three samples, and a 6.964 g (3.8 mℓ) portion was diluted with Pyrex beads and centered in the reactor. The reactor was purged with nitrogen (60 mℓ/min) for 1 hr and then heated to 180°C at the rate of 1.7°C/min. After being held at 180°C for 2 hr, the reactor was cooled, pressurized, and tested with $H_2/CO$ = 70/30 vol%. The results are given in Table IV. A low carbon conversion was obtained, and the major product was methane. To verify that the catalytic activity was due to the rhodium, the experiment was repeated using only $LaB_6$. With no rhodium present on the catalyst support, no products were formed at temperatures up to 300°C.

Although it has been shown that $Rh_4/LaB_6$ is not an ethanol synthesis catalyst under the reaction conditions that were utilized, the conversion of CO to products was 59 mol/kg Rh/hr. This can be compared to the reported conversion at 245°C and 0.86 atm with $H_2/CO$ = = 2.25 over $Rh_4/MgO$ catalyst of 3 mol/kg Rh/hr, where the molar selectivity was 72% $CH_3OH$, 25% $CH_4$, 2% $C_2H_5OH$, and 1% higher molecular weight products [2]. Both of these catalysts are compared with a (Rh/Fe = 2.5/0.5)/$SiO_2$ catalyst [8,9] in Table V. It can be seen that the $Rh_4/LaB_6$ catalyst has an appreciable methanol synthesis activity for a rhodium catalyst when the yield is expressed in terms of kg of methanol/kg Rh/hr. However, all of these yields are very low when compared with the 1.1 kg/ℓ/hr yield observed with the Cu/ZnO = = 30/70 mol% catalyst [1].

TABLE IV

| | |
|---|---|
| CATALYST: | $Rh_4/LaB_6$ ATOMIC FORMULA: $LaB_6Rh_{0.007}$ |
| PREP. METHOD: | Under nitrogen, $Rh_4(CO)_{12}$ was deposited on $LaB_6$ from n-hexane. |
| BULK DENSITY: | 1.83 g/cc |
| TEST: | 1 |
| Feed, $H_2/CO/CO_2$ | 70/30/0 |
| Temp., °C | 250 |
| Pressure, psig | 1100 |
| GHSV, $l$/hr/kg cat | 2150 |
| CONVERSION: | |
| $(CO+CO_2)$, vol% | 0.80 |
| CO, mol/hr/kg cat | 0.21 |
| CO, kg/kg cat/hr | 0.006 |
| CO, kg/kg Rh/hr | 1.69 |
| SELECTIVITY (%): | |
| $CH_4$ | 76 |
| $CH_3OH$ | 24 |

Compared with other reported rhodium-based catalysts for alcohol synthesis, our highly dispersed rhodium catalysts show some promise. Therefore, work with these catalysts will be continued under other research projects, where the central theme will be catalytic methyl-transfer to produce higher carbon number alcohols.

TABLE V

Methanol and Methane Yields observed over Supported Rhodium Catalysts with a $H_2$ + CO Synthesis Gas

| Catalyst Composition | Temp (°C) | Pressure (atm) | Methanol Yield | Methane Yield | Reference |
|---|---|---|---|---|---|
| $Rh/LaB_6$ | 250 | 75 | 0.004[a]<br>0.15[c] | 0.0044[b]<br>0.19[d] | this work |
| Rh/MgO | 245 | 0.85 | 0.0002[a]<br>0.07[c] | 0.00015[b]<br>0.05[d] | 2 |
| $Rh/Fe/SiO_2$ | 300 | 68 | 0.02[a]<br>0.06[e] | | 8,9 |

[a] Methanol yield in kg/$\ell$ catalyst/hr

[b] Methane yield in kg/$\ell$ catalyst/hr

[c] Yield of methanol in kg/kg Rh/hr

[d] Yield of methane in kg/kg Rh/hr

[e] Yield of $CH_4$ + $CH_3OH$ + $C_2H_5OH$ + $C_2$ chemicals

2. Ternary Cu/ZnO-Based Catalysts.

Fe/Cu/ZnO. Deposition of metal carbonyls such as $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ onto Cu/ZnO catalysts by impregnation results in materials that exhibited poor-to-moderate catalytic activity and poor selectivity to ethanol and higher alcohols, as shown in the previous paragraph.

Since an ethanol synthesis catalyst will require a methyl-forming and -transferring agent, *iron* was chosen as an appropriate additive to methanol synthesis catalysts because it is the usual component in Fischer-Tropsch catalysts. Rather than depositing $Fe(CO)_5$ on the

surface of the binary Cu/ZnO catalyst, a series of Fe/Cu/ZnO catalysts were prepared by coprecipitation from nitrate solutions using our usual procedure [1] and 1.0 M $Na_2CO_3$ as the precipitating agent. After digesting the formed solid for 1 hr, during which the solution cooled from about 85°C to about 35°C, it was washed three times by decantation, filtered, and then washed with 10 portions of distilled water. After drying, the solid was calcined using the standard stepwise procedure [1] and pelletized from an aqueous slurry. Prior to catalytic testing, the catalyst was reduced in a flowing $H_2/N_2$ = 2/98 vol% gas stream at ambient pressure and 250°C until the complete disappearance of water from the exit gas, monitored by gas chromatography.

Initial testing of each catalyst was carried out with the $H_2/CO/CO_2$ = 70/24/6 vol% synthesis gas that is utilized for methanol synthesis. Some of the results of this testing are compiled in Table VI. It is evident that as the iron content of the catalysts increased, the over-all catalytic activity decreased and the yield of methanol declined. However, the production of $C_2$-$C_5$ alcohols increased, as did the yields of olefins.

TABLE VI

*Conversion of $H_2/CO/CO_2$ = 70/24/6 vol% Synthesis Gas to Products at 250°C, 75 atm, and GHSV = 5000 $hr^{-1}$*

| Cu/Zn/Fe (mol %) | 30/70/0.1 | 30/70/1 | 30/70/10 |
|---|---|---|---|
| Alcohol Yield ($kg/kg/hr \times 10^{-3}$) | 520 | 56.5 | 28.6 |
| $C_2$-$C_5$ Alcohol Yield ($kg/kg/hr \times 10^{-3}$) | 1.6 | 15.6 | 18.3 |
| Hydrocarbon Yield ($kg/kg/hr \times 10^{-3}$) | 11.2 | 85.7 | 65.2 |
| Alcohols/Hydrocarbons (mole ratio) | 38.9* | 0.51 | 0.31 |
| Olefins/Parafins (mole ratio) | 0 | 0.10 | 0.47 |

* This high alcohol/hydrocarbon mole ratio is due to the fact that the main product is methanol

The Cu/Zn/Fe = 30/70/1 mol% catalyst was studied in greater detail to determine the directions for catalyst optimization. The Schulz-Flory distribution for carbon-containing products formed from synthesis gas by a chain growth mechanism can be expressed by equation 1, where $W_f$ is the weight fraction of oligomers, $C_n$ is the

$$\log(W_f/C_n) = \log(Zn^2\alpha) + C_n \log \alpha \qquad (1)$$

carbon number of the compound formed, and $\alpha$ is the probability of chain growth. The Schulz-Flory distribution for the alcohols synthesized over this catalyst using the conditions given in Table VI is shown in Figure 2. The parameter $\alpha$ can be derived from both the slope and the intercept of the extrapolated line.[a] The small value of $\alpha$ indicates that termination of chain growth tends to be favored over polymerization. The Schulz-Flory distribution for the hydrocarbons is shown in Figure 3, and it can be seen that the $\alpha$ value is appreciably greater than that determined for the alcohol distribution. However, the value of 0.55 is less than the $\alpha$-value typically observed for a Fischer-Tropsch synthesis, e.g. 0.75. These experiments demonstrate that the addition of approximately 1 mol% iron to the Cu/ZnO catalyst decreases the catalytic activity of the catalyst for methanol and causes the formation of hydrocarbons, but it also leads to the formation of higher molecular weight alcohols (see Table VI). Since the $\alpha$-value for the alcohols is lower than the $\alpha$-value for the hydrocarbons, the alcohol $(C_1+C_2)/C_3^+$ ratio is higher than the same hydrocarbon ratio.

[a] A more appropriate distribution to be used here is the Flory distribution $\log (N/N_o) = \log (1-\alpha)^2 + (C_n-1)\log \alpha$, where N is the number of $C_n$ molecules formed and $N_o$ is the number of initial monomer units, because only short chains are produced. This distribution gives values of $\alpha$ comparable to those above.

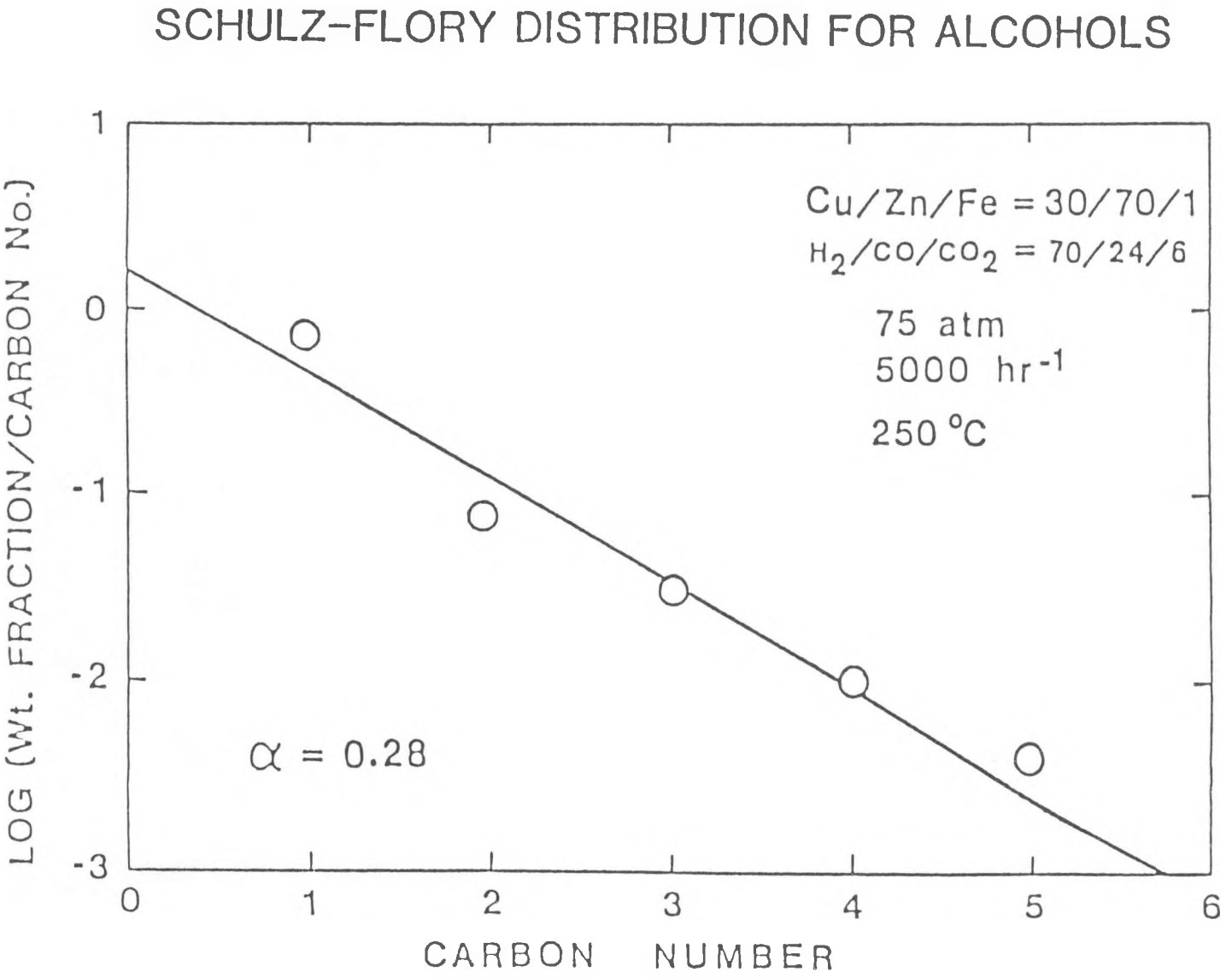

SCHULZ-FLORY DISTRIBUTION FOR ALCOHOLS
LOG (Wt. FRACTION/CARBON No.)
1
0
-1
-2
-3
0
1
2
3
4
5
6
CARBON NUMBER
Cu/Zn/Fe = 30/70/1
H2/CO/CO2 = 70/24/6
75 atm
5000 hr-1
250 °C
α = 0.28

