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METHANOL AND METHYL FUEL CATALYSTS

Final Technical Report for September 1980—August 1983

By
Kamil Klier
Richard G. Herman
Gary W. Simmons

December 1983

Work Performed Under Contract No. FG22-80PC30265

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Prepared For The United States Department of Energy

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I. ABSTRACT

Copper-based alcohol synthesis catalysts were prepared, tested for catalytic activity and selectivity, and characterized. These catalysts include Cu/ZnO, Cu/Co/ZnO, Cu/Co/Cr₂O₃, Cu/Co/Cr₂O₃/K₂O, and Cu/ZnO/KOH. The chromia-containing catalysts exhibited a low activity and selectivity, while the Cu/ZnO catalyst was verified to be a very active and selective methanol synthesis catalyst. Cobalt imparted a methanation function to the catalysts, while potassium suppressed the activity and the selectivity. Over the quaternary catalyst, higher pressure and lower GHSV enhanced the selectivity to higher alcohols.

Low concentrations of carbon dioxide in H₂/CO synthesis gas over Cu/ZnO catalysts promote methanol synthesis, while at high concentrations it behaves as a retardant of the synthesis. This effect of CO₂ has been kinetically modelled, and a general rate equation for methanol synthesis has been developed. It has been shown that the water gas shift reaction readily proceeds over the Cu/ZnO catalyst. Analogous to the CO₂ effect, the presence of water in the synthesis gas has a profound effect on the synthesis of methanol. However, H₂O acts as a more effective promoter at low concentrations and a more severe retardant at high concentrations than does equimolar CO₂ at the same experimental conditions.

It has been demonstrated that the Cu/ZnO catalyst is a good hydrogenation catalyst. Olefins, aldehydes, and acids are hydrogenated at a faster rate than CO is hydrogenated to methanol, but aromatics are hydrogenated at slower rates. In mixtures of these reactants, it is shown that competitive hydrogenations are occurring, and this indicates that the same active surface sites are involved in all of these hydrogenations.

Chemical trapping of the intermediates on these surface sites with amines demonstrates that a kinetically significant intermediate in methanol synthesis is a surface formyl or hydroxycarbene species. These species can be formed from synthesis gas or by alcohols in the reactant stream, and they readily alkylate amines in the reactant gas stream. Over an Fe/Cu/ZnO catalyst, amines inhibit the production of alcohols by trapping the precursor intermediates, while changing the hydrocarbon selectivity from paraffins to predominantly olefins.

II. INTRODUCTION

This research project was based on the desirability of making alcohol fuels from synthesis gas derived from coal and using the low alcohols as major energy chemicals. Currently, most methanol is produced from natural gas via partial oxidation or steam reforming to synthesis gas as shown by equations 1-3. Naphta is also

used as a feedstock since it has approximately the ideal hydrogen-to-carbon ratio of 2. It is reformed as shown by equation 4. Nearly all industrially used ethanol is produced from ethylene that is

converted to ethanol as indicated by equation 5. On the other hand,

the ethanol that has been blended with gasoline to produce a high octane fuel (gasahol) has been produced by fermentation of grains due to governmental incentives and regulations.

To produce ethanol and low alcohol fuels from coal-derived synthesis gas, new catalysts are required. It is well-known that copper-based catalysts are very active and selective for the synthesis of methanol [1,2], while cobalt-based catalysts exhibit Fischer-Tropsch activity with high selectivities to hydrocarbons. Mixed

copper-cobalt catalysts have been shown to produce a mixture of hydrocarbons and higher alcohols [3-5]. Recently, the Institut Francais du Petrole (IFP) has patented quaternary copper-cobalt-based catalysts that exhibit fairly good selectivities toward higher alcohols [6]. These catalysts also contain aluminum, chromium, or zinc and small amounts of alkali, e.g. potassium.

While the quaternary catalysts show good promise for producing alcohol fuels, further research is required to improve these catalysts. The main areas for further investigation encompass the following:

1) The yields of low alcohols over the Cu/Co/M/A catalysts, where M = Al, Cr, or Zn and A = alkali, are 4-5 times lower than the yields of methanol over the commercial Cu/ZnO/Al₂O₃, although the alcohol yields are higher than those of Fischer-Tropsch processes. Thus, even higher activities are desirable and should be achievable.

2) Within the C₁-C₄ alcohol range, the selectivity is not very high; methanol is produced in amounts of at least half that of ethanol, which may be an undesirable feature for some applications. Therefore, the selectivity to C₂-C₄ alcohols should be improved.

3) It has not been disclosed whether water or carbon dioxide is the product of the synthesis, e.g. as exemplified by equations 6 and 7. In addition, it is not known if the water gas shift

reaction proceeds readily over these catalysts. Reaction 7 is more desirable than reaction 6 for synthesis of alcohols from coal because (i) it uses a low hydrogen-to-carbon monoxide ratio in the synthesis gas and (ii) the products are readily separable and do not require distillation. Of course, reaction 7 can be achieved by reaction 6 followed by the water gas shift reaction (equation 8).

To clarify these points of interest, a program in determining the identity and nature of the reactive intermediates present on copper-based catalysts was initiated. Identification of the intermediates, as well as the sites where the intermediates are formed, will assist in explaining the mechanistic role of synthesis gas additives in altering or controlling the observed activities and selectivities.

III. OBJECTIVES

From perspectives gained from the open literature, from patent disclosures, and from our prior research in the area of methanol synthesis catalysts, this research program was set up to examine alcohol synthesis catalysts with the aim of understanding the synthesis mechanism so that directions for the improvement of C_2 - C_4 alcohol activities and selectivities could be clarified. The general areas to be pursued were (i) characterization of the quaternary Cu/Co/M/A catalysts and of model catalysts and (ii) investigation of the water gas shift activity and of the nature of carbon-containing intermediates over copper-based catalysts. The following specific objectives were formulated:

- 1) To prepare Cu/Co/Cr/K catalysts and model catalysts using previously established techniques.
- 2) To carry out catalytic testing and characterization of the catalysts to determine the effects and the roles of the components on the activity and selectivity.
- 3) To determine the effect of synthesis gas composition in terms of:
 - a) alcohol production as a function of the ratios of $H_2/CO/CO_2$ in the synthesis gas,
 - b) carrying out a kinetic treatment of the data obtained when the CO/CO_2 ratio was varied from 0 to 100% in a

$\text{H}_2/(\text{CO}+\text{CO}_2) = 70/30$ vol% synthesis gas over the

$\text{Cu/ZnO} = 30/70$ mol% catalyst,

- c) Determining if the water gas shift reaction occurs over these catalysts when the synthesis gas stream contains water as an additive, and
- d) Obtaining mechanistic information about surface intermediates by adding various reagents to the synthesis gas stream that react with the intermediates.

IV. TECHNICAL REPORT

A. EFFECTS OF Co AND K IN ALCOHOL SYNTHESIS CATALYSTS

Introduction

A successful catalyst for the production of alcohol fuels must have selectivity toward the C_1 - C_8 alcohols, especially the C_2 - C_4 fraction. Furthermore, the most desirable catalysts should not produce methane or other hydrocarbons. Most laboratory catalysts that have been shown to produce alcohols from synthesis gas at relatively low pressures have been based on copper [1-7] or rhodium [8-11]. The reaction conditions and selectivities for the copper catalysts are compiled in Table 1. It is evident that the Cu/Zn catalysts produce methanol in good yield, and these catalysts have recently been well characterized [1,2,12-16]. Addition of cobalt to these Cu-based catalysts give rise to selectivities directed toward ethanol and higher alcohols [3-6], and addition of alkali to the Cu/Co/M catalysts, where M = Cr, Fe, V, or Mn, suppresses methane formation [6]. Supported rhodium catalysts are also used for low alcohol synthesis [8-11], but they are expensive, usually produce appreciable quantities of hydrocarbons, have relatively low activities, and appear to deactivate when CO_2 is present. Rhodium catalysts, therefore, were not studied in the proposed program. The Cu/Co catalysts, on the other hand, are the more likely catalysts to be used for generating alcohol fuels from coal-produced syngas. The Cu/Co/M/A catalysts have therefore been chosen for the present study.

TABLE 1

Copper-Based Synthesis Gas Conversion Catalysts - A Comparison of Selectivities

Catalyst Composition	Reactants (H ₂ /CO/CO ₂)	Temp. (°C)	Pres. (atm)	Product Yield ^a	Ref.
1) Cu/Zn (3/7)	70/24/6	250	75	100% CH ₃ OH ^b	1
2) Cu/Zn/Al (52.4/24.3/23.3 at%)	70/24/6	250	75	100% CH ₃ OH ^c	15
3) Cu/Zn/Al (60,23.3,16.7 at%)	80/10/10	250	50	≈99% CH ₃ OH	7
4) Cu/Co/Al (8.8,6.4, x wt%)	67/33/0	275	51	6% alcohol 42% C ₂ -C ₄ 26% C ₅ ⁺ 26% CH ₄	5
5) CuO/CoS/MnO (1/0.1/1)	67/33/0	400	200	17% CH ₃ OH 22% C ₂ H ₅ OH 11% C ₃ H ₇ OH ⁺ C ₄ H ₉ OH 47% CH ₄	4
6) CuO/CoO/MnO (1/0.01/1)	67/33/0	≈ 400	200	54% CH ₃ OH 8% C ₂ H ₅ OH 8% C ₃ H ₇ OH ⁺ C ₄ H ₉ OH 30% CH ₄	3
7) Cu/Co/Cr/K (1/1/0.8/0.09)	66/19/13	250	60	0.076 ^d CH ₃ OH 0.125 ^d C ₂ H ₅ OH 0.069 ^d C ₃ H ₇ OH 0.045 ^d C ₄ H ₉ OH	6
8) Cu/Co/Mn/K (1/1/0.8/0.12)	66/19/13	250	60	0.065 ^d CH ₃ OH 0.108 ^d C ₂ H ₅ OH 0.064 ^d C ₃ H ₇ OH 0.039 ^d C ₄ H ₉ OH	6

a) % Carbon Distribution

b) 1.35 kg/kg/hr with GHSV = 5000 hr⁻¹

c) 1.37 kg/kg/hr with GHSV = 5000 hr⁻¹

d) kg/kg/hr with GHSV = 4000 hr⁻¹

The nature of the Cu/Co catalysts has not been well established. The interaction of the various components in the Cu/Co/M/A catalysts markedly affects their activities and selectivities. The uniqueness of this interaction is evidenced in the dependence of selectivity on the third element M and on the method of catalyst preparation. The very active Cu/Co/Al catalyst prepared by coprecipitation gives 90% conversion of CO to C_1 - C_4 alcohols and hydrocarbons [5], while in contrast the coprecipitated Cu/Co/Mn catalyst yielded almost pure methanol and no methane [3]. The distribution of products has been shown to vary for catalysts that have identical composition but were prepared by different methods. The Cu/Co/Mn catalyst, prepared by ignition of a mixture of the nitrate salts, gave the product distribution shown in Table 1 (No. 6), which differs from that over the coprecipitated Cu/Co/Mn catalyst.

It is evident that the characterization of these catalysts is needed to determine the interactions between components that give rise to the specific activities and selectivities. For example, the form of cobalt is presently unknown and the effect of the method of catalyst preparation on the form of cobalt has not been clarified.

A weight loss study of the Cu/Co/Al catalyst indicated that all of the Cu and Co ions were reduced to the metals, but the presence of cobalt metal could not be detected by X-ray diffraction [5]. In the absence of copper, the formation of the spinel $CoAl_2O_4$ was reported, while in the presence of copper this compound was not

identified [5]. In the working Cu/Co/Mn catalyst, the cobalt oxidation state was unknown, but it was assumed that at least part of the cobalt held a positive valence [3]. Studies of the chemical form and dispersion of cobalt in these catalysts in conjunction with testing are needed to optimize activity and selectivity.

Experimental

The copper-and/or cobalt-containing catalysts were synthesized by coprecipitation from nitrate media or citrate media by the addition of carbonate or oxalate solution or by evaporation of the solution. The preparation of the CuO, ZnO, CuO/ZnO, CoO/ZnO, and CuO/CoO/ZnO catalysts listed in Table 2 using sodium carbonate followed the procedure given previously [1,14]. In brief, this involved dissolving the nitrate salts in water, heating to 80-90°C, and while stirring continuously, 1.0 M Na₂CO₃ was added dropwise until a solution pH of 6.8 - 7.0 was achieved. During a one hour cooling period, continuous stirring of the solution was maintained. After allowing the solution to stand for 5 - 15 min, the supernatant was decanted from the settled precipitation, which was then washed with 300 - 600 ml distilled water. After standing, this water was decanted and the procedure was repeated two more times. The solid was then filtered onto Whatman #2 filter paper, washed with 10 portions of distilled water, and air-dried. Calcination of the dry materials was achieved by heating to 150°C for 30 min, increasing the temperature every 30 min by 50°C to a maximum of 350°C, and equilibrating at the latter temperature for 3 hr.

The preparations in which oxalate was used as the precipitating agent utilized the nitrate salts of the catalyst components. CoO/ZnO = 30/70 wt% samples were prepared by two different procedures. In Prep. No J72, 1500 ml of saturated sodium oxalate solution was heated to 85°C. While maintaining continuous stirring, 100 ml of an aqueous solution containing the nitrates of cobalt and zinc was

rapidly added. Following the usual procedure, a light pink supernatant was obtained, which was then titrated with 1.0 M Na_2CO_3 at 85°C.