Figure 2

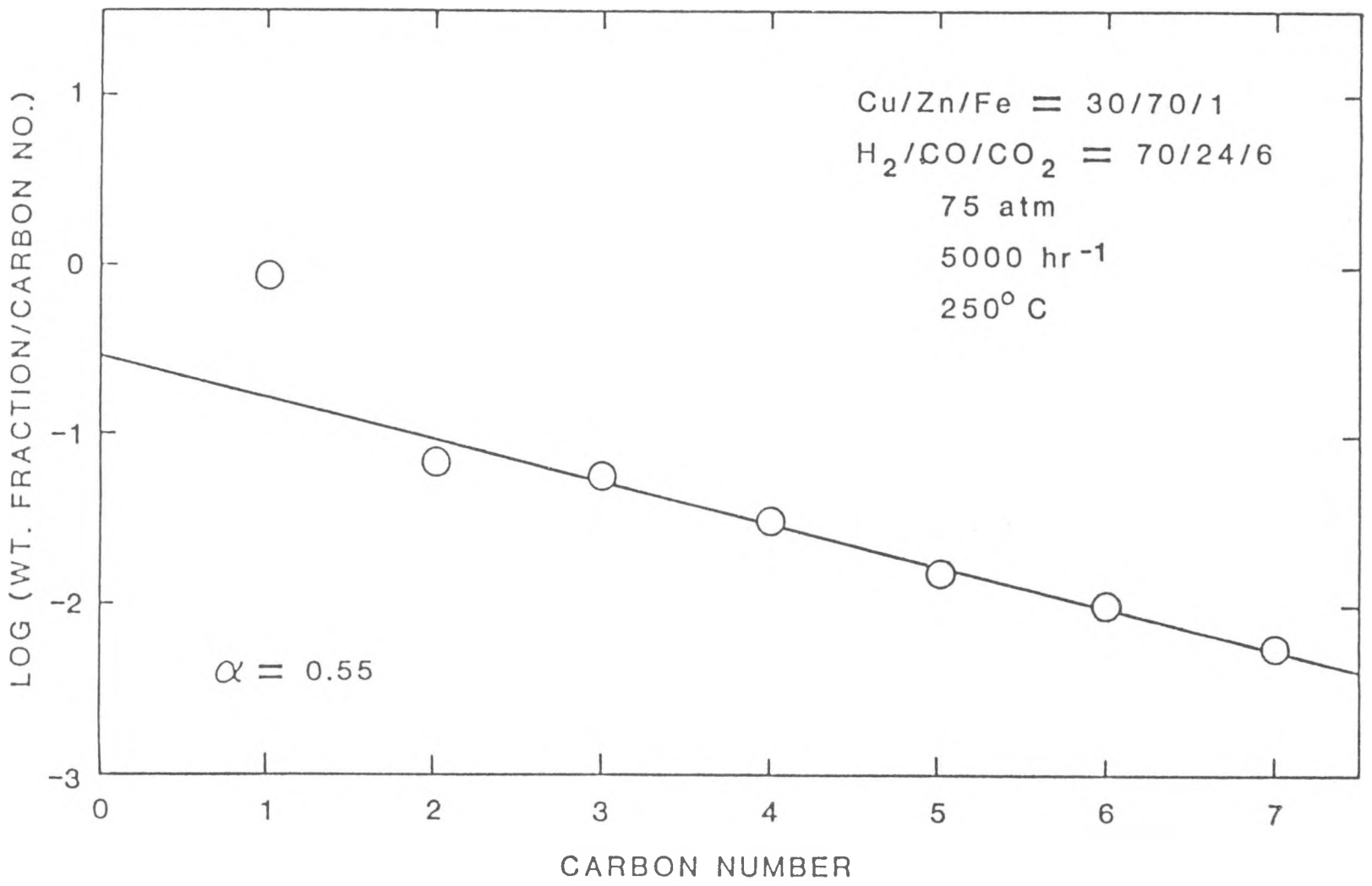

SCHULZ-FLORY DISTRIBUTION FOR HYDROCARBONS
Cu/Zn/Fe = 30/70/1
H2/CO/CO2 = 70/24/6
75 atm
5000 hr-1
250° C
α = 0.55
LOG (WT. FRACTION/CARBON NO.)
CARBON NUMBER
1
0
-1
-2
-3
0
1
2
3
4
5
6
7

Figure 3

The selectivity to higher alcohols relative to the methanol yield was hardly affected by varying the temperature in the range of 225-300°C with the $H_2/CO/CO_2$ = 70/24/6 vol% synthesis gas. However, with a $H_2/CO/CO_2$ = 70/28/2 vol% synthesis gas, the $C_2$-$C_5/C_1$ alcohol molar ratio showed an increasing trend as the temperature was increased from 220°C to 265°C, as illustrated in Figure 4. At the same time, the $C_2$-$C_7/C_1$ hydrocarbon molar ratio increased dramatically from approximately 0.14 to 1.0, while the alcohol/hydrocarbon molar ratio exhibited a maximum value of about 0.42 at 250°C. At this temperature, the $C_2$-$C_5/C_1$ alcohol ratio could be enhanced by lowering the reactor pressure, as shown in Figure 5. However, as the pressure was lowered, the catalytic activity decreased accordingly. This effect was more pronounced for the formation of alcohols than for the production of hydrocarbons. Therefore, the alcohols/hydrocarbons molar ratio decreased with decreasing pressure as shown in Figure 6, and this is caused by promotion of $C_2$-$C_7$ hydrocarbon formation relative to methane, methanol, and $C_2$-$C_5$ alcohols.

Total carbon conversion to hydrogen-containing products was a direct function of the gas hourly space velocity and contact time. An example is given in Figure 7 for the Cu/Zn/Fe = = 30/70/1 catalyst with a $CO_2$-free 1:1 $H_2/CO$ synthesis gas. Thus, the longer the synthesis gas was in contact with the catalyst, the greater was the yield of products. However, the faster the gas flow and the shorter the contact time (points labelled as 1 in Figures 7 and 8), the greater was the yield of alcohols relative to hydrocarbons. This observation indicates

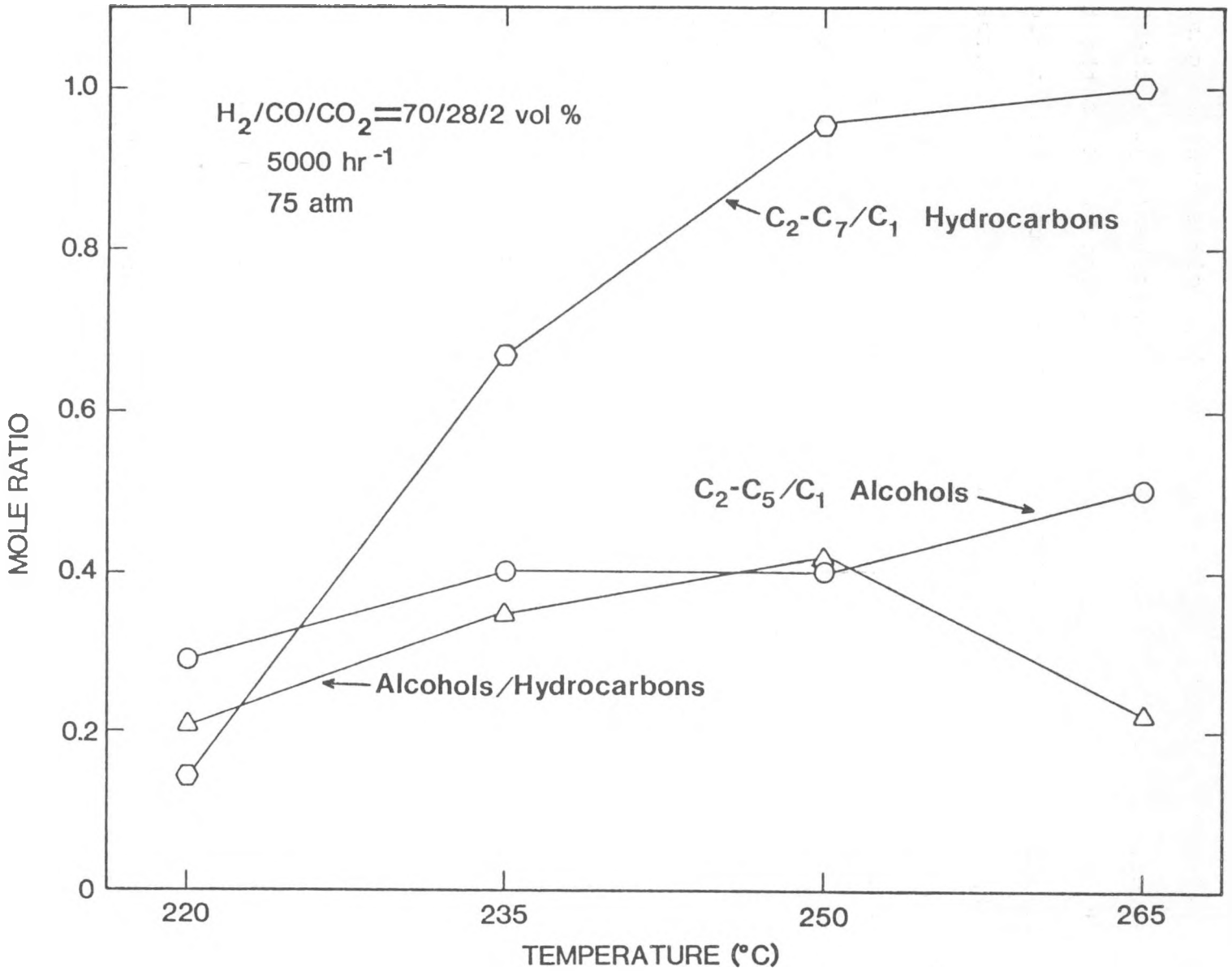

$H_2/CO/CO_2$=70/28/2 vol %
5000 hr$^{-1}$
75 atm
$C_2$-$C_7$/$C_1$ Hydrocarbons
$C_2$-$C_5$/$C_1$ Alcohols
Alcohols/Hydrocarbons
MOLE RATIO
1.0
0.8
0.6
0.4
0.2
0
220
235
250
265
TEMPERATURE (°C)

FIGURE 4

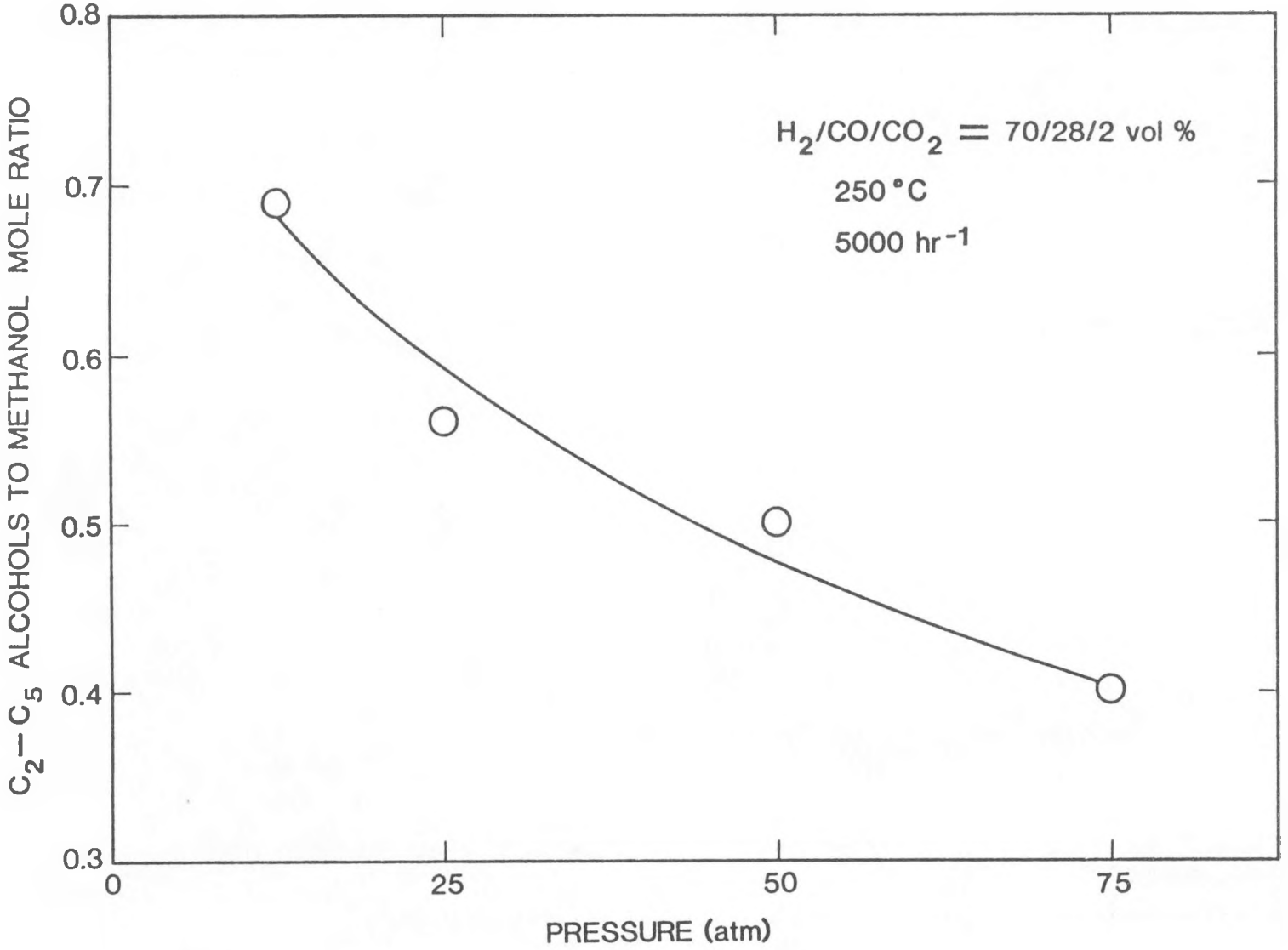

0.8
0.7
0.6
0.5
0.4
0.3
0
25
50
75
$C_2 - C_5$ ALCOHOLS TO METHANOL MOLE RATIO
PRESSURE (atm)
$H_2/CO/CO_2$ = 70/28/2 vol %
250 °C
5000 $hr^{-1}$

FIGURE 5

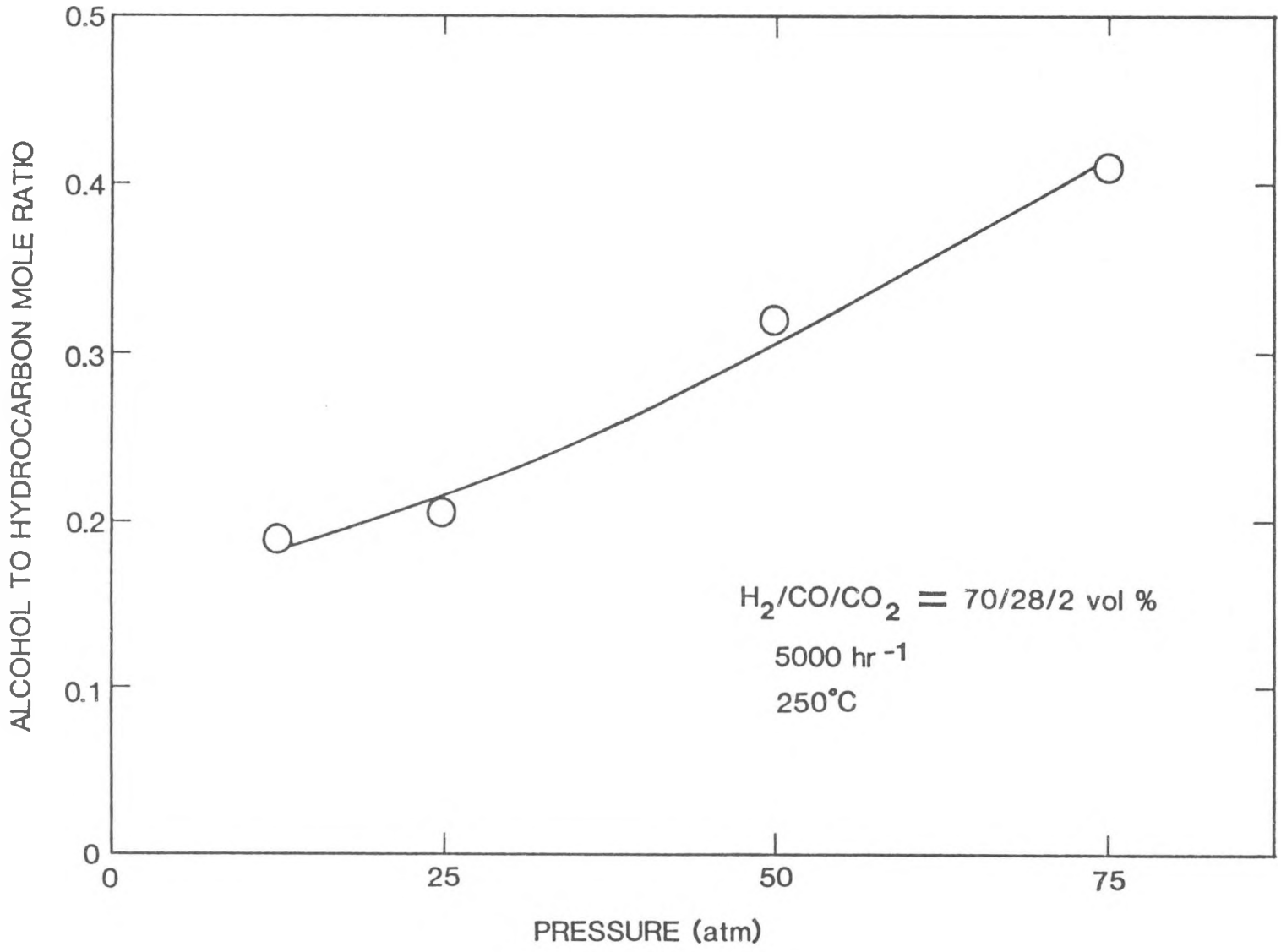

ALCOHOL TO HYDROCARBON MOLE RATIO
0.5
0.4
0.3
0.2
0.1
0
0
25
50
75
PRESSURE (atm)
H2/CO/CO2 = 70/28/2 vol %
5000 hr -1
250°C

FIGURE 6

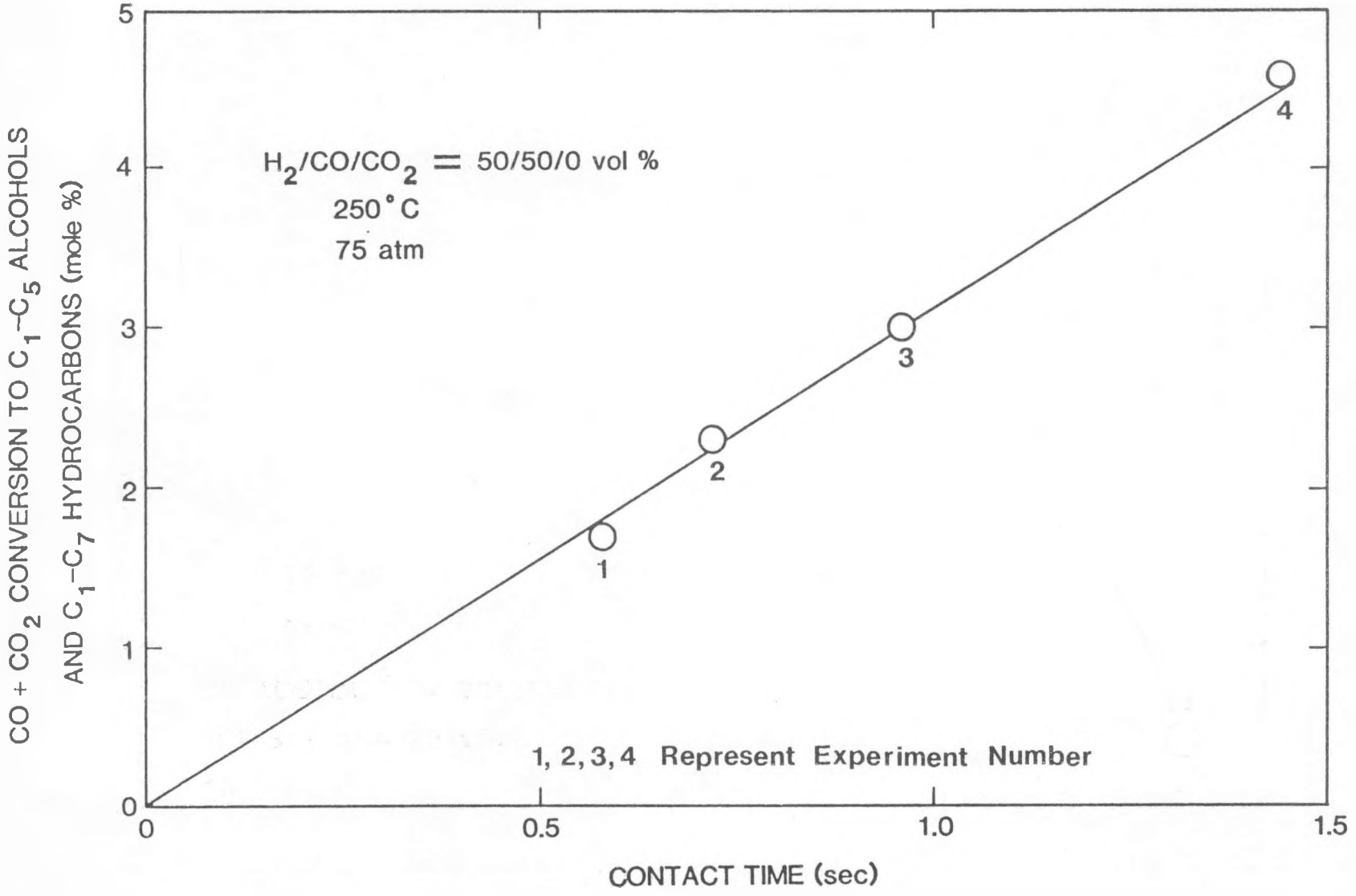

CO + CO2 CONVERSION TO C1–C5 ALCOHOLS
AND C1–C7 HYDROCARBONS (mole %)
H2/CO/CO2 = 50/50/0 vol %
250°C
75 atm
1, 2, 3, 4 Represent Experiment Number
CONTACT TIME (sec)
0
0.5
1.0
1.5
1
2
3
4
5