The oxalate precursor was pink (typical of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), while the carbonate precursor was light purple. The weights of the products indicated that approximately 93% of the cobalt and zinc was precipitated as oxalates and about 7% were precipitated as carbonates. Calcination of the latter yielded a black solid whose X-ray diffraction pattern showed that ZnO, composed of 70 Å diameter crystallites, was the major component present. A broad peak, indicative of a 40 Å crystallite size, located at $2\theta = 44.1^\circ$ seemed to be due to metallic cobalt (strongest line at $2\theta = 42.4^\circ$). Decomposition of the oxalate precursor by calcination in air yielded a green solid whose X-ray diffraction powder pattern contained lines only attributable to ZnO (crystallite size was about 80 Å).

Prep. No. MF2 was prepared by dissolving the cobalt and nitrate salts in 1250 ml of water, heating to 85°C, and then adding saturated sodium oxalate solution in 100 ml portions until a total of 1500 ml had been added. Colors and X-ray diffraction observations were identical to those noted for Prep. No. J72.

Prep. No. MF3 was attempted using the same procedure that was followed with MF2. However, only 1400 ml of saturated $\text{Na}_2\text{C}_2\text{O}_4$ solution was added, at which time a light blue precipitate was evident. After digesting for 1 hr, the supernatant was removed from the solid by decantation. The solid was washed and filtered

TABLE 2

Alcohol Synthesis Catalysts That Have Been Prepared During
This Research Project

Prep.No.	Catalyst	Composition (wt%)	Precipitating Agent	Comments
P8	CuO	100	Carbonate	
J65	ZnO	100	Carbonate	
VC7	CuO/ZnO	30/70	Carbonate	
GV	CuO/ZnO	30/70	Carbonate	
N4	CuO/ZnO	30/70	Carbonate	
N14	CuO/ZnO	30/70	Carbonate	
N2	CuO/ZnO	30/70	Carbonate	
J72	CoO/ZnO	30/70	Oxalate	
MF2	CoO/ZnO	30/70	Oxalate	
MF3	CuO/CoO/ZnO	23/23/54	Oxalate	Separation of phases
MF4	CuO/CoO/ZnO	23/23/54	Carbonate	
PD1	CuO/CoO/Cr ₂ O ₃ /K ₂ O	28/27/43/2	Evaporation	From citrate media
PD2	CuO/CoO/Cr ₂ O ₃ /K ₂ O	28/26/43/3	Carbonate	From nitrate media

using the normal decantation procedure. The supernatant was treated at 85°C with an additional 1400 ml of the oxalate solution, in 100 ml increments. A pink precipitate resulted. By X-ray powder diffraction, it was observed that the blue precursor consisted of $\text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ and $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, while the pink solid was $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. These assignments were verified by preparing the pure single oxalate compounds and obtained their experimental diffraction patterns, which were compared with those reported in the literature [17]. No separation of compounds occurred in the carbonate preparation, MF4.

Prep. Nos. PD1 and PD2 followed the instructions in U.S. Patent 4,122,110 for catalysts B1 and B3, respectively [6]. Of the necessary starting materials, the basic cobalt carbonate was not readily available and had to be synthesized.

The cobalt hydroxycarbonate was prepared by precipitation from a cobalt nitrate solution using sodium carbonate, which is the method described by Sidgwick [18]. In 2000 ml of water was dissolved 336 g (1.15 moles) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, which gave a rose colored solution that was heated to 95°C and stirred with a magnetic stirrer. A slow addition of 1.0 M Na_2CO_3 was used to precipitate the cobalt carbonate. A total of 1235 ml of sodium carbonate solution was used, raising the pH to a final value of 7.5. Stirring was continued for 0.5 hr and the solution was allowed to stand overnight. The precipitate was then collected by filtration and washed with water to give a dark violet solid. This compound was spread out on a watchglass to dry and after a few days gave a dry, light violet solid, shown by X-ray diffraction to be the desired compound - $2\text{Co}(\text{CO}_3), 3\text{Co}(\text{OH})_2 \cdot n\text{H}_2\text{O}$.

The PD1 catalyst was then prepared. Mixed in a large beaker were: 116.6 g of cobalt hydroxycarbonate (0.20 moles); 80.1 g of CrO_3 (0.80 moles) and 241.6 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.99 moles). To this was added 225 ml of water, which caused a gas to be evolved. A dark black solution was formed, with some undissolved compounds in the bottom of the beaker. After 4 hr, with the gas evolution completely finished, 50.0 g (0.26 moles) of citric acid was added, giving a brown solution and again some solid in the

bottom of the beaker. The water was removed by placing the solution in a flask on a rotary evaporator at 45°C for 1.5 hr. About one half of the resulting dry compound was then scraped from the flask, heated on a hotplate set at maximum for 3 hr, and calcined in a furnace at 450°C for 3 hr. This yielded a dark grey compound. An aqueous paste of the calcined product was made and used to shape the catalyst into 5mm long cylindrical pellets using a die. To induce the potassium content, 50 ml of a 2% by weight solution of KOH was placed in a beaker with the same weight of catalyst pellets, which did not keep their shape. The mix was then allowed to stand for a few days and then the water was evaporated off by placing the solution in a teflon beaker on a hotplate. When dry, the solid was placed in a furnace at 400°C for 2 hr, which gave a final product that was dark grey and granular.

The catalyst designated as B3 in the patent was also prepared by following the patent procedure as closely as possible in Prep. No. PD2. To 100 ml of water were added 24.1 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.10 moles) and 29.1 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.10 moles) which gave a dark purple-black solution. A carbonate solution, 150 ml containing 26.5 g (0.25 moles) of Na_2CO_3 , was heated to 60°C and stirred vigorously. The cobalt-copper solution was then quickly added to it over a period of about 15 sec. A copious lavender precipitate was formed immediately and some gas was evolved. The precipitate was filtered and washed with water; the supernatant liquid had a very slight violet tint. The solid dried to a light

lavendar color and was crushed to a fine powder. Upon being heated in a furnace at 200°C for 2 hr, this material turned to a light green color. In order to impregnate the solid with potassium, a solution of 0.84 g (0.0043 moles) of K_2CrO_4 in the minimum amount of water for solvation was added to 90% of the green compound, and then let set. The water was slowly evaporated off by heating over a hotplate, giving a light olive colored compound. A solution of 8.15 g of $(NH_4)_2Cr_2O_7$ (0.032 moles) was added to 90% of the olive compound. After being allowed to stand overnight, the water was evaporated off. This yielded a light brown compound that was crushed and then heated in the furnace at 200°C for 2 hr and then, at 450°C for an additional 2 hr. The dark grey colored catalyst was pressure pelletized using a 1/2 inch die and hydraulic press, with 2.5 tons pressure applied on the die for 30 sec, giving a disc 1/2 inch in diameter and 1-2 mm high. This was then broken and sized to 10-20 mesh.

The role of potassium in the quaternary alcohol synthesis catalysts is unknown. In an attempt to clarify this role, potassium ions were impregnated into the intensively studied $CuO/ZnO = 30/70$ wt% methanol synthesis catalyst. The deposition of KOH was carried out stirring 6 g of the calcined catalyst with 100 ml of KOH solution having a certain known pH. The solution was then evaporated to dryness at 70°C. The resultant catalysts were mixed with distilled water at a weight ratio of 6 to 10 to form a slurry, which was then pressed through a die with 3 mm holes. After drying in a hood for several days, the pellets were

cut and sieved to 10-20 mesh. The samples prepared for this investigation are listed in Table 3.

TABLE 3

Potassium Hydroxide Impregnated CuO/ZnO = 30/70 Catalysts

Catalyst Utilized	Sample No.	pH of KOH Solution	% of Surface Area Covered by KOH ^a
VC7	GV1	11.83	28.3
VC7	GV2	10.82	2.8
GV	GV3	11.30	8.4
GV	GV4	11.82	28.3
VC7	GV5	-	0

^a Area per KOH = $16.7 \text{ \AA}^2$

Results

Zinc Oxide. This pure material that had been obtained by precipitation and calcination was tested for methanol synthesis using a synthesis gas of $\text{H}_2/\text{CO}/\text{CO}_2 = 70/24/6$ vol% and a gas hourly space velocity (GHSV) of 5000 l/hr/l of catalyst. The results of the catalytic testing are given in Table 4. The used material was white and had a surface area of $25.2 \text{ m}^2/\text{g}$. X-Ray diffraction demonstrated that the zinc oxide crystallite size was approximately $170 \text{ \AA}$ in diameter. The weight of ZnO tested was 1.594 g, and this resulted in an area of 40 m^2 of catalyst surface exposed to the syngas.

TABLE 4

Catalyst: ZnO

Prep Method: Precipitation from the nitrate with Na_2CO_3 .
Calcined at 350°C in air, reduced in 2% H_2 /98% N_2
at 1 atm and 250°C .

Feed: $\text{H}_2/\text{CO} = 2.92$ CO_2 : 6 vol%

Bulk Density: 0.76 g/cc

Test No.:	1	2	3	4
Temp., $^\circ\text{C}$	250	275	300	325
Pressure, psig	1100	1100	1100	1100
GHSV, l/hr/kg cat	6590	6590	6590	6590

Conversion:

CO + CO_2 , vol%	0	<0.01	0.4	1.5
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Selectivity(%):

CH_4	-	-	?	20
CH_3OH	-	-	100	75
C_2H_4	-	-	-	3.5
C_2H_6	-	-	-	1.5

Copper. This sample was prepared by precipitation from nitrate medium by the dropwise addition of 1.0 M Na_2CO_3 . The green product was $\text{Cu}_2(\text{OH})_3\text{NO}_3$, which was decomposed by calcination at 350°C using the stepwise heating procedure. X-Ray diffraction showed the calcined product to be crystalline CuO (tenorite). The CuO catalyst (20 g) was loaded into the reactor in powder form (held in place by Pyrex wool and Pyrex beads) and reduced in a gas stream of 2% H_2 /98% N_2 at atmospheric pressure and 250°C . The reduction process was monitored by gas chromatographic analysis of the exit gas and was stopped when the water content had decreased to 0.001%.

The catalyst was subjected to a standard methanol synthesis test by passing the $\text{CO}_2/\text{CO}/\text{H}_2 = 6/24/70$ vol% synthesis gas at 75 atm and 250°C at the flow rate of 15 liters (STP) per hour over the copper catalyst. The testing was carried out at steady state for 24 hr, during which time no trace of methanol was detected by the on-line gas chromatograph that used an automatic sampling valve. The red catalyst was removed from the reactor under nitrogen. The BET surface area of the sample was found to be $0.6 \text{ m}^2/\text{g}$, so that the tested catalyst exposed a copper surface area of 9.6 m^2 to the syngas.

CuO/ZnO. All of the $\text{CuO}/\text{ZnO} = 30/70$ wt% catalysts listed in Table 2 were tested for methanol synthesis activity using the standard testing conditions. The catalysts had comparable activities and all were 100% selective to methanol. To illustrate the activity of these catalysts, some results for catalysts N14 and VC7 are tabulated in Table 5, where each entry was obtained with a fresh sample. The bulk density of N14 was 0.49 g/cc . The methanol yield over this binary catalyst as a function of the CO_2 content of the synthesis gas has been previously reported [16,19].

TABLE 5

<u>Catalysts:</u>	Cu/ZnO		<u>Atomic Formula:</u> ZnCu _{0.43}			
<u>Prep. Method:</u>	Coprecipitation from the nitrates with Na ₂ CO ₃ . Calcined at 350°C in air, reduced in 2% H ₂ /98%N ₂ at 1 atm and 250°C.					
<u>Feed:</u>	H ₂ /(CO + CO ₂) = 2.33					
<u>GHSV:</u>	6120 l/hr/kg cat.					
<u>Pressure:</u>	1100 psig					
<u>Test No.:</u>	1	2	3	4	5	6
Catalyst	N14	N14	N14	VC7	VC7	VC7
Temp., °C	235	250	250	250	250	250
% CO ₂	6	6	2	6	6	2
<u>Conversion:</u>						
CO + CO ₂ , vol%	37.3	51.9	69.8	53.0	55.6	66.4

CoO/ZnO. The pink MF2 catalyst precursor (9.246 g) was loaded into the reactor and a programmed procedure was used to calcine the material. Maintaining a flow of nitrogen (0.86 l/hr) over the precursor, the temperature was increased from ambient to 250°C over a period of 3 hr, at which time a 24-hr equilibration under these conditions was carried out. The nitrogen flow rate was then doubled and the temperature was increased to 370°C over a span of 11 hr. The temperature was then immediately lowered to 270°C and maintained at this point for 10 hr. After decreasing the temperature to 250°C , the N_2 was replaced with H_2 flowing at the rate of 4.0 l/hr at ambient pressure. After 2.5 hr, the temperature was reduced and the reactor was pressurized for testing the activity of the catalyst.

Catalytic testing was carried out at the usual conditions, and steady state conditions were maintained at each designated temperature for 5 to 14 hr. The results are presented in Table 6. It is evident that this binary catalyst is a good methanation catalyst but a poor methanol synthesis catalyst. The used catalyst was dark grey.

The initial reduction procedure was studied by placing 4.268 g of the J72 precursor in a glass reaction chamber. A flow of 2% H_2 /98% N_2 at 2.4 l/hr was established and the temperature was increased to 250°C at the rate of approximately 2°C/min. Water was given off by the sample and was collected in a cold trap. After 22 hr, the

TABLE 6

<u>Catalyst:</u>	Co/ZnO		<u>Atomic Formula:</u> ZnCo _{0.43}	
<u>Prep. Method:</u>	Coprecipitation from the nitrates with Na ₂ C ₂ O ₄ Calcined at 370°C in N ₂ , decomposed at 250°C in 1 atm H ₂ .			
<u>Feed:</u>	H ₂ /CO:2.92		CO ₂ :6 vol%	
<u>Bulk Density:</u>	0.62 g/cc for the precursor			
<u>Test No.:</u>	1	2	3	4
Temp., °C	180	200	235	250
Pressure, psig	1100	1100	1100	1100
GHSV l/hr/kg cat.	6560	5410	4920	4460
<u>Conversion:</u>				
CO + CO ₂ , vol%	0.27	0.35	22	32
<u>Selectivity (%):</u>				
CH ₄	-	-	91	79
CH ₃ OH+C ₃ H ₈	0.094 ^a	0.21 ^a	1.6	2.5
CH ₃ OCH ₃ +C ₂ Alcohols	0.22 ^a	0.06 ^a	0.5	10.7
C ₂ -C ₄ hydrocarbons	0.12 ^a	0.26 ^a	6.2	5.3
C ₅ hydrocarbons	0	0	0.7	2.3

^a Estimates

sample was cooled and removed from the reaction apparatus under nitrogen. The solid was a light lavender, and the color change from pink indicated that dehydration occurred but that reduction to cobalt metal had not proceeded.

A portion of the pink J72 precursor was calcined to 350°C to yield a green solid. Charged to the glass reactor was 1.36 g of this material. After establishing a flow of 2% H_2 /98% N_2 of 3.6 l/hr over the solid, the temperature was increased at 2°C/min to 250°C. The temperature was maintained for 22 hr, at which time the sample was cooled. The color of the solid remained an intense green, which is the color of a CoO/ZnO solid solution [20].

A follow-up experiment using the same apparatus, gas flow, and heating rate was carried out with the pink J72 precursor. However, the exit gas was monitored by continual analysis by an on-line gas chromatography. While heating the sample to 250°C, it was observed that water and carbon dioxide were given off by the solid prior to reaching 180°C. After being maintained at 250°C for 21 hr, no water was detected in the exit gas but CO and CO_2 were observable. These gases were still detected after the sample had been equilibrated at 250°C for 45 hr. Therefore, the temperature was increased to 275°C for 24 hr and then increased further to 300°C. As the temperature approached 300°C, there was an appreciable discharge of CO_2 from the solid. The sample was equilibrated at 300-305°C for 27 hr and then cooled and removed from the reactor under nitrogen. The resultant powder was dark green. Its X-ray diffraction pattern showed the presence of ZnO in 95 Å diameter crystallites, but lines due to a cobalt compound

were not evident. Plotting and integrating the chromatographic data, using the appropriate thermal response factors [21], yielded the result that the CO_2/CO ratio = 1.00/1.07 or approximately 1. All of these observations indicate that the cobalt/zinc oxalate mixture is quite stable against decomposition and reduction at temperatures less than 250°C at ambient pressure, even in a $2\%\text{H}_2/98\%\text{N}_2$ gas mixture. However, decomposition to the oxides to form a highly dispersed solid solution does occur when the temperature reaches about 300°C . This reaction can be represented by the following equation ($\text{M} = \text{Co}, \text{Zn}$): $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{MO} + \text{CO}_2 + \text{CO} + 2\text{H}_2\text{O}$. Upon catalytic testing at 75 atm pressure with $\text{H}_2/\text{CO}/\text{CO}_2 = 70/24/6$ vol%, reduction of at least some of the cobalt does occur since the color of the tested catalyst was dark gray, which is the color of metallic cobalt derived from cobalt oxalate [22].

CuO/CoO/ZnO. The black calcined MF4 catalyst (3.18 g) was loaded in the reactor and reduced in a stream of $2\%\text{H}_2/98\%\text{N}_2$ long enough to reduce all of the copper oxide. The reactor was then cooled to ambient temperature, pressurized, and heated to 200°C at the uniform rate of about $45^\circ\text{C}/\text{hr}$. Testing was carried out at 200, 235, and 250°C for an average of 15 hr at each temperature. The temperature was then lowered to 180°C and activity was measured for a period of 35 hr. At the low observed conversion, the methane peak in the chromatogram was not resolved from that of carbon monoxide. However, it appeared that the carbon conversion was nearly 100% selective toward the formation of methane. The

results are given in Table 7. The used catalyst was pitch black. It is notable that this catalyst is a poor ethanol (and methanol) catalyst but a good methanation catalyst.

TABLE 7

<u>Catalyst:</u>	Co/Cu/ZnO	<u>Atomic Formula:</u> ZnCu _{0.43} Co _{0.42}			
<u>Prep. Method:</u>	Coprecipitation from the nitrates with Na ₂ CO ₃ . Calcined at 370°C, reduced in 2%H ₂ /98%N ₂ at 1 atm and 250°C				
<u>Feed:</u>	H ₂ /CO = 3.21	CO ₂ :5.6 vol%			
<u>Bulk Density:</u>	0.265 g/cc				
<u>Test No.:</u>	1	2	3	4	
Temp., °C	180	200	235	250	
Pressure, psig	1100	1100	1100	1100	
GHSV l/hr/kg cat.	3880	4700	4700	4700	
<u>Conversion:</u>					
CO + CO ₂ , vol%	0.223	23.7	31.9	48	
<u>Selectivity (%):</u>					
CH ₄	-	95.0	91.0	86.4	
CH ₃ OH + C ₃ H ₈	0.11 ^a	1.2	2.5	4.3	
CH ₃ OCH ₃ +C ₂ ⁺ Alcohols	0.04 ^a	0.4	0.7	0.5	
C ₂ -C ₄ Hydrocarbons	0.16 ^a	3.0	6.0	6.8	
C ₅ Hydrocarbons	0	0	0	2.0	

^a Estimates

CuO/CoO/Cr₂O₃/K₂O. The testing of the PDI catalyst involved placing 4.5 g of the granular calcined product diluted with 7 ml of Pyrex beads in the reactor. The catalyst was reduced using the standard procedure for a time sufficient to reduce all of the divalent copper to the metal. Testing was carried out at 250°C

with a synthesis gas containing 7.8 vol% CO₂ for 72 hr. While being heated to 250°C and reaching a steady state at that temperature, an appreciable quantity of water was detected in the exit gas. Since the hydrocarbon production was very low at this stage of the testing, the water represents further reduction of the catalyst. During the initial period of testing, the selectivity was at least 50% to methanol but no ethanol was detected, where the detection sensitivity is at least 0.001% ethanol in the exit gas, exclusive of hydrogen. With time, the selectivity to methanol decreased, while the yield of ethanol, methane, and other hydrocarbons increased. The results of the catalytic testing at steady state are presented in Table 8.

TABLE 8

<u>Catalyst:</u>	Cu/Co/Cr ₂ O ₃ /K ₂ O	<u>Atomic Formula:</u> CuCoCr _{0.8} K _{0.1}
<u>Prep. Method:</u>	According to Catalyst B ₁ in U.S. Patent 4,122,110 Utilized citric acid Final calcination at 400°C reduced in 2%H ₂ /98%N ₂ at 1 atm and 250°C	
<u>Feed:</u>	H ₂ /CO = 3.17	CO ₂ :7.8 vol%
<u>Bulk Density:</u>	1.50 g/cc	
<u>Test:</u>		
Temp., °C	250	
Pressure, psig	1100	
GHSV, l/hr/ kg cat.	4430	
<u>Conversion:</u>		
CO + CO ₂ , vol%	1.14	
<u>Selectivity (%):</u>		
CH ₄	61.0	
CH ₃ OH	20.0	
C ₂ H ₅ OH	6.8	
C ₂ -C ₄ Hydrocarbons	12.2	
C ₅ ⁺ Hydrocarbons	0	

The catalyst was removed from the reactor under nitrogen and portions were placed into an X-ray diffraction holder and a quartz diffuse reflectance cell under nitrogen for further characterization. The X-ray diffraction powder pattern showed the presence of Cr_2O_3 , metallic cobalt and metallic copper. The optical spectra of the catalyst were obtained by diffuse reflectance spectroscopy (DRS) with a Cary 14 spectrophotometer using both the single scan mode and the multiscanning facility. The spectrum in the visible region exhibited peaks at 5500 and 6500 Å, which are characteristic of metallic cobalt, and a weak band at approximately 7500 Å that is due to metallic copper.

Catalyst PD2 was pelletized after calcination using a hydraulic press rather than from an aqueous slurry. A catalyst charge of 3.061 g was used, which was diluted with about 7.5 ml of Pyrex beads. The reduction of the catalyst utilized the standard procedure, and the water content of the exit gas was followed by on-line gas chromatography analyses. The reduction proceeded slower than does the reduction of the binary CuO/ZnO catalysts, as determined by the water content of the exit gas. The reduction was carried out for twice the time calculated for stoichiometric reduction of the CuO , at which time the water content of the exit gas was decreasing and $\text{N}_2/\text{H}_2/\text{H}_2\text{O} = 98/1.8/0.2$ vol%. The longer time was expected since the reduction proceeded slower than initially expected.

Testing was carried out at 60 atm pressure (880 psig) with a $\text{H}_2/\text{CO}/\text{CO}_2 = 70/20/10$ vol% synthesis gas flowing at 4000 l/l cat./hr, which are conditions specified in the patent description of the analogous testing [6]. The reactor was heated at 3°C/min, and at

approximately 200°C the conversion to methanol was 2.3%. At this temperature, the exit gas contained 0.3% water (exclusive of hydrogen). With further heating, the methanol yield decreased while the production of water increased. As the temperature reached 250°C, the water content of the exit gas was 6 vol%, exclusive of hydrogen, and methane, ethane, and propane began to be synthesized. The production of these four products reached a maximum and began to decrease. At the same time, the yield of methanol, ethanol, and methyl formate increased. Ethylene and propylene were also present, but there was no evidence for the presence of CH_3OCH_3 , $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$, and HCHO in the exit gas.

While maintaining the temperature at 250°C, the pressure was increased to 75 atm and then to 90 atm. The results for the three tests are tabulated in Table 9. In each of these tests, the CO_2 content of the exit gas was greater than the CO_2 content of the initial synthesis gas. Therefore, the water gas shift reaction was occurring over this catalyst and it appeared to be independent of pressure. No decay of catalytic activity was observed during each of these tests.

After Test 3 listed in Table 9, the pressure was decreased to 880 psig again. The carbon conversion fell to 1.4 vol%, but the selectivity to alcohols increased relative to Test 1. The selectivities to methanol and ethanol were 14.6 and 10.2%, while those to methane and $\text{C}_2\text{-C}_4$ hydrocarbons decreased to 36.5 and 24.1%, respectively. While maintaining the temperature and pressure, the synthesis gas was changed to $\text{H}_2/\text{CO}/\text{CO}_2 = 70/24/6$ vol%. The

TABLE 9

<u>Catalyst:</u>	Cu/Co/Cr ₂ O ₃ K ₂ O		<u>Atomic Formula:</u> CuCoCr _{0.8} K _{0.09}
<u>Prep. Method:</u>	According to Catalyst B ₃ in U.S. Patent 4,122,110 No citric acid present (nitrate media) Calcined at 450°C, reduced in 2%H ₂ /98%N ₂ at 1 atm and 250°C		
<u>Feed:</u>	H ₂ /CO = 3.5	CO ₂ :10 vol%	
<u>Bulk Density:</u>	1.18 g/cc		
<u>Test:</u>	1	2	3
Temp., °C	250	250	250
Pressure, psig	880	1100	1320
GHSV, l/hr/kg cat.	3400	3400	3400
l/hr/l cat.	4000	4000	4000
Time, hr	20.5	24.5	46.5
<u>Conversion:</u>			
CO + CO ₂ , vol%	1.6	1.8	2.1
<u>Selectivity(%):</u>			
CH ₄	45.2	44.2	40.1
CH ₃ OH	8.4	10.5	11.8
C ₂ H ₅ OH	6.4	8.8	10.4
C ₂ -C ₄ Hydrocarbons	27.1	24.3	25.9
HCOOCH ₃	12.9	12.2	11.8

activities and selectivities were then determined at GHSV = 2000, 4000, and 8000 l/l cat./hr. A final test was carried out with a H₂/CO/CO₂ = 70/28/2 vol% synthesis gas at 250°C with a flow rate of 4000 l/l cat./hr at a pressure of 880 psig. A summary of the selectivities of this catalyst to the formation of ethanol under the various experimental conditions that were employed in this study is presented in Table 10. It is clear from this Table that the yield of ethanol relative to methane is enhanced by utilizing the higher pressure, lower GHSV, and lower concentration of CO₂ in the syngas. However, the actual production of methane is greater than that of ethanol in all cases. Similar trends are observed

for the yield of ethanol relative to methanol and methyl formate with the exception that higher concentrations of CO_2 in the synthesis gas enhance the production of ethanol relative to methanol. The proportion of ethanol to methyl formate appears to be independent of the CO_2 content of the syngas.