FIGURE 7

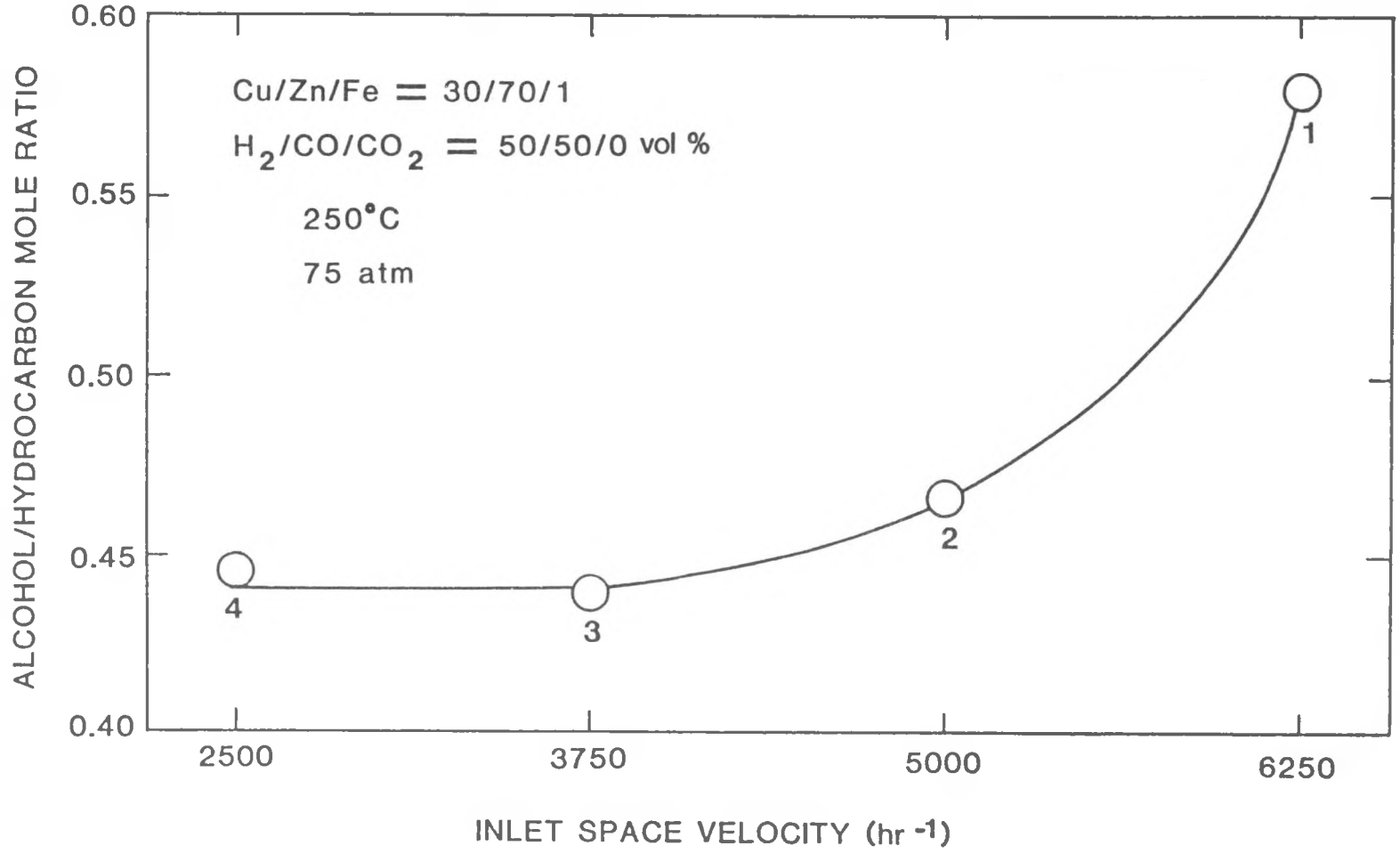

0.60
0.55
0.50
0.45
0.40
ALCOHOL/HYDROCARBON MOLE RATIO
Cu/Zn/Fe = 30/70/1
H2/CO/CO2 = 50/50/0 vol %
250°C
75 atm
1
2
3
4
2500
3750
5000
6250
INLET SPACE VELOCITY (hr -1)

FIGURE 8

that alcohols are primary products formed from the synthesis gas; they are not secondary products formed from the hydrocarbons.

It should be pointed out that the iron in these catalysts is in a highly dispersed state. Even in the calcined catalysts, iron compounds are not detected by X-ray powder diffraction. In the catalytically tested catalysts, the presence of iron is not detected by Auger spectroscopy, but this technique demonstrated that a large amount of carbon is on the surface of the catalyst. Auger lines for copper, zinc, and oxide are present, and scanning Auger micrographs show that copper is highly dispersed over the catalyst.

Mn/Cu/ZnO. Another transition metal ion, in addition to iron, that can behave as a catalyst modifier is *manganese*. Therefore, a MnO/CuO/ZnO = 8/27/65 wt% catalyst was synthesized in an inert environment from the nitrate salts. The usual preparation techniques were employed [1], and the dried catalyst precursor was calcined to 350°C in a nitrogen atmosphere. The catalyst was pelletized under nitrogen from an aqueous slurry that was prepared with degassed distilled water. After drying, 2.45 g of the catalyst (10-20 Mesh) was charged to the reactor in a nitrogen filled glove-bag. The catalyst was reduced at 250°C with a $H_2/N_2$ = = 2/98 vol% gas mixture for the period of time that was sufficient to reduce the CuO to Cu. After cooling, the reactor was pressurized to 75 atm with $H_2/CO/CO_2$ = 70/24/6 vol% synthesis gas, and the flow rate was adjusted to 6120 $\ell$/kg catalyst/hr. The reactor was heated to 250°C, and the initial catalytic activity during the first few hours of testing corresponded to 29.6% carbon conversion

to methanol, as illustrated in Table VII. A gradual decrease in the activity was noted for about 100 hr, at which time a rather steady conversion was observed. Decreasing the $CO_2/CO$ ratio in the synthesis gas led to an increase in methanol yield, which was constant during the 12 hr test. At the same time, the yield of water, produced by ethanol formation and the reverse water gas shift reaction, decreased by approximately 50%.

The synthesis gas flow was stopped (GHSV < 40 $\ell$/hr/kg cat) for approximately 10 hr while maintaining all other reaction conditions. Analyses every 75 min by gas chromatography demonstrated that $H_2$ was gradually depleted from the synthesis gas in the system and the $CO_2/(CO+CH_3OH)$ ratio remained relatively constant. Re-establishing the gas flow resulted during the first 20 min in an excess of $CO_2$ in the exit gas, traces of methane, ethane, and ethanol in the exit gas, and enhancement of the yield of methanol. After that short period of time, the $CO_2$ concentration decreased such that $H_2/CO/CO_2$ = 70/28.4/1.6 vol% and the traces of the minor products listed above disappeared. However, the methanol yield remained high and constant. It is evident that the treatment at 250°C with the $CO/CO_2$ = 93/7 vol% gas mixture benefitted the catalyst by increasing the methanol synthesis activity.

Further examination of this catalyst involved altering the $CO_2$ content in the synthesis gas as described for tests 5 and 6 in Table VII. The final test duplicates test 2 and demonstrates that the catalyst had not irreversibly deactivated. Although the selectivity of this ternary catalyst was very high, its activity was

TABLE VII

CATALYST: Mn/Cu/ZnO ATOMIC FORMULA: $ZnCu_{0.43}Mn_{0.14}$

PREP. METHOD: Coprecipitation from nitrate solution with $Na_2CO_3$ Calcined at 350°C under nitrogen. Reduced at 250°C with 2% $H_2$/98% $N_2$

BULK DENSITY: 0.82 g/cc

| TEST: | 1 | 2[a] | 3[b] | 4[c] | 5[d] | 6 |
|---|---|---|---|---|---|---|
| Feed, $H_2/CO/CO_2$ | 70/24/6 | 70/24/6 | 70/28/2 | 70/28.4/1.6 | 70/30/0 | 70/24/6 |
| Temp., °C | 250 | 250 | 250 | 250 | 250 | 250 |
| Pressure, psig | 1100 | 1100 | 1100 | 1100 | 1100 | 1100 |
| GHSV, l/hr/kg cat | 6120 | 6120 | 6120 | 6120 | 6120 | 6120 |
| CONVERSION: | | | | | | |
| (CO + $CO_2$), vol% | 29.6 | 9.1 | 20.7 | 35.6 | 12.6 | 10.5 |
| CO, mol/hr/kg cat. | 22.2 | 6.8 | 15.6 | 26.7 | 9.5 | 7.9 |
| CO, kg/kg cat/hr | 0.62 | 0.19 | 0.44 | 0.75 | 0.27 | 0.22 |
| SELECTIVITY (%): | | | | | | |
| $CH_3OH$ | 99.8 | 99.8 | 99.9 | 100.0 | 100.0 | 100.0 |
| $C_2H_5OH$ | 0.2 | 0.2 | 0.1 | 0.0 | 0.0 | 0.0 |

[a] After continuous testing for 115 hr

[b] Constant yield for 12 hr

[c] Gas flow was stopped for 10 hr prior to this test

[d] Constant yield for 21 hr following a 20 hr equilibration period

significantly lower than the parent Cu/ZnO catalyst. The comparisons at steady state conversions at 250°C are shown in Figure 9.

The low methanol synthesis activity of the Mn/Cu/ZnO catalyst is not a function of a physical alteration of the basic Cu/ZnO catalyst. The BET surface area of the tested ternary catalyst, as determined by argon adsorption at -195°C, was 36.7 $m^2/g$, as compared with 40 $m^2/g$ for a tested sample of the binary Cu/ZnO catalyst. X-Ray powder diffraction patterns demonstrated that severe sintering did not occur and that the Cu and ZnO crystallite sizes were of the order of 8 and 13 mn, respectively. Auger spectra of the calcined and the tested managnese-containing catalysts were more-or-less identical with the triplet for Mn centered at 580 eV and having intensities, relative to the Cu and Zn line intensities, corresponding to the Mn bulk concentration. However, the X-ray photoelectron spectra (XPS) of the calcined and the tested catalysts did not exhibit lines for Mn. The XPS spectrum obtained with the calcined sample indicated that a small quantity of carbon was present, while the spectrum for the tested catalyst contained a sharper C 1s line (as well as more intense lines due to Cu $2p\frac{1}{2}$ and Cu $2p\frac{3}{2}$). These observations might indicate that the manganese moiety was covered by carbon. However, it is expected that the manganese is present as MnO since the standard reduction potentials for the reaction $M^{2+} + 2e^- \quad M°$ with $Mn^{2+}$, $Zn^{2+}$, and $Cu^{2+}$ are -1.029, -0.7628, and +0.3402 V, respectively, and it is known that at least part of the copper can be reduced to the metallic state under reduction and testing conditions, while the zinc is not [1,6,7].