TABLE 10

Summary of the Selectivity of the PD2 Catalyst
($\text{CuCoCr}_{0.8}\text{K}_{0.09}$) to the Synthesis of Alcohols

Experimental Variable	$\frac{\text{C}_2\text{H}_5\text{OH}}{\text{CH}_3\text{OH}}$	$\frac{\text{C}_2\text{H}_5\text{OH}}{\text{CH}_4}$	$\frac{\text{C}_2\text{H}_5\text{OH}}{\text{HCOOCH}_3}$	%Selectivity to Alcohols	Constants
<u>Pressure (atm)</u>					
60	0.76	0.14	0.50	15	70/20/10% 250°C 4000 hr ⁻¹
75	0.84	0.20	0.71	19	
90	0.88	0.26	0.91	22	
<u>GHSV (hr⁻¹)</u>					
2000	0.76	0.37	1.08	54	70/24/6 250°C 60 atm
4000	0.53	0.23	0.53	25	
8000	0.19	0.03	0.09	19	
<u>[CO₂] (%)</u>					
2	0.36	0.26	0.53	32	250°C 4000 hr ⁻¹ 60 atm
6	0.53	0.23	0.53	25	
10	0.76	0.14	0.50	15	

$\text{CuO/CoO/Cr}_2\text{O}_3$. A portion of the PD1 catalyst was tested for catalytic activity prior to impregnation with potassium. A 4.51 g portion of the powder was weighed, diluted with about 5.5 ml of Pyrex beads, and centered in the reactor. With nitrogen flowing through the reactor at a rate of 60 ml/min, the catalyst was heated to 350°C at a rate of about 3°C/min. After being calcined at this temperature for 3 hr, the sample was cooled to ambient temperature.

Using the same heating and flow rates, but with a 2% H_2 /98% N_2 gas stream, the catalyst was heated to 250°C and held at this temperature until the production of water was near zero, at which time the reactor was cooled to room temperature. The reactor was pressurized to 75 atm with a $\text{H}_2/\text{CO}/\text{CO}_2 = 70/20/10$ vol% synthesis gas and testing was carried out at 250°C. The results are given in Table 11 for run times of 4 hr and 24 hr. The pressure was then decreased to 60 atm, and then the CO_2 content of the synthesis gas was decreased by changing to a $\text{H}_2/\text{CO}/\text{CO}_2 = 70/24/6$ vol% feed gas mixture.

It is evident that this ternary catalyst is similar to the previously tested B1 and B3 catalysts that contained potassium in regard to the low degree of carbon conversion to products. However, there are marked differences in selectivities. Over the potassium-containing catalysts, about 12% of the carbon-containing products was methyl formate. Over the ternary catalyst, no methyl formate was produced. Over the potassium-containing catalysts, the $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ and $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ ratios were approximately equal to 2. Over the ternary Cu/Co/Cr catalyst, these ratios became approximately the following: $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6 \approx 0.1$ and $\text{C}_3\text{H}_6/\text{C}_4\text{H}_8 \approx 0.5$. The water gas shift reaction was occurring over this catalyst because the CO_2 content of the exit gas was greater than the CO_2 content of the initial synthesis gas, and this was also observed with the potassium impregnated catalysts. With respect to the latter catalysts, the potassium-free catalyst exhibited a higher overall carbon conversion, a higher carbon conversion to alcohols, and a lower selectivity to C_2 - C_4 hydrocarbons.

TABLE 11

<u>Catalyst:</u>	Cu/Co/Cr ₂ O ₃		<u>Atomic Formula:</u> CuCoCr _{0.8}	
<u>Prep. Method:</u>	According to Catalyst B ₁ in U.S. Patent 4,122,110 Utilized citric acid Final calcination at 350°C, reduced in 2%H ₂ /98%N ₂ at 1 atm and 250°C			
<u>Bulk Density:</u>	1.02 g/cc			
<u>Feed:</u>	H ₂ /CO = 3.5	CO ₂ = 10 vol%	Tests 1-3	
	H ₂ /CO = 3.0	CO ₂ = 6.6 vol%	Test 4	
<u>Test:</u>	1	2	3	4
Temp., °C	250	250	250	250
Pressure, psig	1100	1100	880	880
GHSV, l/hr/kg cat.	3900	3900	3900	3900
Time, hr	4	24	15	
<u>Conversion:</u>				
CO + CO ₂ , vol%	6.60	8.36	4.62	3.38
<u>Selectivity(%):</u>				
CH ₄	55.6	33.0	49.6	50.5
CH ₃ OH	8.6	30.8	28.2	32.6
C ₂ H ₅ OH	18.3	26.0	11.9	9.8
C ₂ -C ₄ Hydrocarbons	17.5	7.6	8.7	5.3
C ₃ H ₈ OH	-	2.6	1.6	1.8

CuO/ZnO/KOH Each of the five samples (2.45 g) tested for catalytic activity were reduced with 2%H₂/98%N₂ flowing at 3.6 l/hr for the time calculated to give stoichiometric reduction of CuO to metallic copper. Testing was carried out using the standard procedure, and the results obtained are tabulated in Table 12. A small quantity of potassium on the surface of the catalyst led to the formation of a small quantity of ethanol. Adding more potassium led to enhanced methane formation but less ethanol

synthesis. Table 12 and Figure 1 demonstrate that coverage of the catalyst surface by potassium led to inhibition of the catalytic activity.

The tested catalysts were removed from the reactor under nitrogen and were examined by scanning Auger analyses. This technique analyzes the surface components of a material and employs a high vacuum chamber. To obtain data by scanning Auger microscopy (SAM), areas on the catalyst particles were found by Auger spectroscopy that were rich in zinc or in copper. Auger images of zinc and potassium and of copper and potassium were then obtained for these areas. Qualitatively, it appeared

TABLE 12

<u>Catalysts:</u>	Cu/ZnO/KOH		<u>Atomic Formula:</u> $\text{ZnCu}_{0.43}\text{K}_n$		
<u>Prep. Method:</u>	Coprecipitation of Cu, Zn nitrates with Na_2CO_3 . Calcined at 350°C in air, imprenated with KOH, pelletized, reeuced in 2%H ₂ /98%N ₂ at 1 atm and 250°C.				
<u>Feed:</u>	H ₂ /CO = 2.92		CO ₂ : 6 vol%		
<u>Test Conditions:</u>					
Temp. °C	250				
Pressure, psig	1100				
GHSV, l/hr/kg cat	6120				
<u>Test:</u>	GV5	GV2	GV3	GV1	GV4
% surface area covered by KOH	0	2.8	8.4	28.3	28.3
<u>Conversion:</u>					
CO + CO ₂ , vol%	53.0	48.6	36.9	0.8	0.4
<u>Selectivity (%):</u>					
CH ₄	0	-	0.33	≈6	-
CH ₃ OH	100	99.7	99.5	≈94	≈100
C ₂ H ₅ OH	0	0.23	0.14	0	0
C ₂ -C ₄ Hydrocarbons	0	0.06	0.02	-	-

evident that the potassium was closely associated with the zinc oxide phase, rather than with the metallic copper phase. On a semi-quantitative scale, the average concentrations of potassium, expressed as K/Zn and K/Cu, in the areas rich in zinc or rich in copper are given in Table 13, along with the average K/Zn ratios observed for the bulk materials. The intensities have been corrected by the sensitivity factors for the elements at 5 keV.

TABLE 13

Average Concentrations of Potassium Calculated on
Basis of the Intensities of the K, Zn, and Cu Auger Signals

Catalyst	K/Zn	K/Cu	Bulk Average K/Zn
GV2	0.089	0.013	0.066
GV3	0.099	0.018	-
GV1	0.145	-	0.88
GV4	0.143	-	0.66

Since the impregnation of these catalysts was carried out with potassium hydroxide, rather than with a salt such as potassium nitrate, the possible role of the OH moiety was investigated. Portions of each catalyst were leached with distilled water prior to or after catalytic testing. The procedure was to add 0.12 g of catalyst to 2 ml of distilled water and to stir occasionally over a period of 2.5 hr, at which time the pH of the solution was measured. The results are tabulated in Table 14. Continued leaching of the GV1 catalyst produced a pH of 10.0 after 24 hr and a pH of 10.2 after 48 hr.

TABLE 14

pH after Leaching Potassium-doped Cu/ZnO = 30/70 Catalysts

Catalyst	pH after Leaching of the Unreacted Catalyst	pH after Leaching of the Tested Catalyst
GV2	10.37	7.45
GV3	10.70	7.80
GV1	11.34	9.40

Tables 13 and 14 indicate that the major proportion of potassium is on the zinc oxide surface and that at least part of the hydroxide groups are recoverable from the catalyst by leaching with water. The active site for the formation of reactive intermediates on the catalyst surface is probably a Lewis acid center, e.g. Cu^+ in the ZnO lattice. The role of KOH on the surface of these catalyst could be as a neutralizing agent, the mechanism of which could follow one or more of the following equations:

It has previously been proposed that CO adsorbs on the Cu^+ ions that are in solid solution with the ZnO matrix [1]. The adsorption involves binding of the CO to the Cu^+ ion via σ -bonding with donation of electrons from the CO 3σ orbitals into the Cu^+/ZnO lowest lying empty energy band and π -bonding with back-donation of electrons from the unscreened filled Cu 3d orbitals into the empty CO π^* orbital. It is well-known that addition of

potassium to an iron- and cobalt-based Fischer-Tropsch catalyst shifts the selectivity to higher molecular weight products. This effect was attributed to the increase in electron density of the transition metal [23], which strengthens the metal-carbon monoxide bond, and to the attraction of the oxygen end of the molecule to potassium. However, this effect was not observed in the present investigation with the Cu/ZnO catalyst. Instead, only a gradual retardation of the methanol synthesis occurred upon controlled surface-doping of the catalyst with KOH. However, addition of K to the Cu/Co/Cr₂O₃ catalyst did result in enhanced selectivities to C₂-C₄ hydrocarbons.

It has often been suggested that the low pressure, as well as the high pressure, methanol synthesis proceeds via formate and methoxy intermediates, in which the first step is the insertion of CO into the O-H bond of a surface hydroxyl group [24]. The present research demonstrated that K was well distributed over the zinc oxide surface and that OH groups, which were recoverable by aqueous leaching, were placed on the catalyst surface by the impregnation treatment. However, the methanol synthesis rate decreased, rather than increase as predicted by the CO-OH insertion mechanism. The dominant effect of KOH on the low pressure methanol synthesis catalysts is the blockage of active centers that do not themselves involve hydroxyl groups that take part in the CO insertion steps. The blocked sites are probably predominantly the hydrogen-activation sites on the zinc oxide.

Summary

Once again it has been demonstrated that the Cu/ZnO = 30/70 mol% catalyst is a very active and selective catalyst for forming methanol from synthesis gas. In contrast, the pure individual components exhibit no activity for this reaction under the same experimental conditions. The analogous binary Co/ZnO catalyst has a lower activity than the copper-based catalyst, and the major product is methane. A Cu/Co/ZnO catalyst having equal quantities of copper and cobalt exhibited a catalytic activity intermediate between those of the binary catalysts. Both methanol and methane were formed, but methane was the predominant product. This is similar to the observation that >1 wt% cobalt impregnated onto a Cu/ZnO/Al₂O₃ decreased the catalytic activity and changed the selectivity from methanol to hydrocarbons (plus a small amount of higher alcohols) at 270°C, 65 atm pressure, and GHSV = 8000 hr⁻¹ with a H₂/CO/CO₂/N₂ = 60/28/10/2 vol% synthesis gas [25]. In fact, even 0.17 wt% of cobalt placed onto the catalyst decreased the yield of methanol by 74%, while the selectivity and surface area of the catalyst was unaffected [25].

The Cu/Co/Cr₂O₃ and Cu/Co/Cr₂O₃/K₂O catalysts prepared and tested during this project had very low activities, with the former catalyst being more active than the latter. In both cases, methane was the major product. Over the Cu/Co/Cr₂O₃ catalyst, the yield of C₂-C₃ alcohols was larger than the C₂-C₄ hydrocarbons and the catalytic activity and alcohol selectivity increased with testing time at 250°C, 1100 psig, and GHSV = 3900 l/kg cat/hr.

Over the Cu/Co/Cr₂O₃/K₂O catalyst, the yield of ethanol relative to methane was enhanced by increasing the reaction pressure, decreasing the GHSV, and decreasing the CO₂ content of the synthesis gas. All of these alterations to the experimental testing conditions increased the overall selectivity to alcohols.

Addition of small amounts of KOH to the Cu/ZnO catalyst by impregnation caused a decrease in catalytic activity with no appreciable change in selectivity. The decrease in activity was directly proportional to the surface coverage of the catalyst by KOH. When the surface coverage was about 28%, the carbon conversion to products at 250°C was less than 1%, and this contrasts with the 53% carbon conversion observed initially with the catalyst with the H₂/CO/CO₂ = 70/24/6 vol% synthesis gas prior to potassium impregnation. Therefore, the potassium blocks specific sites necessary for the catalytic formation of methanol. These appear to be hydrogen activation sites on the ZnO since the potassium was observed to be preferentially located on the ZnO component of the catalyst system.