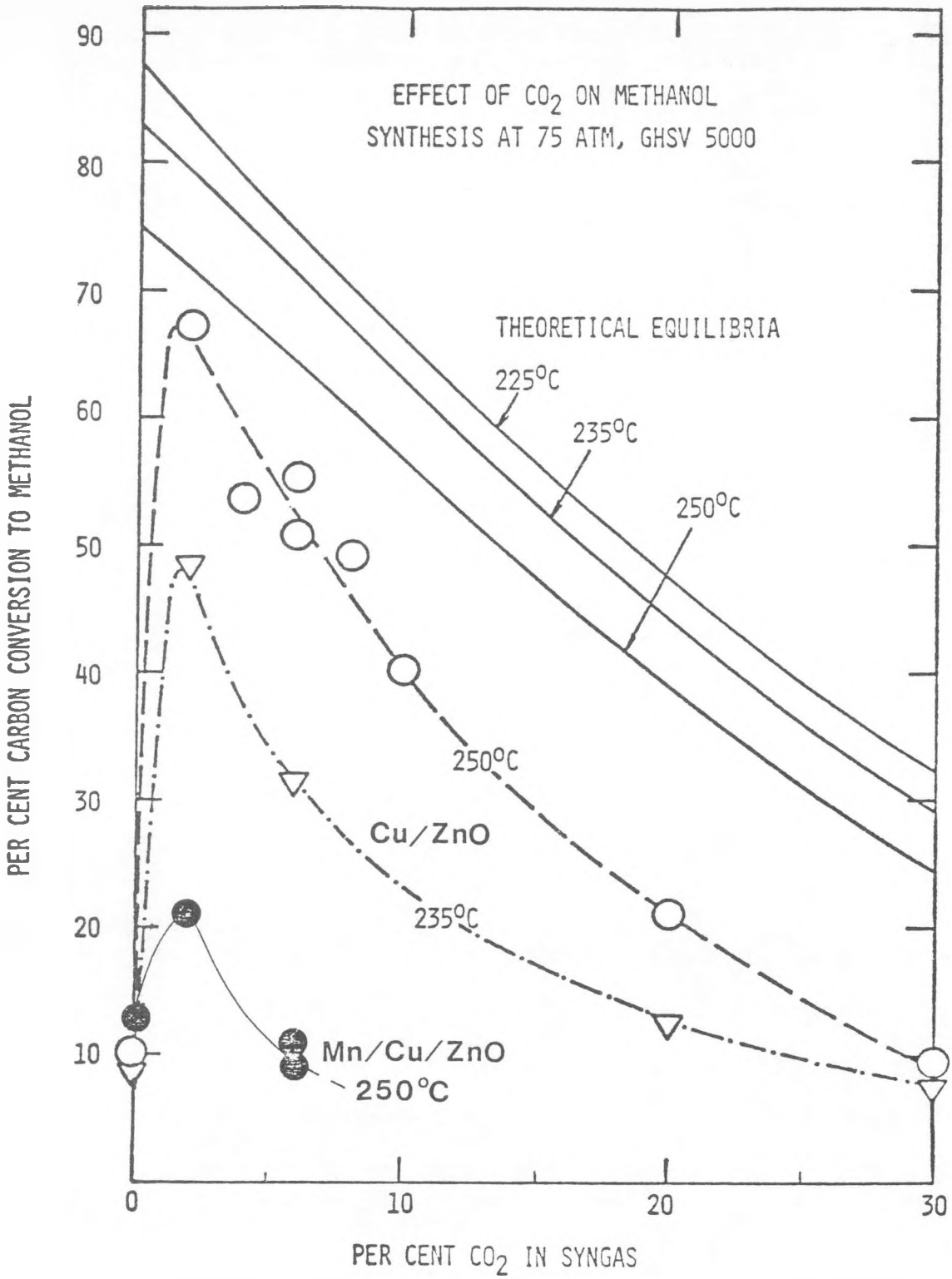



FIGURE 9. The effect of carbon dioxide on the formation of methanol from $H_2/(CO + CO_2)$ = 70/30 vol% synthesis gas over a Cu/ZnO = 30/70 mol% catalyst (open symbols) and a Mn/Cu/Zn = 8/27/65 mol% catalyst (solid circles).

Pd/Cu/ZnO. Another approach to synthesizing $C_2^+$ alcohols is to combine the Cu/ZnO catalyst with an additive that is a known catalyst for methanol synthesis, but which usually operates in a non-selective manner. It has been demonstrated that *palladium* supported on silica behaves as a methanol synthesis catalyst [10]. However, the formation of methanol is very sensitive to the choice of the palladium carrier [11], and depending on the support that is utilized, fairly high yields of $CH_3OCH_3$, $CH_4$, and $C_2^+$ can be generated [12,13]. Therefore, Pd/ZnO and Pd/Cu/ZnO catalysts were prepared and tested in this project.

The Pd/Cu/ZnO = 27/64/9 mol% catalyst was prepared by co-precipitation from nitrate solution by the addition of 1.0 M $Na_2CO_3$ using the standard procedure [1]. After calcination and pelletization, 2.627 g of the oxides were loaded into the reactor and reduced with the $H_2/N_2$ = 2/98 vol% reducing gas mixture. Subsequent catalytic testing was carried out at 250°C and the resultant activity and selectivity data are tabulated in Table VIII. During the reactor start-up, the reactor was pressurized with $H_2/CO/CO_2$ = 70/24/6 vol%, the GHSV was set at the designated flow rate of 5000 $hr^{-1}$, and the temperature was increased from ambient to 250°C at the rate of approximately 3.5°C/min. During the heating process, catalytic conversion of CO was initiated with the production of methanol and methane. As the catalyst bed temperature passed through the 220-230°C range, a carbon conversion of about 3.5% was observed and the product, exclusive

TABLE VIII

CATALYST: Pd/Cu/ZnO ATOMIC FORMULA: $ZnCu_{0.43}Pd_{0.14}$

PREP. METHOD Coprecipitation from nitrate solution with $Na_2CO_3$ Calcined at 350°C, pelletized, and reduced at 250°C with 2% $H_2$/98% $N_2$

BULK DENSITY: 0.88 g/cc

| TEST: | 1 | 2 | 3 |
|---|---|---|---|
| Feed, $H_2/CO/CO_2$ | 70/24/6 | 70/30/0 | 70/28/2 |
| Temp., °C | 250 | 250 | 250 |
| Pressure, psig | 1100 | 1100 | 1100 |
| GHSV, $\ell$/hr/kg cat | 5710 | 5710 | 5710 |
| CONVERSION: | | | |
| (CO + $CO_2$) vol% | 10.48 | 4.46 | 17.85 |
| CO, mol/hr/kg cat | 7.34 | 3.06 | 12.43 |
| CO, kg/kg cat/hr | 0.21 | 0.09 | 0.35 |
| SELECTIVITY(%): | | | |
| $CO_2$[a] | 0.0 | trace | 1.8 |
| $CH_3OH$ | 97.6 | 98.2 | 96.0 |
| $CH_4$ | 1.5 | 0.2 | 0.1 |
| $C_2$-$C_3$ HC | 0.9 | 1.6 | 2.1 |

[a] In addition to any $CO_2$ in the feed gas.

of water, consisted of 64.3% $CH_3OH$, 12.2% $CH_4$, 22.2% $C_2$-$C_3$ hydrocarbons, and about 1.3% excess $CO_2$ produced by the water gas shift reaction. A steady state conversion was rapidly reached at 250°C, and as shown in Table VIII, the resultant hydrocarbon synthesis rate was low. The transient hydrocarbon synthesis was not recovered in subsequent testing.

The dependence of the carbon conversion to methanol over the Pd/Cu/ZnO catalyst as a function of the $CO_2$ content of the synthesis gas was similar to that observed with the binary Cu/ZnO catalyst, as shown in Figure 10. Therefore, the principal effect of the Pd addition to the catalyst was to decrease the catalytic activity, and this was also observed with the Mn additive (see Figure 9).

In contrast, no maximum in carbon conversion to products as a function of the $CO_2$ content of the synthesis gas was observed with a Pd/ZnO = 30/70 mol% catalyst. The activity of this catalyst at 250°C, 1100 psig, and GHSV = 5350 $\ell$/kg/hr with a $H_2/CO/CO_2$ = = 70/24/6 vol% synthesis gas corresponded to only 0.16% carbon conversion to methanol. At the same time, traces (<0.01%) of methane, ethane, propane, and ethylene were also present and, in fact, were the dominant (but less than 0.09% conversion to any one product) products formed during the initial heat-up period. Increasing the temperature to 275°C, increased the carbon conversion to 0.36%, and the products included $CO_2$ formed by the water gas shift reaction, as well as the hydrogen-containing products. Although true steady state conversions were not established, it was clear that decreasing the content of $CO_2$ in the synthesis gas from