B. EFFECTS OF CARBON DIOXIDE IN THE SYNTHESIS GAS
OVER Cu/ZnO = 30/70 CATALYST

It was previously shown [16,19,26] that small concentrations of CO₂ in the synthesis gas have a true promotion effect on the methanol synthesis rate rather than increasing it by direct hydrogenation of carbon dioxide to methanol, which would have to be faster than the hydrogenation of carbon monoxide. It was established that the methanol yield decreased substantially upon completely replacing CO in the ternary synthesis gas by CO₂ or by inert gas. Hence, a gradual replacement of CO by CO₂ produced a maximum in the synthesis rate; at low concentrations CO₂ acts as a promoter, while at high concentrations it behaves as a retardant of the synthesis. Such an influence of the CO/CO₂ ratio on the synthesis is of both fundamental and practical interest as it allows the catalyst to be optimized for various compositions of the synthesis gas.

In addition to mechanistic elucidation of the effects of carbon dioxide, it is desirable to formulate a kinetic equation that described these effects quantitatively and contains temperature-dependent factors that allow the concentration and temperature distribution in industrial reactors to be predicted. Such equations were formulated before, but none of them described satisfactorily the synthesis patterns over the copper-based catalysts.

During this research project, we initiated a study to determine phenomena that give rise to the maximum synthesis rate at a certain concentration of carbon dioxide. In the process of doing so,

models were formulated that quantitatively interpret the observed rates for various compositions of the synthesis gas. Thermodynamic functions derived from the comparison of the model-based kinetic equations with experiment give insight into the competitive adsorption of reactants in determining the synthesis rate at a given CO_2/CO ratio and temperature. It is possible that these data will lead to further development of catalysts for synthesis gases of various composition and origin. We have focused on a single catalyst of the composition $\text{Cu}/\text{ZnO} = 30/70$ mol%, described and characterized in our earlier work [1,12-14], because this catalyst operates in a well-defined structural, morphologic, and electronic state while retaining high activity and selectivity to methanol.

The kinetic model that was put forward has been published [16], and it was based on the following observations concerning the chemical and physical properties of the Cu/ZnO catalyst:

(1) The methanol conversion rates from H_2/CO synthesis gas increase substantially with the addition of CO_2 , H_2O or even small amounts of O_2 [1]. The catalyst is irreversibly deactivated by prolonged exposure to synthesis gas containing only H_2 and CO .

(2) A catalyst that has been reduced by H_2 at 250°C can be further reduced by CO at the same temperature with the appearance of CO_2 . When this CO -reduced catalyst is exposed to CO_2 at 250°C , it is reoxidized and the CO_2 is partially converted to CO . The CO/CO_2 equilibria are established in a time frame of hours [27].

(3) The activity of the catalyst increases as a high power of the concentration of X-ray amorphous copper, which was earlier identified as a solute species in the zinc oxide phase [1,12-14]. The catalyst activity to methanol formation is not proportional to nor monotonously dependent on the surface area of crystalline copper particles that are also present in the catalyst. This latter finding has been a matter of controversy [15,28], but additional support for this is provided by chemisorption of CO and O₂ on the Cu/ZnO catalyst [27].

(4) Carbon dioxide is adsorbed quite strongly on the binary catalyst. The reactant adsorption strengths are estimated to decrease in the order CO₂ > CO > H₂.

The general form of the methanol synthesis rate equation is

$$r = \text{const} \left(1 + \frac{1}{K'} \frac{p_{\text{CO}}}{p_{\text{CO}_2}} \right)^{-3} \times \frac{(p_{\text{CO}} p_{\text{H}_2}^2 - p_{\text{MeOH}}/K_{\text{eq}})}{(F + K_{\text{CO}_2} p_{\text{CO}_2})^n} + k' \left(p_{\text{CO}_2} - \frac{1}{K'_{\text{eq}}} \frac{p_{\text{MeOH}} p_{\text{H}_2\text{O}}}{p_{\text{H}_2}^3} \right) \quad (9)$$

where K' is the equilibrium constant for the reaction of a reduced catalytic surface species with CO₂, i.e. A_{red} + CO₂(g) ⇌ A_{ox} + CO(g), p is the pressure of the gaseous reactants and products, K_{eq} is the equilibrium constant for the reaction represented by equation 3, F is a linear function of pressures of H₂ and CO, K_{CO₂} is the equilibrium constant for the surface equilibrium CO₂(g) ⇌ CO₂(a), n is an exponent that ranges from 1 to 3, k' is a constant empirically obtained for the low direct conversion of CO₂ into methanol where K'_{eq} is the equilibrium constant for equation 10.

Rate equation 9 can be used in its integral form to calculate carbon conversion to methanol in an integral isothermal flow reaction, as detailed elsewhere [16]. The model and rate equation briefly described here yield the theoretical curves shown in Figure 2, which fit the experimental data points very well. The derived kinetics primarily reflect the catalytic promotion by CO_2 and the retarding effects of CO_2 at high concentration through its relatively strong adsorption, but do not depend on whether CO and H_2 adsorption is competitive or noncompetitive. Despite the resultant uncertainty as to whether the CO and H_2 adsorption is competitive or not, all of the successful kinetic models require nearly identical adsorption energies and entropies and a constant ratio of residence times of the reactants. It is these properties that determine the relative surface coverages of CO , H_2 and CO_2 . The conversion is then visualized as occurring by relatively infrequent reactive encounters resulting in a very unstable intermediates that are rapidly converted to the products.

A more detailed description of the model, the method of determining the kinetic and thermodynamic constants, and interpretation of the data has been published elsewhere [16].

FIGURE 2

The dependence of carbon conversion to methanol in a CO₂/CO/H₂ synthesis gas containing 70% H₂ and a variable ratio of CO₂ 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 CO₂/Ar/H₂ = 6/24/70 synthesis gas, expressed in terms of equivalent conversion of (CO₂ + Ar) to methanol. The dotted line represents the rate of CO₂ hydrogenation $r_{CO_2} = k'p_{CO_2}$.

C. WATER GAS SHIFT REACTION OVER Cu/ZnO CATALYSTS

One of the sub-tasks of this research program was "to determine if the water gas shift reaction or a modified internal shift reaction occurs over these catalysts when the syngas stream contains water." These possibilities were investigated over a CuO/ZnO = 30/70 wt% catalyst by utilizing a Gilson pump that delivers a steady liquid stream to the synthesis gas stream at the top of the reactor. The exit gas was continually monitored by means of a heated automated sampling valve on a HP gas chromatograph. The apparatus has been described in greater detail elsewhere [1].

The catalyst was prepared by coprecipitation, dried, calcined, pelletized, and reduced using our standard procedures [1,16]. The catalyst was then tested at 250°C with a H₂/CO/CO₂ = 70/24/6 vol% synthesis gas, and the expected CO conversion to methanol was observed, as shown in Table 15. Removing the carbon dioxide from the synthesis gas greatly reduced the activity of the catalyst as expected. Injecting water into the synthesis gas at various flow rates resulted in the production of CO₂ according to equation 8 and in the enhanced catalytic conversion of CO to CH₃OH. Periods of water injection, which were maintained for 5.5

to 20 hr, were interspersed with periods of running only the H₂/CO = 70/30 vol% synthesis gas.

TABLE 15
SUMMARY FOR RUN Water Gas
DATE 9/81

CATALYST NO. N 15 ATOMIC FORMULA ZnCu_{0.43}
MOLECULAR FORMULA CuO/ZnO = 30/70
PREP. METHOD Standard coprecipitation
WEIGHT OF CATALYST USED 2.45 g BULK DENSITY 0.89 g/ml
FORM OF CATALYST LOADED IN REACTOR 10-20 Mesh Pellets

TEST NO.	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
H ₂ /CO/CO ₂	<u>70/24/6</u>	<u>70/30/0</u>	<u>70/30/0</u>	<u>70/30/0</u>	<u>70/30/0</u>	<u>70/30/0</u>
Temp., °C	<u>250</u>	<u>250</u>	<u>250</u>	<u>250</u>	<u>250</u>	<u>250</u>
Pressure, psig	<u>1100</u>	<u>1100</u>	<u>1100</u>	<u>1100</u>	<u>1100</u>	<u>1100</u>
GHSV, 1/l/hr	<u>5360</u>	<u>5360</u>	<u>5360</u>	<u>5360</u>	<u>5360</u>	<u>5360</u>
1/kg/hr	<u>6120</u>	<u>6120</u>	<u>6120</u>	<u>6120</u>	<u>6120</u>	<u>6120</u>
Liquid Injected			H ₂ O	H ₂ O	*	H ₂ O
Rate, µl/min			<u>10</u>	<u>5</u>	<u>5</u>	<u>15</u>
mol/min			<u>5.6x10⁻⁴</u>	<u>2.8x10⁻⁴</u>	<u>2.8x10⁻⁵</u>	<u>8.4x10⁻⁴</u>
g/min			<u>0.01</u>	<u>0.005</u>	<u>0.0005</u>	<u>0.015</u>
CONVERSION						
CO + CO ₂ , vol%	<u>55.9</u>	<u>5.5</u>	<u>37.2</u>	<u>28.0</u>	<u>10.1</u>	<u>26.2</u>
CO, mol/kg cat/hr	<u>42.0</u>	<u>4.2</u>	<u>28.0</u>	<u>21.0</u>	<u>7.6</u>	<u>4.4</u>
kg/kg cat/hr						
SELECTIVITY (vol%)						
CO ₂			<u>31.6</u>	<u>19.6</u>	<u>8.6</u>	<u>79.7</u>
CH ₃ OH	<u>99.8</u>	<u>100</u>	<u>68.0</u>	<u>80.0</u>	<u>91.4</u>	<u>20.0</u>
C ₂ H ₅ OH	<u>0.2</u>		<u>0.4</u>	<u>0.5</u>	<u>-</u>	<u>0.2</u>
C ₃ H ₇ OH						
CH ₄						
C ₂ -C ₃ HC						
% H ₂ O in Exit Gas	<u>1.6</u>	<u>0.0</u>	<u>0.25</u>	<u>0.07</u>	<u>0.02</u>	<u>0.70</u>
Others: 1 CO ₂			<u>11.8</u>	<u>5.5</u>	<u>0.87</u>	<u>20.9</u>
2 CH ₃ OH			<u>25.3</u>	<u>22.4</u>	<u>9.2</u>	<u>5.2</u>
3						

* Solution of 10% H₂O/90% C₂H₅OH

Table 15 shows that adding 0.0005 g H₂O per minute to the H₂ + CO syngas nearly doubled the methanol synthesis activity. Injecting water at the rates of 0.005 and 0.01 g/min resulted in approximately the same yields of methanol. Considering the formation of CO₂ from the injected H₂O according to equation 8, the synthesis gas at these two injection rates would correspond to H₂/CO/CO₂ $\approx$ 70/28.3/1.7 and 70/26.4/3.6 vol%, respectively. Injecting water at a higher flow rate produced a larger concentration of carbon dioxide, and the yield of methanol was retarded. This experiment demonstrated that the water gas shift reaction proceeds readily over the Cu/ZnO methanol synthesis catalyst and that the maximum methanol synthesis activity was observed for CO₂ concentrations in the synthesis gas in the neighborhood of 2-3 vol%.

The presence of water in the synthesis gas clearly has a profound effect on the synthesis of methanol over the Cu/ZnO catalyst. Therefore, the influence of water on the methanol yield was studied further at 235°C. It was observed that water was indeed a very effective promoter for the formation of methanol from H₂/CO = 70/30 vol% synthesis gas. However, as shown in Figure 3, water is also effective for retarding the synthesis when it is present in the synthesis gas at relative high concentrations. A comparison of the H₂O and CO₂ addition experiments, given in Figure 3, demonstrates that water behaves as a more effective promoter at low concentrations and a more severe retardant at high concentrations than does equimolar carbon dioxide at the same experimental conditions.

FIGURE 3. Comparison of the carbon conversion to methanol effected by the addition of CO₂ (□) to H₂(CO+CO₂) = 70/30 vol% synthesis gas and of H₂O (○) to H₂/CO = 70/30 vol% synthesis gas at 235°C.

The maximum in the methanol formation rate as a function of water content of the synthesis gas was also observed during the non-steady state reactions that occurred when the water addition was terminated. The results obtained at 225°C are shown in Figure 4, where the initial water addition (0.01 g/min) was 245 g/kg catalyst/hr. It is evident from Figure 4 that the transient conversions sequentially follow the trend in steady state conversions given in Table 15 as water is removed from the synthesis gas. The methanol yield during the transient conversion was 90 times the quantity that would be produced by simply sweeping the methanol precursor from the catalyst surface. Therefore, water had conditioned the catalyst surface for enhanced synthesis rates that persist for 1-2 hr after water is removed from the gas phase. Eventually the low steady state conversion in the water free synthesis gas is attained.

These preliminary experiments indicated that the water gas shift reaction proceeded at least 95% to completion under the experimental conditions utilized and that no maximum in the water gas shift reaction rate occurred. In contrast, a pronounced maximum in methanol yield was observed at low water concentrations. Since the water gas shift reaction and the water effect on the methanol yield required more extensive investigation, the mechanistic relationships between these two reactions has been examined and is being resolved under DOE/SERI Subcontract No. XX-200217301.

FIGURE 4. The transient production of methanol at 225°C. after the addition of water at the rate of 33 mmol/2.45 g cat/hr to the $H_2/CO = 70/30$ vol% synthesis gas was terminated over the Cu/ZnO catalyst.