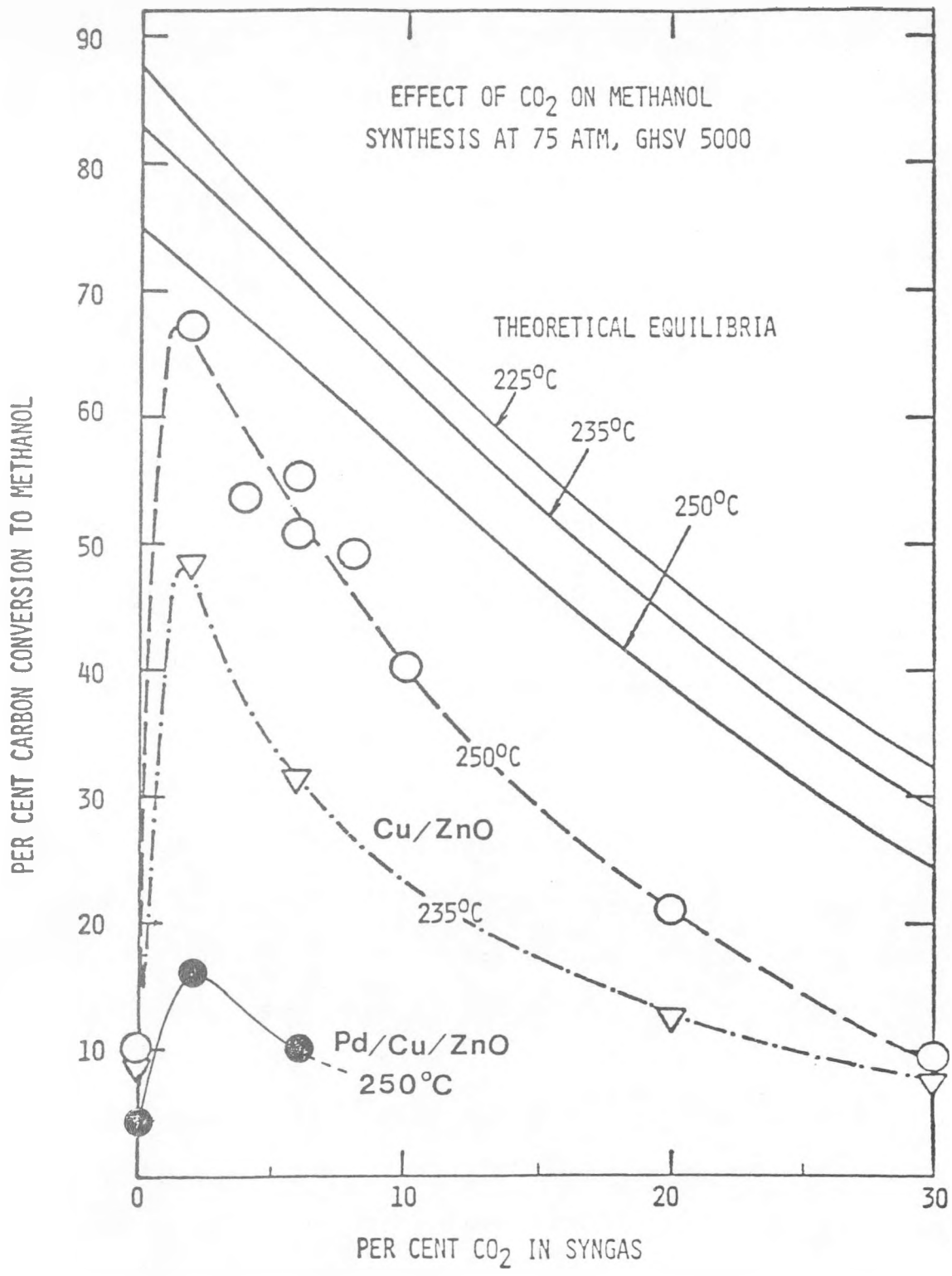



Figure 10. The effect of carbon dioxide on the formation of methanol from $H_2/(CO+CO_2)$ = 70/30 vol% synthesis gas over a Pd/Cu/Zn = 8/27/65 mol% catalyst (solid circles). This effect can be compared with methanol synthesis observed over a binary Cu/ZnO = 30/70 mol% catalyst (open symbols).

6 vol% to 0.3 vol% caused a decrease in the conversion of CO to methanol and hydrocarbon products.

These experiments involving Pd demonstrate that palladium is a less active and less selective catalyst than is the Cu-ZnO catalyst. When both Pd and Cu are incorporated together into ZnO, the principal catalyst consists of the copper species, which is moderated in its methanol synthesis activity by the palladium.

## 3. Iron Group Metal Carbonyls Dispersed on Cu/ZnO for Alcohol Synthesis

Since Fischer-Tropsch hydrocarbon products are produced from synthesis gas over bulk iron and cobalt catalysts, the aim of this part of the project was to form fine dispersions of the iron group metals, particularly *cobalt*, on methanol synthesis catalysts. Following the preparation of these catalysts, testing was carried out using the catalyst testing unit depicted in Figure 1, and the activities and selectivities of these catalysts in synthesis gas reactions were determined.

Two $Co_2$/Cu/ZnO catalysts were prepared and tested for alcohol synthesis activity. Their preparations were patterned after the rhodium catalysts, and the cobalt reagent used was $Co_2(CO)_8$. The Cu/ZnO catalyst was synthesized in the usual way [1], and the observed methanol synthesis activity corresponded to 57% carbon conversion to methanol using the experimental conditions described for Test 1 in Table III. The tested catalyst (initially 2.45 g of the oxides) was removed from the reactor in a nitrogen-filled

glove bag and added to a beaker containing 0.1145 g $Co_2(CO)_8$ dissolved in 40 ml tetrahydrofuran. The solution was periodically gently stirred while the tetrahydrofuran was evaporated with the aid of a stream of nitrogen. The dry catalyst was reloaded into the reactor for subsequent testing.

The reactor was pressurized with $H_2/CO/CO_2$ = 70/24/6 vol% synthesis gas; the flow rate established at GHSV = 5920 l/kg cat/hr, and the temperature was gradually increased to 250°C. A very low activity was observed and the methanol selectivity was decreased such that methane and ethane were produced, as shown in Table IX. On the basis of the cobalt content of the catalyst, the 0.55% carbon conversion corresponds to 0.885 kg CO converted/kg Co/hr. In Test 3, the $CO_2$ partial pressure of the synthesis gas was reduced to a low value, while the total pressure was reduced in Test 4, in which the catalytic activity decreased as expected. These results indicate that the cobalt clusters probably block the active sites on the Cu/ZnO catalyst, but the clusters did not exhibit a high hydrogenation activity during the 91 hr test program.

Another preparation of the Co/Cu/Zn catalyst was made in which the cobalt content was reduced to one-half that of the previous catalyst. The $Co_2(CO)_8$ was deposited under a nitrogen atmosphere on a reduced, but untested, sample of Cu/ZnO that was from the same preparation batch as that utilized previously. After being replaced in the reactor, the catalyst was heated to 118°C in flowing nitrogen at ambient pressure for 2 hr. The reactor was cooled, pressurized

TABLE IX

CATALYST: $Co_2Cu/Zn$ ATOMIC FORMULA: $ZnCu_{0.43}Co_{0.03}$

PREP. METHOD: Coprecipitation from Cu, Zn Nitrates with $Na_2CO_3$ Calcined, reduced, and tested (Test 1). Under nitrogen, $Co_2(CO)_8$ was deposited on Cu/ZnO from tetrahydrofuran.

BULK DENSITY: 0.71 g/cc

| TEST: | 1 | 2* | 3* | 4* |
|---|---|---|---|---|
| Feed, $H_2/CO/CO_2$ | 70/24/6 | 70/24/6 | 70/29.9/0.1 | 70/29.7/0.3 |
| Temp., °C | 250 | 250 | 250 | 250 |
| Pressure, psig | 1100 | 1100 | 1100 | 735 |
| GHSV, $\ell$/hr/kg cat. | 5800 | 5920 | 5920 | 6160 |
| CONVERSION: | | | | |
| (CO + $CO_2$), vol% | 55.3 | 0.55 | 0.63 | 0.29 |
| CO, mol/hr/kg cat | 39.4 | 0.40 | 0.46 | 0.22 |
| CO, kg/kg cat/hr | 1.41 | 0.014 | 0.016 | 0.007 |
| SELECTIVITY (%): | | | | |
| $CH_3OH$ | 100 | 65 | 83 | 57 |
| $CH_4$ | | 27 | 13 | 33 |
| $C_2H_6$ | | 8 | 2 | 7 |
| $C_2H_4$ | | | 2 | 3 |

* After deposition of $Co_2(CO)_8$

TABLE X

CATALYST: $Co_2/Cu/Zn$ ATOMIC FORMULA: $ZnCu_{0.43}Co_{0.015}$

PREP. METHOD: Coprecipitated from Cu, Zn Nitrates with $Na_2CO_3$ Calcined and Reduced. Under nitrogen, $Co_2(CO)_8$ was deposited on Cu/ZnO from tetrahydrofuran. Carbonyl was decomposed in flowing nitrogen at 118°C prior to pressurizing with synthesis gas.

BULK DENSITY: 0.72 g/cc

| TEST: | 1 | 2 |
|---|---|---|
| Feed, $H_2/CO/CO_2$ | 70/29.8/0.2 | 70/24/6 |
| Temp., °C | 250 | 250 |
| Pressure, psig | 1100 | 1100 |
| GHSV, l/hr/kg cat | 5620 | 5740 |
| CONVERSION: | | |
| (CO + $CO_2$), vol% | 0.68 | 0.40 |
| CO, mol/hr/kg cat | 0.47 | 0.28 |
| CO, kg/kg cat/hr | 0.017 | 0.010 |
| SELECTIVITY (%): | | |
| $CH_3OH$ | 66 | >90 |
| $C_2H_5OH$ | 6.5 | |
| $CH_4$ | 23 | <10 |
| $C_2H_6$ | 4.5 | |

with $H_2/CO$ = 70/30 vol% synthesis gas, and heated to 250°C. The testing results are presented in Table X: the activities and selectivities are similar to those observed for the first cobalt catalyst (Table IX).

These catalysts, which had cobalt deposited on the surface of the reduced Cu/ZnO samples, exhibited much less catalytic activity than the coprecipitated $ZnCu_{0.43}Co_{0.42}$ catalyst that was described in a previous report for this project. When tested under conditions comparable to Tests 2 in Table IX and Table X, the latter catalyst yielded a 48% carbon conversion, but the selectivity was 86% to methane, 4.3% to methanol, and 0.5% to ethanol + dimethylether. Thus, the cobalt cluster catalysts produced a more desirable selectivity in product composition than did the bulk coprecipitated ternary catalyst.

A dispersed iron carbonyl on Cu/ZnO catalyst was prepared by depositing the anionic $[C_5H_5Fe(CO)_2]^-$ complex on the reduced Cu/ZnO = 30/70 mol% under an inert atmosphere. The complex was prepared [14] from $[C_5H_5Fe(CO)_2]_2$ that was purchased from Strem Chemicals. A 1.198 g portion of the dimer was dissolved in 25 mℓ of filtered tetrahydrofuran (THF) in a 50 mℓ Wheaton bottle fitted with a tight teflon septum. While this solution was being shaken, 8 mℓ of a Hg/Na amalgam, which had been previously prepared by adding 1.202 g Na metal to 15 mℓ of triple distilled mercury, was placed in a similar Wheaton bottle. While this bottle was being continuously purged with flowing nitrogen via needles through the septum, all of the THF solution was transferred to this bottle by means of a syringe. When the transfer was completed, all of the needles were withdrawn and the THF, dimer, and amalgam mixture

was shaken vigorously for 15 min. A dark orange-brown solution resulted.

A 5 g portion of pelletized CuO/ZnO catalyst had been previously reduced with a $H_2/N_2$ = 2/98 vol% gas mixture at 250°C. After cooling, the catalyst was removed from the reactor in a nitrogen-filled glove bag and added to a Wheaton bottle, which was then capped. In consecutive steps, 10 mℓ THF was added to the catalyst, then 1 mℓ of the filtered THF, iron complex, amalgam mixture, followed by 10 mℓ THF. The solution was swirled and then the THF was evaporated by flowing a stream of nitrogen through the bottle, which was still contained in the glove bag. A 2.724 g portion of the resultant dry catalyst was placed in the reactor under nitrogen. The reactor was then placed in the furnace of the catalyst testing unit (refer to Figure 1) and purged with nitrogen flowing at a rate of 3.75 ℓ/hr. Over a period of 80 min, the reactor was heated from ambient temperature to 200°C, and the latter temperature was maintained for 35 min before the reactor was cooled.