D. COMPETITIVE HYDROGENATION REACTIONS OVER Cu/ZnO CATALYSTS

A comparison of hydrogenation rates of various substrates over the same catalyst has sometimes been used to yield mechanistic information concerning the type of attack the substrate undergoes on the catalyst surface. Moreover, when two hydrogenable substrates and hydrogen are allowed in contact with the catalyst simultaneously, their relative conversions reflect the extent to which these reaction components compete for the active sites. We report herein on the relative hydrogenation rates, both of the individual substrates and of their mixtures with carbon monoxide, over the Cu/ZnO catalyst for methanol synthesis. A pattern that emerges for the Cu/ZnO catalyst is then compared with those for nickel, cobalt, and rhodium to demonstrate some significant differences in the function of these catalysts.

Using the Cu/ZnO = 30/70 catalyst described earlier (1), the substrates 1-hexene, propionic acid, propanaldehyde, benzene, toluene, ethylbenzene, and carbon monoxide were hydrogenated in vapor phase under the pressure, temperature, and flow rate conditions at which CO is hydrogenated to methanol. The results are summarized in Table 16, which shows that the hydrogenation rates were substrate dependent in the order: olefin > aldehyde > CO + CH₃OH > carboxylic acid > ethylbenzene ~ toluene > benzene.

It is noteworthy that carbon monoxide is hydrogenated faster than the aromatic ring over the Cu/ZnO catalyst. The order of hydrogenation rates of CO and aromatics is just the opposite over nickel: while Vannice reports a turnover rate of $3.2 \times 10^{-2} \text{ s}^{-1}$ at

TABLE 16

Relative Hydrogenation Rates of Carbon Monoxide, Hydrocarbons, and Oxygenates over the Cu/ZnO Catalyst^a

Substrate	Percentage conversion ^b	Turnover rate ^c (s ⁻¹)	Substrate feed rate (mol/hr)	Ionization potential (eV)
Benzene	16.6	4.95×10^{-3}	0.0068	9.24
Toluene	25	6.27×10^{-3}	0.0057	8.82
Ethylbenzene	29	6.24×10^{-3}	0.0049	8.76
Propionic acid	63	1.48×10^{-2}	0.0080	
Propanaldehyde	99	4.23×10^{-1}	0.2922	
1-Hexene	100	4.33×10^{-1}	0.2957	
Carbon monoxide	55	2.96×10^{-1}	0.147	

^a Cu/ZnO = 30/70 catalyst and testing conditions are described in Ref. (1). The hydrogenation products were cycloparaffins from aromatics, paraffins from olefins, primary alcohols from oxygenates, and methanol from CO.

^b Conversion was measured at 250°C, 75 atm, over 2.45 g catalyst using a feed of 10.5 liters (STP) of hydrogen per hour (0.43 mol H₂/hr) and that of the substrate indicated in the fourth column of this table.

^c The turnover rate was calculated from the measured conversion rates assuming 2×10^{18} sites/m² of ZnO on the Cu/ZnO catalyst having 23.3 m² ZnO surface per gram of catalyst. The turnover rate is defined as the number of conversions per site per second per hydrogen molecule consumed. Hence the substrate turnover is two (three) times smaller in the case where the substrate is hydrogenated by two (three) hydrogen molecules.

TABLE 17

Hydrogenation Rates of Carbon Monoxide, Hydrocarbons, and Oxygenates when CO plus an Additional Substrate and Hydrogen Were Admitted to the Cu/ZnO Catalyst^a

Reaction mixture	Molar ratio	Percentage MeOH from the hydrogenation of CO	Percentage hydrogenation of the hydrogenable substrate other than CO or CO ₂
CO/CO ₂ /H ₂	24/6/70	55	—
1-Hexene/CO/CO ₂ /H ₂	4.4/22.9/5.8/66.8	25–42 ^b	100% to <i>n</i> -hexane
Propanaldehyde/CO/CO ₂ /H ₂	3.9/23/5.8/67.2	32–51 ^b	99% to <i>n</i> -propanol
Acrolein/CO/CO ₂ /H ₂	1.5/23.6/5.9/69.0	13.6 ^b	99% to <i>n</i> -propanol
Propionic acid/CO/CO ₂ /H ₂	1.3/23.7/6.0/69.0	0.6 ^b	63% to <i>n</i> -propanol
Ethylbenzene/CO/CO ₂ /H ₂	0.8/23.8/6.0/69.4	31.3 ^b	0% to ethylcyclohexane (traces of toluene)
Toluene/CO/CO ₂ /H ₂	0.9/23.8/6.0/69.3	34.0 ^b	0% to methylcyclohexane
Benzene/CO/CO ₂ /H ₂	1.1/23.7/6.0/69.2	30.5 ^b	0% to cyclohexane

^{a,b} See footnotes of Table 1-6. The CO/CO₂/H₂ = 24/6/70 mixture was used at 250°C, 75 atm, and total flow rate of 15 liters/hr over 2.45 g of the Cu/ZnO = 30/70 catalyst. The substrate was admitted from a liquid feed valve to produce concentrations indicated in the second column.

275°C for hydrogenation of CO to methane over nickel catalysts (29), those for benzene hydrogenation can be estimated as $4.6 \times 10^{-1} \text{s}^{-1}$ at 275°C and $3.4 \times 10^{-1} \text{s}^{-1}$ at 250°C from the report by Danes et al. (30)¹ and these compare well with the values estimated from Richardson (31) and Taylor and Staffin (32). The above comparison suggests that *on those catalysts on which carbon monoxide is hydrogenated to methanol, this reaction proceeds faster than the hydrogenation of aromatics, while on catalysts which steer the CO hydrogenation to hydrocarbons, the hydrogenation of aromatics is the faster of the two reactions.* The latter pattern may result from the requirement that the CO molecule dissociates in the course of methanation. This is supported by the observation of higher activation energy of methanation than of methanol synthesis on those catalysts which guide CO hydrogenation to both methane and methanol (33).

¹ The turnover rate for benzene hydrogenation on nickel was calculated using the data in Ref. 30: 92.2% conversion at 66°C over 1.49 g Ni of surface area ca. $10 \text{ m}^2/\text{g}$, flow rate $21 \text{ cm}^3/\text{min}$ of $\text{H}_2/\text{benzene} = 7/1$ feed gas. A surface density of $1 \times 10^{15} \text{ sites}/\text{cm}^2$ was assumed. The minimum turnover rate at 275°C was estimated using the minimum activation energy of 7.3 kcal/mol derived from data in Table 2 of the given reference.

A further point of difference between the Cu/ZnO and transition metal catalysts is the relative rate of hydrogenation of substituted aromatics. Völter et al. (34) have found that over nickel, cobalt, and rhodium catalysts, the rate of hydrogenation of substituted benzenes *decreases* with increasing electron density on the aromatic ring (although activation energies varied in a manner that differed from one metal to another). The Cu/ZnO catalyst behaves, once again, in an opposite fashion: ethylbenzene and toluene are hydrogenated faster than benzene showing that the aromatic ring hydrogenation rate *increases* with increasing electron density. Such behavior is strong evidence in favor of π -bonded intermediates, the surface concentration of which increases with increasing electron-donating ability of the π -electron system, and indicates that hydrogenation might involve an electrophilic attack of the surface intermediate. A simple explanation of the observed pattern is provided by a model wherein the aromatics are π -bonded to the surface cations of the Cu/ZnO catalyst followed by a facile stepwise addition of hydrogen. Because the hydrogenation rates are proportional to the stability of the π -donor complexes, no σ -bonded intermediates need to be invoked for the Cu/ZnO catalyst as it was deemed necessary to explain the inverse proportionality between the hydrogenation rates and the stability of π -donor complexes on Ni, Co, and Rh (34). Additional evidence that supports the proposed model is the observed increase in the rate of hydrogenation with decreasing ionization potential. The ionization potentials and the turnover rates of ethylbenzene and toluene are nearly equal, 8.76 and 8.82 eV, but there is a significant increase of ionization potential and decrease of hydrogenation rate between these two substituted aromatics and

benzene (ionization potential, 9.24 eV). The criterion for a π -complex is its increasing stability with decreasing ionization potential, and it is suggested that the hydrogenation rate increases where increased stability of the π -complex increases its surface coverage. However, this argument can only be used to compare hydrogenation rates within one class of compounds such as aromatics, since other variables such as steric influence, resonance energy, dipole moments, etc., would differ significantly from one class of substrates to another and offset simple correlations that may exist in one homolog series.

Further experiments, in which a hydrogenable substrate and carbon monoxide were simultaneously admitted to the catalyst, showed that aromatics, carbon monoxide, carboxylic acids, aldehydes, and olefins compete for the same active sites. The results, summarized in Table 17, demonstrate clearly that the addition of a small percentage of the substrate results in a suppression of the methanol yield, while the hydrogenation of the benzene ring is completely inhibited by the presence of carbon monoxide. The results of Table 17 thus show that the same active sites are involved in activating aromatics, olefins, carboxylic acids, aldehydes, and carbon monoxide. The notion that these sites are surface cations is entirely consistent with our earlier suggestion that carbon monoxide is activated for methanol synthesis by copper ions in the zinc oxide surface [1]. The data and discussion presented in this section of the report have been published elsewhere [35].

E. CHEMICAL TRAPPING OF SURFACE INTERMEDIATES ON THE Cu/ZnO CATALYST

Introduction

The intermediates involved in the synthesis of methanol from carbon monoxide and hydrogen over Cu/ZnO catalysts are of interest both for formulating kinetic equations that adequately describe the rate of this important industrial reaction and for being utilized as building blocks in organic syntheses. Although surface formate and methoxide have been identified by spectroscopic and chemical means on related catalysts [36], it has also been proposed that a formyl, hydroxycarbene, or aldehydic intermediate plays a key role in the synthesis [1]. There is a precedent for homogeneous catalyzed transformations of synthesis gas mixtures to oxygen-containing organic compounds to probably occur via metal formyl intermediates [37-44]. A variety of formyl complexes have been synthesized [45-54], and at least some of them can be reduced to yield formaldehyde or methanol [54,55]. Infrared spectroscopic evidence for the formation of formyl by coadsorbed CO and H₂ on Cu/ZnO at near-ambient conditions has been reported [56].

In general, amines are known to react with aldehydes and ketones to produce alkyl substituted amines and water [57]:

where R=H or alkyl. The reaction is a typical nucleophilic addition of the electron-rich (base) nitrogen of the amine attacking the electron-deficient (acid) carbonyl carbon of the aldehyde

or ketone. Secondary amines are more basic, and therefore, more reactive than primary amines which are more reactive than ammonia:

On the other hand, the oxygenates of the lowest molecular weight are the most reactive due to a combination of electronic and steric factors:

With these ideas in mind, ammonia, isopropylamine, and diethylamine were added to the reactant feed gases in an attempt to trap the oxygenated intermediate.

In this section of the report, we present evidence that a reactive intermediate involved in the formation of methanol from carbon monoxide and hydrogen is of the aldehydic or hydroxycarbenoic type. At the same time, the nature of the intermediate formed during the alkylation of amines with synthesis gas and alcohols is clarified.

Chemical trapping with Ammonia

A CuO/ZnO = 30/70 mol% catalyst was coprecipitated from a (Cu/Zn) nitrate solution by 1.0 M sodium carbonate, filtered, washed, dried, calcined to 350°C, and pelletized to 10-20 Mesh as described previously [1]. A 2.45 g (4.8 ml) portion of the dry pelletized solid was diluted with an equal volume of Pyrex beads, centered in the 316 stainless steel reactor, and reduced at 250°C and ambient pressure with a $H_2/N_2 = 2/98$ vol% gas mixture. After

cooling to ambient temperature, the reaction system was pressurized to 840 psig with hydrogen, and the flow rates of hydrogen and carbon monoxide were adjusted to the desired values with the resultant composition being $H_2/CO = 2/1$. The reactor was heated to $120^\circ C$, and heated ammonia gas was added to the synthesis gas stream at the top of the reactor. The catalyst was then initially tested at the conditions specified in Table 18.

TABLE 18

The Results of the Reaction of Synthesis Gas
With Ammonia ($NH_3/CO = 2.1$) over 2.45 g (4.8 ml) of $Cu/ZnO = 30/70$
Catalyst at $300^\circ C$, a Pressure of 840 psig, and with GHSV = 1040 hr^{-1}

	H_2	CO	CO_2	NH_3	CH_3NH_2
Moles/hr In	0.0806	0.0401		0.0834	
Moles/hr Out	a	0.0382	0.0009	0.0826	0.0009

^a Not determined

Under these conditions with $NH_3/CO/H_2 = 40.9/19.6/39.5$, approximately 4% of carbon monoxide was converted in equal proportions to methylamine and carbon dioxide. No methanol was detected in the exit gas, nor were dimethylamine and trimethylamine formed under these experimental conditions.

Maintaining the temperature at $300^\circ C$ and the pressure at 840 psig, the flow rate of ammonia was decreased so that the inlet gas stream consisted of $NH_3/CO/H_2 = 28.2/23.8/47.9$. The results of this test are presented in Table 19. About 7.2% CO conversion was observed and the yield of monomethylamine was 0.31 mol/l of catalyst/hr. This can be regarded as a minimum yield because this catalyst was pelle-

tized to give a low bulk density of 0.51 g/ml instead of the usual 0.82 g/ml. The monomethylamine yield corresponds to 0.50 mol/kg of catalyst/hr. A trace of dimethylamine was present in the exit stream, but no water or methanol was detected.