In a $H_2/CO/CO_2$ = 70/24/6 vol% environment, the reactor was pressurized to 1100 psig and then heated to 250°C. Table XI summarizes the subsequent catalytic tests that were carried out. It is evident that the observed conversions of CO to products were low. For each set of experimental conditions, a gradual decline in catalytic activity was noted. The highest degree of carbon conversion was found in Test 7 that utilized a $H_2/CO$ = 1:1 synthesis gas at a low GHSV. Traces of a variety of products were evident, and these included ethanol, propane, and ethylene. The water that was formed by the hydrocarbon syntheses was converted

TABLE XI

CATALYST: Fe/Cu/ZnO ATOMIC FORMULA: $ZnCu_{0.43}Fe_{0.006}$

PREP. METHOD: Impregnation of reduced Cu/ZnO = 30/70 mol% catalyst in THF with $Na[C_5H_5Fe(CO)_2]$ prepared from $[C_5H_5Fe(CO)_2]_2$

BULK DENSITY: 0.65 g/cc

| TEST: | 1 | 2[a] | 3 | 4[b] | 5[c] | 6[b] | 7 |
|---|---|---|---|---|---|---|---|
| Feed, $H_2/CO/CO_2$ | 70/24/6 | 70/24/6 | 70/24/6 | 70/24/6 | 70/29.9/0.1 | 50/50/0 | 50/50/0 |
| Temp., °C | 250 | 250 | 250 | 250 | 250 | 250 | 300 |
| Pressure, psig | 1100 | 1100 | 1100 | 1100 | 1100 | 1100 | 100 |
| GHSV, l/hr/kg cat | 5500 | 5500 | 2800 | 2800 | 2800 | 1650 | 1650 |
| CONVERSION: | | | | | | | |
| $(CO+CO_2)$, vol% | 2.2 | 1.3 | 1.6 | 1.5 | 1.3 | 1.6 | 9.6 |
| CO, mol/hr/kg cat | 1.5 | 0.88 | 0.55 | 0.52 | 0.45 | 0.54 | 3.2 |
| CO, kg/kg cat/hr | 0.042 | 0.025 | 0.015 | 0.014 | 0.013 | 0.015 | 0.091 |
| SELECTIVITY(%): | | | | | | | d |
| $CH_3OH$ | | 95 | | 93 | 100 | 100 | 95 |
| $CH_4$ | e | 5 | e | 7 | trace | trace | 4 |
| $C_2H_6$ | | trace | | trace | 0 | trace | 1 |
| $C_2H_5OH$ | | 0 | | 0 | 0 | 0 | trace |

[a] After 21 hr of continuous operation at these conditions

[b] After 18 hr of operation at these reaction conditions

[c] After 35 hr of operation at these reaction conditions

[d] The water formed was nearly quantitatively converted into $CO_2+H_2$

[e] Not determined

to $CO_2$ by the water gas shift reaction. Therefore, part of the reported carbon conversion to products is due to the conversion of CO into $CO_2$, rather than the conversion of CO totally to hydrogen-containing products.

4. Further Characterization of the Cu/ZnO Catalyst Function in the Presence of Water and $CO_2$.

Prior to this research project, it was known that the concentration of $CO_2$ in the $H_2/CO$ synthesis gas had a profound effect on the yield of methanol produced over binary Cu/ZnO catalysts [15]. Some of the data are shown in Figures 9 and 10 for comparison with some of the catalysts prepared and tested during this project. However, additional data points were required and a mechanistic interpretation of the data was desired. Therefore, a few additional experiments were carried out.

A CuO/ZnO = 30/70 mol% catalyst was prepared using the usual carbonate coprecipitation, filtration, and calcination method (1). The catalyst was pelletized from an aqueous slurry and dried. A 2.45 g 4.7 mℓ charge, diluted with 5.3 mℓ Pyrex beads, was centered in the reactor and reduced in a stream of $H_2/N_2$ = 2/98 vol% at 250°C until the absence of water in the exit gas was noted by gas chromatography. The reactor was then cooled to ambient temperature and pressurized to 75 atm with a $H_2/CO/CO_2$ = 70/24/6 vol% synthesis gas. The gas hourly space velocity (GHSV) was then adjusted to 6120 ℓ/kg catalyst/hr, and the temperature was increased to 235°C. After 18 hr, the synthesis gas was changed to $H_2/CO/CO_2$ = 70/20/10 vol%, and the catalytic activity was determined at 235, 225, and 250°C

TABLE XII

CATALYST: Cu/ZnO ATOMIC FORMULA: $ZnCu_{0.43}$

PREP. METHOD: Coprecipitation from Cu, Zn Nitrates with $Na_2CO_3$ Calcined at 350°C in air, reduced in 2% $H_2$/98% $N_2$ at 1 atm and 250°C

BULK DENSITY: 0.52 g/cc

FEED: Test 1 $H_2/CO = 2.92$ $CO_2 = 6$ vol%
Test 2-4 $H_2/CO = 3.50$ $CO_2 = 10$ vol%

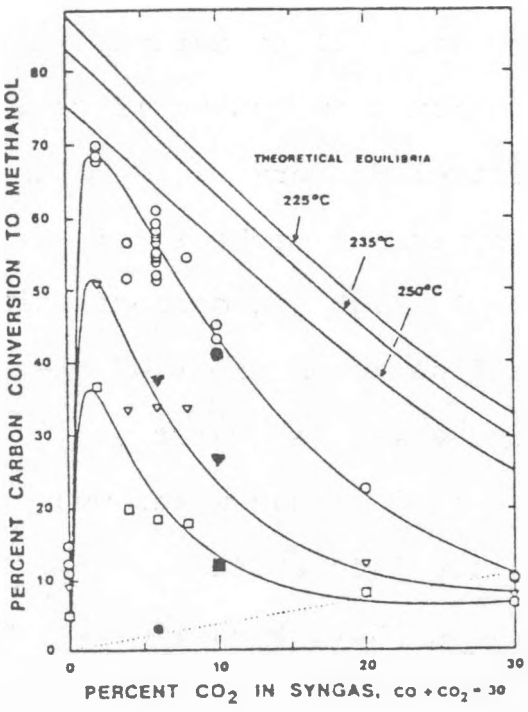
| TEST NO.: | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Temp., °C | 235 | 235 | 225 | 250 |
| Pressure, psig | 1100 | 1100 | 1100 | 1100 |
| GHSV, *l*/hr/kg cat. | 6120 | 6120 | 6120 | 6120 |
| CONVERSION: | | | | |
| (CO + $CO_2$) vol% | 37.3 | 26.5 | 11.9 | 40.5 |
| CO, mol/hr/kg cat. | 28.0 | 19.9 | 8.9 | 30.4 |
| CO, kg/kg cat/hr | 1.0 | 0.71 | 0.32 | 1.1 |
| SELECTIVITY (%): | | | | |
| $CH_3OH$ | 100 | 100 | 100 | 100 |

over a period of two days. The experimental results are tabulated in Table XII and are shown in Figure 11 as the four larger darkened symbols.

Another experiment carried out with a fresh portion of the Cu/ZnO = 30/70 catalyst involved using a synthesis gas in which the CO was replaced by argon, i.e. $H_2/Ar/CO_2$ = 70/24/6 vol%. This experiment was conducted at 250°C and at the same pressure and GHSV as the previous experiment (see Table XII). The resultant data point is shown in Figure 11 as the filled circle that lays on the dotted line. Also shown in this figure are equilibrium conversions calculated from known equilibrium constants and fugacity ratios of methanol synthesis [16] from carbon monoxide and hydrogen and of the water gas shift reaction.

Figure 11

The dependence of carbon conversion to methanol in a $CO_2/CO/H_2$ synthesis gas containing 70% $H_2$ and a variable ratio of $CO_2$ and CO. Experimental data are shown for 250°C(○), 235°C(▽), and 225°C(□). Lines drawn through the data points are theoretical curves derived from the model described in text. Theoretical equilibrium methanol conversions for the three temperatures studied are also shown as heavy lines in the upper portions of the figure. The point ● denotes the yield in $CO_2/Ar/H_2$ = 6/24/70 synthesis gas, expressed in terms of equivalent conversion of ($CO_2$ + Ar) to methanol. The dotted line represents the rate of $CO_2$ hydrogenation $r_{CO_2} = k' p_{CO_2}$.



Details of this $CO_2$ effect on the catalytic synthesis of methanol over the Cu/ZnO catalysts has recently been published [17]. It is evident from Figure 11 that the maximum conversion of CO to methanol occurs with a $H_2/CO/CO_2$ = 70/28/2 vol% synthesis gas. At lower concentrations of $CO_2$, the catalyst is deactivated by over-reduction, and at higher concentrations of $CO_2$ the synthesis is retarded by a strong adsorption of this gas, which prevents the activation of CO. A kinetic model has been presented that quantitatively describes the observed patterns in the indicated range of synthesis gas compositions and at temperatures between 225 and 250°C [17]. A rate equation has been derived that incorporates the $CO_2$ effect, and the solid lines that fit the experimental data points in Figure 11 are calculated curves generated by the rate equation. The proposed kinetic model is consistent with all physical characteristics of the Cu/ZnO catalysts and corroborates earlier findings [1,6,7] that an intermediate oxidation state of the catalyst is its active state. However, this model is incomplete and will be extended to consider the mechanism of methanol formation from synthesis gas. Intermediates on the catalyst surface include formate and aldehydic species. It will be shown that the synthesis mechanism involves a formate-formyl conversion step.

At high $CO_2$ concentrations in the synthesis gas, water was a significant component of the exit gas stream. Since it was evident that the reverse water gas shift reaction was occurring ($CO_2 + H_2 \rightarrow H_2O + CO$), that water would be generated by the formation of $C_2$-$C_4$ alcohols from synthesis gas, and that the forward water gas shift reaction could then proceed under the utilized experimental conditions, the study of the influence of water in the synthesis gas on

methanol synthesis was initiated. This investigation is being carried out with the Cu/ZnO = 30/70 mol% catalyst and a $H_2/CO$ = = 70/30 vol% synthesis gas. Water was injected into the gas stream just above the preheater section of the reactor by means of a Gilson high pressure pump (shown schematically in Figure 1), which provided a steady known rate of water addition. The exit gas was continually monitored by gas chromatography via a heated sampling valve that was controlled by a HP-3380A Reporting Integrator.

The methanol synthesis and water gas shift activities of the catalyst were observed to be very strongly dependent on the water content in the $H_2/CO$ synthesis gas, as shown in Figure 12. It is evident from this figure that the water gas shift reaction was proceeding over 90% to completion to produce $CO_2$. No maximum in the $CO_2$ yield is observed, but rather the degree of reaction is a linear function of the initial water content in the synthesis gas. However, the methanol yield exhibits a pronounced maximum as a function of the concentrations of water in the incoming synthesis gas stream. At water contents greater than about 4 vol%, the methanol synthesis activity is severely inhibited.