TABLE 19

The Results of the Reaction of Synthesis Gas With Ammonia ($\text{NH}_3/\text{CO} = 1.2$) over 2.45 g (4.8 ml) of $\text{Cu}/\text{ZnO} = 30/70$ Catalyst at 300°C , a Pressure of 840 psig, and with GHSV = 870 hr^{-1}

	H_2	CO	CO_2	NH_3	CH_3NH_2
Moles/hr In	0.0806	0.0401		0.0474	
Moles/hr Out	a	0.0372	0.0014	0.0459	0.0015

^a Not Determined

A 2.45 g (4.8 ml) portion of the $\text{Cu}/\text{ZnO} = 30/70$ catalyst was prepared for testing using the procedure described above, but it was tested under different experimental conditions. Using a reactant gas stream consisting of $\text{NH}_3/\text{CO}/\text{H}_2 = 5.2/31.5/63.3$, the results in Table 20 were obtained.

TABLE 20

The Results of the Reaction of Synthesis Gas with Ammonia ($\text{NH}_3/\text{CO} = 0.16$) over 2.45 g (4.8 ml) of $\text{Cu}/\text{ZnO} = 30/70$ Catalyst at 300°C , a Pressure of 840 psig, and with GHSV = 650 hr^{-1}

	H_2	CO	CO_2	NH_3	H_2O	CH_3OH	$\text{CH}_3\cdot\text{NH}_2$	$\begin{smallmatrix} (\text{CH}_3)_2 \\ \text{NH} \end{smallmatrix}$	$\begin{smallmatrix} (\text{CH}_3)_3 \\ \text{N} \end{smallmatrix}$
Moles/hr In	0.0806	0.0401		0.0067					
Moles/hr Out	a	0.0150	0.0107	0.0023	0.0027	0.0013	0.00006	0.0008	0.0042

^a Not Determined

It is evident that about 63% of the CO reactant was converted to products that consisted of carbon dioxide, methanol, monomethylamine, dimethylamine, and trimethylamine. About 66% of the inlet ammonia was converted to methylated products with a 96.8% selectivity to trimethylamine. No higher alkyl amines, e.g. ethylamine, were found in the exit gas. The yield of trimethylamine corresponded to 0.88 mol/l of catalyst/hr (1.7 mol/kg of catalyst/hr).

Chemical Trapping with Isopropylamine

A CuO/ZnO = 30/70 catalyst was prepared in the same way and the calcined powder was pelletized from a thick aqueous slurry. A 2.45 g (3.0 ml) portion of the dry pelletized solid was centered in the reactor and reduced at 250°C with a H₂/N₂ = 2/98 vol% gas mixture at ambient pressure. After cooling, the reactor was pressurized to 1100 psig with a H₂/CO = 70/30 vol% synthesis gas. Maintaining a gas flow of GHSV = 5000 hr⁻¹, the reactor was heated to 225°C and the isopropylamine was injected continuously into the gas stream as the top of the reactor. The conversion results are given in Table 21.

TABLE 21

The Results of the Reaction of Synthesis Gas Containing CO/H₂ = 30/70 vol% at GHSV = 5000 hr⁻¹ and a Pressure of 1100 psig with Isopropylamine over 2.45 g (3.0 ml) of Cu/ZnO (30/70) Catalyst

	Temp- era- ture	CO	CO ₂	H ₂ O	CH ₃ OH	Isopro- pyl- amine	Methyl Isopro- pyl- amine	Dimethyl Isopropyl- amine
Moles/hr In	225°C	0.1840				0.0282		
Moles/hr Out		0.1372	0.0146	0.0009	0.0165	0.0154	0.0101	0.0027
Moles/hr In	190°C	0.1840				0.0423		
Moles/hr Out		0.1699	0.0040	0.0003	0.0056	0.0383	0.0040	0.0000

When the reaction was carried out at 225°C with a pumping rate of 40 μ l/min (0.0282 mol/hr) of isopropylamine, about 25% of the CO was converted to products and 45% of the primary amine was converted to secondary and tertiary amines with 79% selectivity for the secondary methylisopropylamine. The selectivity is defined as $100 \times (\text{mol fraction of methylisopropylamine}) / (\text{mol fractions of methylisopropylamine plus dimethylisopropylamine})$. At this temperature, the yield of methylisopropylamine is 3.37 mol/l of catalyst/hr. At the temperature of 190°C and with a reactor inlet stream of $(\text{CH}_3)_2\text{C(H)NH}_2/\text{CO}/\text{H}_2 = 6.4/28.1/65.5$, about 10% of the amine reactant was converted to methylisopropylamine with 100% selectivity. No disproportionation of the amine reactant was observed at either temperature.

The methanol synthesis activity of the Cu/ZnO = 30/70 catalyst at 225°C, 1100 psig, and GHSV = 5000 hr^{-1} with a $\text{H}_2/\text{CO} = 70/30$ vol% synthesis gas corresponds to 30 mmol CH_3OH formed per hour [16]. Adding isopropylamine to the reactant, with the amine/CO molar ratio = 1.0/6.5, decreased the yield of methanol by 45% but increased the total number of methyl groups formed as methanol and methylated amines to 32 mmol/2.45 g catalyst/hr (Table 21). In order to compare the activation energies for methanol and methylamine syntheses, while avoiding the conditions where methanol synthesis is substantially suppressed as in the above example, a small concentration of amine amounting to 3.86% of the CO content was added to the synthesis gas, and the rates of methylation of the amine, as well as of methanol synthesis, were measured in the temperature range of 150-215°C (Table 22).

The Arrhenius plots in Figure 5 demonstrate that the apparent activation energies for the two competing reactions are identical (74.9 ± 0.4 kJ/mol), and this is the same apparent activation energy that was observed prior to the addition of isopropylamine to the binary CO/H₂ synthesis gas. Therefore, methanol and methylated amine are formed from a common intermediate such as the formyl, formaldehyde, or hydroxycarbene species. It should be noted that formaldehyde was never observed in the gaseous phase under the presently employed synthesis conditions, so that the amine trapping is selective for surface intermediates.

TABLE 22

The Results of the Reaction of Synthesis Gas Containing CO/H₂ = 30/70 vol% at GHSV = 5000 hr⁻¹ and a Pressure of 1100 psig with Isopropylamine over 2.45 g (3.0 ml) of Cu/ZnO (30/70) Catalyst

	Temp- era- ture	CO	CO ₂	H ₂ O	CH ₃ OH	Isopro- pyl- amine	Methyl isopro- pyl- amine	Dimethyl- isopropyl- amine
Moles/hr In	215°C	0.1840				0.0071		
Moles/hr Out		0.1409	0.0094	0.0006	0.0239	0.0013	0.0029	0.0028
Moles/hr In	180°C	0.1840						
Moles/hr Out		0.1756	0.0016	0.0000	0.0053	0.0058	0.0013	0.0000
Moles/hr In	159°C	0.1840						
Moles/hr Out		0.1807	0.0007	0.0000	0.0019	0.0066	0.0005	0.0000
Moles/hr In	150°C	0.1840				0.0071		
Moles/hr Out		0.1820	0.0002	0.0001	0.0015	0.0068	0.0003	0.0000

The results summarized in Table 22 show that at 215°C about 82% of the amine was methylated, where half of the amine product was dimethylisopropylamine. At the same time when methylation was occurring, methanol synthesis (but not methane formation) was

FIGURE 5. An Arrhenius activation energy plot for the formation of methylisopropylamine (□) and methanol (O) from an isopropylamine/CO/H₂ = 1.14/29.67/69.18 mol% gas mixture at 1100 psig and GHSV = 5000 hr⁻¹ over the Cu/ZnO catalyst.

observed. It is evident from Table 22 that the yield of methylisopropylamine is larger at 215°C than that at 180°C, indicating that higher temperatures favor higher yields of methylated amines.

The amine methylation reaction was studied in greater detail at 190°C with isopropylamine as the reactant amine. Flowing a small concentration of this amine in a nitrogen stream over the Cu/ZnO catalyst at 190°C resulted in appreciable disproportionation of the amine, but this was inhibited by the presence of CO (Table 23, Tests 1 and 2). In the presence of synthesis gas, both methylation of the amine and formation of methanol occurred to the extent

TABLE 23

Data for the Catalytic Synthesis of Dialkylamines at 190°C,
GHSV = 5000, and 1100 psig over 2.45 g of Cu/ZnO (30/70) Catalyst

Test No.	MMol/ Hr	Isopropyl- amine, PNH ₂ ^a	CO	H ₂	N ₂	CH ₃ OH	NH ₃	P(NH)CH ₃ ^a	PNH ₂ ^a	H ₂ O
1	In	7.1	0	0	613	0	0	0	0	0
	Out	5.5	0	0	613	0	0.8	0	0.8	0
2	In	7.1	184	0	429	0	0	0	0	0
	Out	7.1 ^b	184	0	429	0	0	0	0	0
3	In	42.3	184	429	0	0	0	0	0	0
	Out	38.3	169.9 ^c	d	0	5.6	0	4.0	0	0.3
4	In	41.3	0	429	0	9.9	0	0	0	0
	Out	39.5	0	429	0	8.2	0	1.7 ^e	0	1.7
5	In	0	184	429	0	0	0	0	0	0
	Out	0	178	420	0	6.2	0	0	0	0

^a p = isopropyl

^b No N-alkylformamide was formed by carbonylation

^c Plus 4.0 mmol/hr carbon dioxide formed via the water gas shift reaction

^d Not determined

^e Plus 0.1 mmol/hr isopropyldimethylamine

of 9.6 mmol CO/2.45 g catalyst/hr converted to methyl groups (Table 23, Test 3). If methanol were the reactive intermediate between CO and the amine, adding the alcohol directly to the gas stream would be expected to increase the yield of the methylated amine. Therefore, the CO was replaced by N_2 , and an amount of methanol (9.9 mmol/2.45 g catalyst/hr) approximately equivalent to the number of methyl groups formed in the previous experiment as methanol plus methylisopropylamine was injected into the gas stream. Table 23 shows that the degree of amine methylation was lower when methanol was the source of methyl groups (Test 4) than when the synthesis gas was the source of the methyl group (Test 3). The total amount of methyl groups synthesized in the absence of the amine but otherwise identical conditions was lower (Table 23, Test 5) than that in the presence of the amine (Tests 3 and 4), but this is due to the water formed during the amine methylation reaction, which promotes the formation of the reactive surface intermediate [58].

Chemical trapping with Diethylamine

During methanol synthesis testing over a Cu/ZnO = 30/70 catalyst at 215°C with H_2/CO = 70/30 vol%, diethylamine (DEA) was added to the inlet stream at the rate of 433 g DEA/kg catalyst/hr. About 77.2% of the amine was methylated, with a 95.7% selectivity, to methyldiethylamine, as represented by equation 12. As shown in Table 24, 97% of the water formed in reaction was converted to CO_2 via the water gas shift reaction (equation 8). Disproportionation of the reactant amine also occurred to a small extent. The steady

state methanol yield prior to the amine addition was 6.8 mmol $\text{CH}_3\text{OH/hr}$, while with H_2O injected at the rate of 12.4 mmol/hr (approximately equal to the quantity of $\text{H}_2\text{O} + \text{CO}_2$ produced when amine was added) into the H_2/CO synthesis gas, the methanol yield was 16.0 mmol $\text{CH}_3\text{OH/hr}$.

TABLE 24

Trapping of the intermediate by diethylamine during methanol synthesis at 215°C and 1100 psig with $\text{H}_2/\text{CO} = 70/30$ vol% synthesis gas at GHSV = 5000 hr^{-1} over 2.45 g of $\text{Cu/ZnO} = 30/70$ catalyst^a

	CO	CO ₂	CH ₄	H ₂ O	CH ₃ OH	(C ₂ H ₅) ₂ NH	(C ₂ H ₅) ₂ NCH ₃	C ₂ H ₅ NHCH ₃	(C ₂ H ₅) ₃ N
mmol/hr IN	184.0	0	0	0	0	14.5	0	0	0
mmol/hr OUT	151.1	11.6	0.2	0.3	7.9	2.7	11.2	0.3	0.2

^a In addition to the products given, 0.1 mmol/hr of ethanol and methyl formate were also observed in the exit stream.

Discussion

It follows from the described experiments with isopropylamine that the methylation of the amine is not proceeding via reaction with methanol, but rather through an intermediate that is common to methanol synthesis and to the methylation of amines. Among the possible intermediates, adsorbed CO, formate, and methoxide are not expected to react with an amine, but formyl or adsorbed formaldehyde will be prone to the nucleophilic attack by the amine. The isomer of formaldehyde, hydroxycarbene HCHO , may be expected to react in a similar manner. Although the estimated activation energy barrier of the isomerization of free gaseous formaldehyde to hydroxy-

carbene, $\text{H}_2\text{CO} \rightarrow \text{HCOH}$, lies in the range of 330-351 kJ/mol [59], the barrier may be significantly lowered by the bonding of the hydroxycarbene to the catalyst surface. In order that hydroxycarbene play a role as an intermediate in methanol and amine syntheses, its binding energy to the catalyst surface would, therefore, have to be ≥ 330 kJ/mol. Such a binding energy might reasonably be achievable.

While evidence is being presented for the existence of a formyl-, formaldehyde, or hydroxycarbene-type intermediate during the synthesis of methanol from carbon monoxide over Cu/ZnO catalysts, it must be pointed out that other reactive species, such as formate and methoxide, also play a role in the mechanistic pathways of the methanol synthesis and water gas shift reactions [58].