The previously observed $CO_2$ effect on the formation of methanol over the Cu/ZnO catalyst did not show a dependence that was as dramatic as the $H_2O$ effect. A comparison of the two experiments demonstrates that water behaves as a more effective promoter at low concentrations and a more severe retardant at high concentrations than does carbon dioxide at the given experimental conditions in Figure 13. Therefore, it appears that the synthesis is promoted by

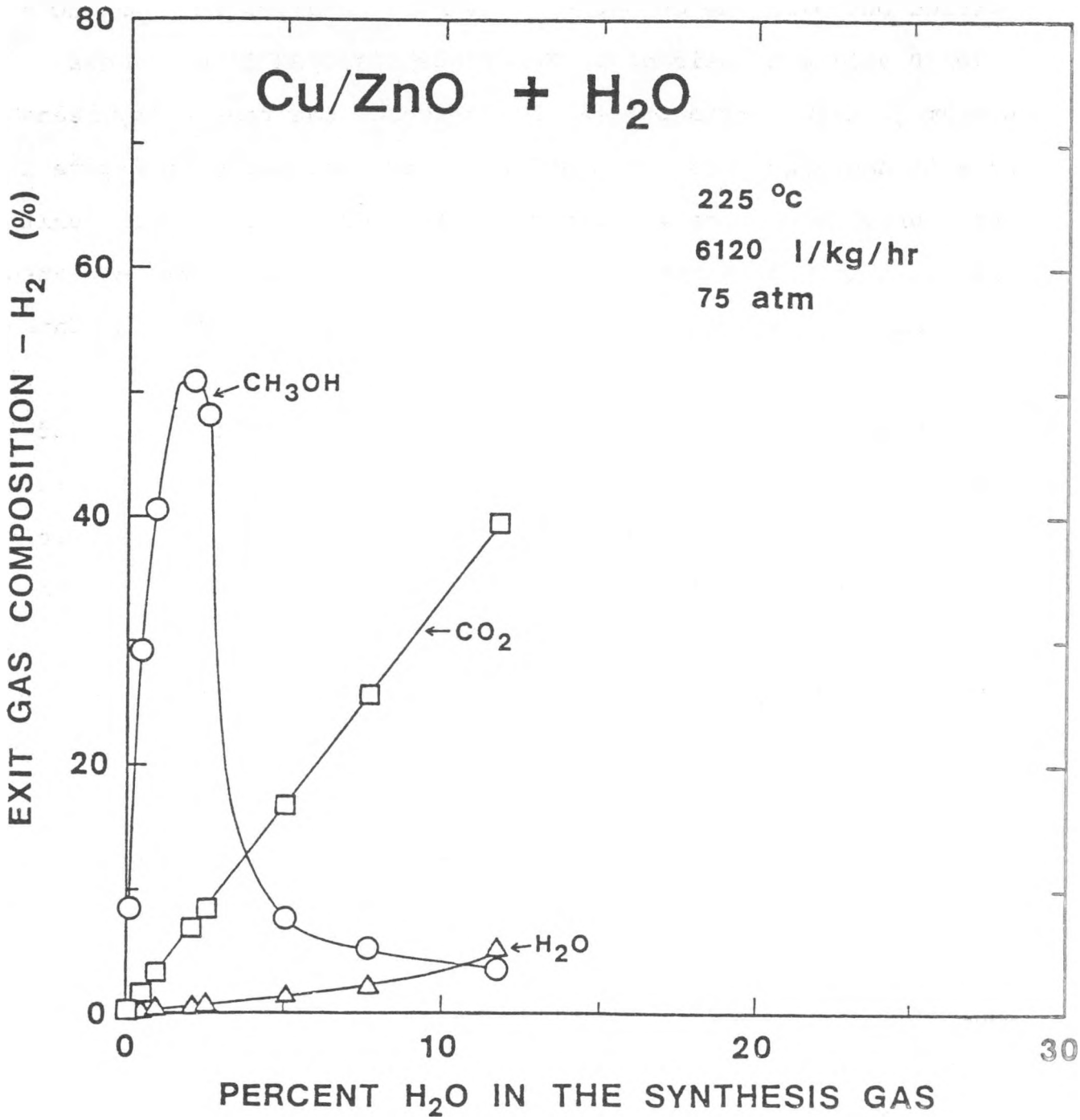



Figure 12. The composition of the exit gas, exclusive of hydrogen, as a function of the initial water content of the $H_2/CO$ synthesis gas as it enters the reactor.

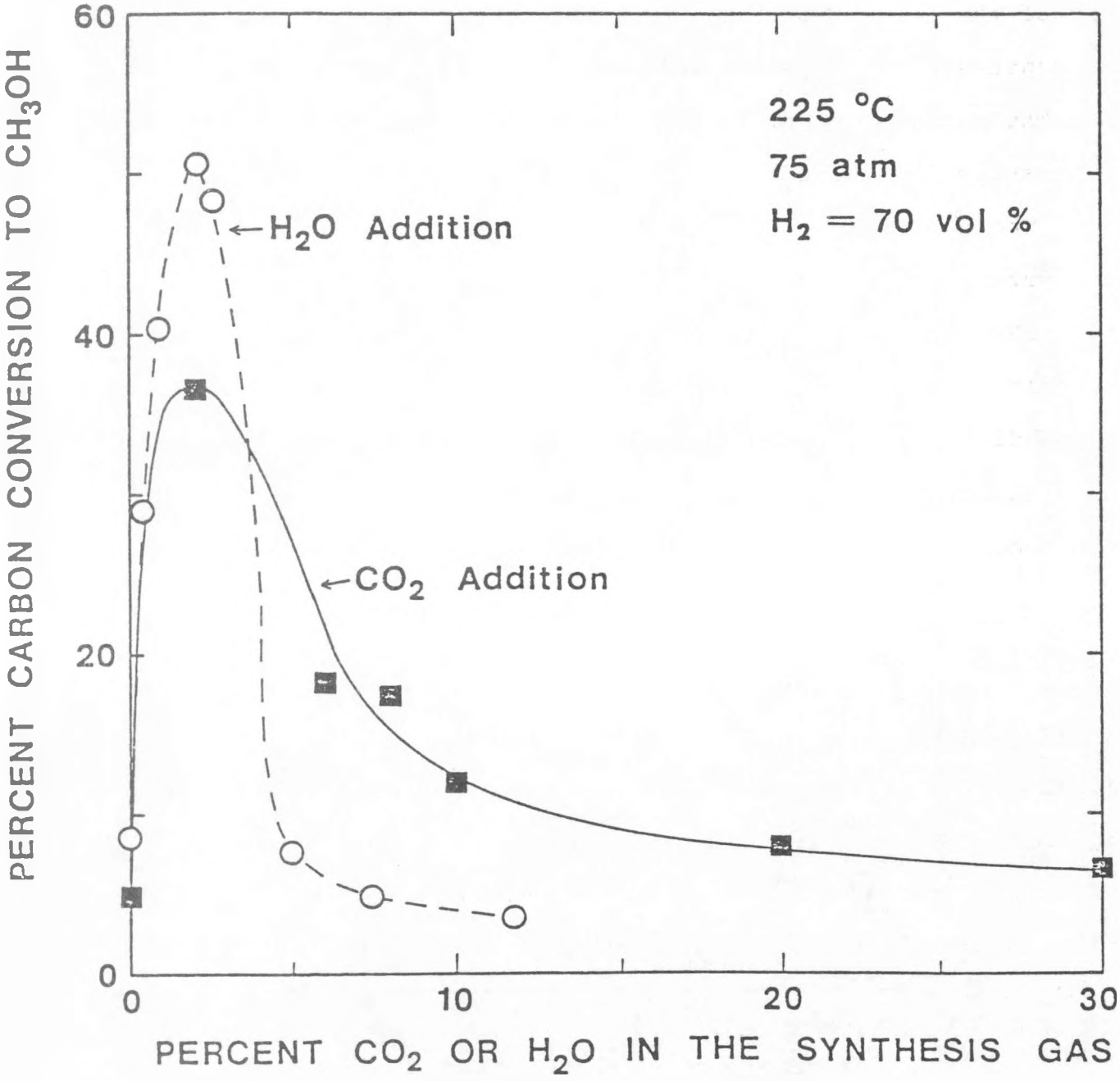



Figure 13. The dependence of carbon conversion to methanol in a $H_2/CO$ = 70/30 synthesis gas at 225°C, 75 atm, and initial gas hourly space velocity of 6120 $l$/kg catalyst/hr over a Cu/ZnO = 30/70 mol% catalyst. Closed symbols correspond to a $H_2/(CO+CO_2)$ = 70/30 vol% synthesis gas, while the open circles are data points obtained by the addition of $H_2O$ to a $H_2/CO$ = 70/30 vol% synthesis gas.

water rather than by carbon dioxide formed from it by the water gas shift reaction. Preliminary experiments in which the temperature of the reactor was varied indicate that the water effect on the synthesis is temperature dependent, as is the $CO_2$ effect, and that the maximum in methanol yield becomes less pronounced as the temperature is lowered.

The water effect on the methanol yield over the Cu/ZnO catalysts will be more intensively studied during the next year under SERI Subcontract No. XX-2002173-01. During that project, the role of water in interacting with catalytically active surface intermediates will be examined by utilizing $D_2O$ and $H_2{}^{18}O$, and these experiments will provide further insight into the mechanism of alcohol synthesis from CO + $H_2$ over copper-based catalysts.

## CONCLUSIONS

During this research project, the modification of the highly active Cu/ZnO = 30/70 mol% methanol synthesis catalyst by incorporation of various metal ions and the alteration of catalytic activity and selectivity over some of these catalysts by additives to the $H_2$/CO synthesis gas were investigated. It was observed that the addition of any metal ion (Fe, Co, Rh, Pd, Mn) to the standard Cu/ZnO = 30/70 catalyst lowered the catalytic activity. This was uniformly found whether the ternary catalyst was synthesized by coprecipitation from aqueous solution or by impregnation of the reduced Cu/ZnO catalyst with metal carbonyls from organic media under an inert atmosphere.

Of the ternary catalysts prepared by coprecipitation, the Mn and Pd catalysts exhibited suppressed activities for methanol synthesis as the major effect (see Figures 9 and 10). However, the Pd/Cu/ZnO catalyst also showed a low activity for the synthesis of methane and the $C_2$-$C_3$ hydrocarbons (Table VIII). On the other hand, the Fe/Cu/ZnO catalysts exhibited a large change in the selectivity of products formed. A ternary catalyst containing only 1 mol% iron showed a pronounced selectivity toward hydrocarbons and higher alcohols. Experimentation demonstrated that the alcohols were primary products and that the $C_2$-$C_5/C_1$ molar ratio could be increased by increasing the temperature and decreasing the pressure (Figures 4 and 5), while the alcohol/hydrocarbon ratio could be increased by increasing the inlet space velocity (Figure 8). It is noted that the higher alcohols are produced at higher rates over this catalyst than over Fischer-Tropsch synthesis catalysts.

Deposition of Rh on the surface of reduced Cu/ZnO catalysts produced a severe inhibition of the methanol synthesis activity and only a small shift in selectivity toward ethanol. However, compared with previously reported data [2,3], it is evident that these high pressure experiments did increase the yields of products (Table V). Impregnation of the binary Cu/ZnO catalyst with very small amounts of Co and Fe carbonyls caused the observed carbon conversions to be suppressed by factors in the range of 33-100 (Tables IX-XI). In general, the lower the coverage by the Co or Fe species, the higher was the selectivity to methanol and the lower it was to methane.

Investigations of the effects of $CO_2$ and of $H_2O$ in the $H_2/CO$ synthesis gas demonstrated that the concentrations of these additives are crucial in determining the resultant methanol synthesis activity of the Cu/ZnO = 30/70 mol% catalyst. The study of the $CO_2$ dependence of carbon conversion to methanol in $H_2/CO/CO_2$ synthesis gas mixtures was completed during this project, and the experimental data are presented in Figure 11. A partial model of methanol synthesis over the binary catalyst has been published [17]. The methanol synthesis dependence is even more severe for the presence of $H_2O$ in the synthesis gas (Figure 3), and most of the water is converted to carbon dioxide via the water gas shift reaction (Figure 12). This water effect is being investigated in detail during the coming year.

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