Addition of diethylamine to the synthesis gas stream resulted in a rapid methylation of the amine, with the concomitant production of water and CO_2 . The formation of water according to equation 12 enhanced the yield of methanol, as well as of CO_2 *via* the shift reaction. However, the quantity of methanol formed (Table 24) was only about 50% that expected for the observed $\text{CO}_2 + \text{H}_2\text{O}$ content of the synthesis gas [16,58]. The total number of methyl groups formed as methanol and methylamines in the presence of amine was approximately equal to the yield of methanol in the absence of amine but with an equivalent amount of water present. Therefore, it is evident that the amination of a surface intermediate is competing with the hydrogenation of the intermediate to form methanol. The amine methylation reaction did not interfere with the water gas reaction,

and the yields of CO₂ and H₂O were exactly those expected for the amine-free synthesis.

Since the methylation of diethylamine did not suppress the water gas shift reaction but did inhibit methanol synthesis, the C₁ intermediate undergoing amination was formed subsequent to the formate. This intermediate is identified as a surface *formyl* or *hydroxycarbene*, the enolic form of formaldehyde, because these species will undergo specific coupling reactions with amines to form a C-N bond, which in the presence of hydrogen will be converted to a methylamine. The coupling reaction involved can be written, based in part on reference [60], as shown in equation 13.

A further diagnostic for formyl or hydroxycarbene is the conversion of propanal to 2-methyl-1-propanol. This reaction is typical of aldol condensation between the surface C₁ aldehydic residue and propanal followed by hydrogenation to yield the β-branched product. This is similar to the conversion of 1-propanol to 2-methyl-1-propanol and of 2-propanol to 2-butanol over alkali- and alkaline earth-doped Cu/ZnO catalysts under the same reaction conditions [61].

F. CHEMICAL TRAPPING OVER AN Fe/Cu/ZnO CATALYST

The catalyst utilized in this study was a Fe/Cu/ZnO = 1.2/31.8/67.0 mol% catalyst that was investigated for higher alcohol synthesis, as described elsewhere [62,63]. It was prepared by coprecipitation from nitrate solution by the addition of sodium carbonate, which is the usual method for preparing Cu/ZnO catalysts [1,14]. A 2.414 g portion of the pelletized catalyst was prepared for catalytic testing by diluting the 3.0 ml catalyst charge with 7.0 ml Pyrex beads and centering the solid mixture in the 316 stainless steel reactor by means of additional Pyrex beads. The reactor was purged with a $H_2/N_2 = 2/98$ vol% gas mixture for 2 hr, and then the catalyst was reduced, at ambient pressure and 250°C with the gas mixture flowing at the rate of 3.6 l/hr, until water was absent from the exit gas, which was monitored every 5 min by gas chromatography. The reactor was then cooled to ambient temperature and pressurized with a $H_2/CO = 70/30$ vol% synthesis gas mixture.

Initially, a steady state conversion was established at 235°C, 75 atm, 5000 hr^{-1} and $H_2/CO = 70/30$ vol% without the addition of isopropylamine. Then, 20 $\mu\text{l/min}$ of liquid isopropylamine was pumped into the feed gas mixture. Within 6 to 8 hr of the start of pumping, a steady state conversion was achieved. Quantitative analysis of the products was obtained by inline gas chromatography, while qualitative data was obtained by mass spectroscopy. Experimental results are summarized in Table 25 and Figures 6 and 7.

TABLE 25

Effects of isopropylamine on product distributions over a 1.2% Fe containing Cu/ZnO catalyst at 235°C, 75 atm, 5000 hr⁻¹, and H₂/CO/CO₂ = 70/30/0 vol%. Catalyst charge = 2.414 g (R = isopropyl)

<u>Isopropylamine in Feed</u> (μl/min)	0	20
H ₂ /CO/RNH ₂ (molar ratio)	2.33/1.00/0	2.33/1.00/0.08
<u>CO Conversion</u> (mol%)	4.45	4.38
(mol/kg/hr)	3.4	3.3
<u>Products</u> (x 10 ⁻⁴ mol/hr)		
C ₁ -C ₅ Alcohols	7.03	0
C ₁ -C ₇ Hydrocarbons	38.43	23.01
Amines:		
R-NH-CH ₃	0	1.01
R-N-(CH ₃) ₂	0	1.34
R-NH-C ₂ H ₅	0	0.70
R-N-(CH ₃ , C ₂ H ₅)	0	7.71
R-N-(C ₂ H ₅) ₂	0	0.35
R-NH-(n-C ₃ H ₇)	0	0.38
<u>Certain Molar Ratios</u>		
Alcohols/Hydrocarbons	0.2	0
Olefins/Paraffins	0.1	1.4

FIGURE 6. Effects of isopropylamine on alcohol and hydrocarbon product distribution at 235°C over a 1.2% Fe/Cu/ZnO catalyst.

FIGURE 7. Effect of amine on the alcohol, paraffin and olefin product distributions over a 1.2% Fe/Cu/ZnO catalyst.

It was observed that the small quantities of isopropylamine pumped into the system had little effect on carbon conversion, however, the product distribution changed significantly. Alcohols were consumed completely by the amines while the rate of hydrocarbon production decrease significantly. There was no additional branching observed in the hydrocarbon product, but it was apparent that the distribution shifted in favor of the longer chain molecules. It was also observed that the olefin to paraffin ratio increased significantly with the addition of the amine. The amine products consisted of methyl, ethyl and n-propyl substituted isopropylamines with a high selectivity for N-methyl, N-ethyl isopropylamine.

Since there were no alcohols in the reactor exit gas, these results indicate that isopropylamine reacts readily with either the alcohol precursor or the alcohols after they have been formed and readsorbed onto the catalyst surface. The fact that the total hydrocarbon product decreased during amine pumping, suggests that there is competition for reactive sites between the hydrocarbon intermediate and isopropylamine. The reason for an increase in the olefin yield as the amine was added to the system could be explained in two ways. The first, is that the presence of isopropylamine, perhaps by competitive adsorption with hydrogen, inhibits the hydrogenation step for the formation of paraffins.

The formation of olefins, however, is uninhibited by the presence of the amine because these compounds form by β -hydrogen elimination [64] and do not need adsorbed hydrogen.

The reduction in the hydrogen step would also explain the shift toward longer chain hydrocarbons. That is, the reaction intermediates do not become hydrogenated to products but continue to polymerize on the catalyst surface. The second explanation to a higher olefin to paraffin ratio is, that α -olefins may be formed by a secondary reaction via a Hofmann elimination [57]:

However, the presence of a Hofmann elimination was explored further in another experiment that involved pumping n-butanol and isopropylamine in a CO-free feed mixture under synthesis conditions similar to those in Table 25. In this reaction the formation of n-butylisopropylamine would be an expected product, since the alcohol would be adsorbed onto the catalyst surface, rearrange to form a stable oxygenated intermediate, and then react with the amine by a nucleophilic addition. If the Hofmann elimination does occur over the Fe/Cu/Zn system, then n-butylisopropylamine would decompose in the presence of a base (OH^-) to 1-butene, isopropylamine and water. The results of this experiment are summarized in Table 26. It is evident that

a large number of products were synthesized including n-butylisopropylamine. However, there was no evidence of butene or other hydrocarbons being formed. Therefore, Hofmann elimination does not occur under the synthesis conditions of this work.

TABLE 26.

Reaction of n-butanol and isopropylamine over the 1.2% Fe catalyst at 235°C, 75 atm and 5000 hr⁻¹. Liquid pumping rate = 40 μ l/min.

<u>N₂/H₂</u> (vol%)	100/0	70/30	100/0
<u>Liquid Feed</u> (mole ratios)			
n-butanol	1	1	1
isopropylamine	1	1	1
water	0	0	0.5
<u>Reactor Effluent</u> ¹ (%)			
n-butanol	28.6	11.7	37.8
isopropylamine	15.3	6.0	16.3
water	3.7	6.7	9.3
acetone	3.5	5.0	5.5
butane nitrile	5.3	3.0	1.7
N-isopropylpyrrolidine	9.7	0	8.8
n-butylisopropylamine	21.9	61.1	12.9
dibutylamine	3.5	6.5	2.2
C ₉ + compounds	8.7	0	5.5
butene + hydrocarbons	0	0	0

¹ percent of all products excluding N₂ as recorded by the inline GC

Figures 8 and 9 refer to the Schulz-Flory distributions for the data collected in the isopropylamine experiments Table 25 and Figure 6. At 235°C and without the influence of isopropylamine, the distributions for alcohols and hydrocarbons give α values of 0.47 and 0.53, respectively. Upon the addition of isopropylamine to the reactor feed gases, the alcohol distribution vanishes because alcohols are completely consumed by the amines, however, the distribution of hydrocarbons shifts in favor of the longer chain products, indicated by a larger propagation constant 0.58. This shift in the hydrocarbon distribution was previously explained as an inhibiting affect on hydrogenation of the hydrocarbon intermediates due to the presence of the amine. The distribution of the alkyl groups, e.g. $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{C}_3\text{H}_7$, on the product amines (excluding the isopropyl group) is plotted in Figure 8 according to the following equation:

$$\log(\text{N}_x/\text{N}_0) = \log((1-\alpha)^2/\alpha) + x \log \alpha. \quad (17)$$

It is apparent from the non-linearity of these points that the formation of alkyl groups do not follow the Schulz-Flory distribution. This indicates that the amines attack the alcohol precursor. If the amines reacted with the alcohols, then the Schulz-Flory distribution of alkyl groups would give exactly the same distribution as the alcohols ($\alpha = 0.47$). The yield of C_2 substituted amines lies above the expected value found for the alcohol distribution and the amount of C_1 and C_3 alkylated amines lies below the expected value. The reason for the low yield of C_1 and higher yield of C_2 could be explained as a methyl transfer reaction similar

FIGURE 8. Schulz-Flory distribution for alcohols and amines formed over the 1.2% Fe catalyst.

FIGURE 9. Effect of amine on the hydrocarbon Schulz-Flory distribution over the 1.2% Fe catalyst.

to that reported by Chen and Feder [65]. That is, isopropylamine reacts with a C_1 intermediate to form a methylated amine, which, in turn, transfers the methyl group to the activated iron center (Fe^*). Following CO insertion, a C_2 oxygenated compound is formed and is readily attacked by the amine. The following scheme illustrates these reactions (R = isopropyl):

Thus, C_2 alkyl amines are created at the expense of C_1 substituted amines. The low yield in C_3 substituted amines is explained as a termination in the chain-growth due to the attack of amine on the C_2 intermediates.

The results of the amine work are in direct contrast to the results of Olivé and Olivé [64] in the production of amines by the reaction of ammonia and synthesis gas over iron catalysts. Unlike the amine distribution found in this work, Olivé and Olivé observe a distribution of amines that obeys the Schulz-Flory law, e.g. at

200°C $\alpha = 0.69$. The products found in that work were exclusively primary amines, whereas in this work, starting with the primary amine, secondary and tertiary amines were formed. Olivé and Olivé proposed that ammonia attacks an alkyl intermediate ($-\text{CH}_x$); however, from this work it is evident that the oxygenated intermediate reacted with the amines and that the hydrocarbon intermediate was essentially left undisturbed. This indicates that Olivé and Olivé may not have observed an ammonia-alkyl reaction, but rather a reaction involving an oxygenated intermediate and ammonia.

G. ALCOHOL/AMINE REACTIONS OVER THE Cu/ZnO CATALYST AND A Pd/SiO₂ CATALYST

Introduction

The data in Table 23 demonstrated that methanol reacted with isopropylamine in the absence of carbon monoxide to form methylisopropylamine over the Cu/ZnO catalyst. Since the formation of methylamines from synthesis gas and from methanol could involve the same surface oxygenate intermediate species, the reactions of amines with alcohols over the Cu/ZnO = 30/70 catalyst was investigated further. In addition, a 4.8 wt% Pd/SiO₂ catalyst was also subjected to the alcohol/amine reaction testing to determine its catalytic activity and to examine whether alkyl-transfer reactions could be induced over this catalyst under mild experimental conditions.

Experimental

The Cu/ZnO = 30/70 catalyst was prepared as described previously [1,14]. When it was tested, a 2.45 g portion ($\approx$ 3.0 ml) was diluted with 7 ml of Pyrex beads and centered in the reactor by means of additional beads. Reduction was then carried out at 250°C and atmospheric pressure with a flowing 2% H₂/98% N₂ gas mixture (3.6 l/hr) until water was absent from the exit gas. The catalyst was cooled to ambient temperature before the reactor was pressurized.

The 4.8 wt% Pd on SiO₂ catalyst was prepared by adding 200 g of 10-20 Mesh silica gel to 200 ml of concentrated HCl containing

16.7 g of PdCl_2 , as described elsewhere [66]. The liquid was evaporated at 60°C with the aid of evacuation, and the sample was dried under vacuum at 150°C for 3 hr and then calcined in air at 400°C for 4 hr. For catalytic testing, a 4 g (10 ml) portion was centered in the reactor with Pyrex beads, and the reactor was extensively purged with hydrogen under ambient conditions. The catalyst was then reduced in flowing H_2 at 300°C for 2 hr and at 500°C for 2.5 hr. The system was cooled to ambient temperature before pressurization was carried out.

A high pressure pump was used to feed liquid reactants into the inlet gas stream at the top of the reactor at system pressures up to 100 atm. The liquids vaporized in the preheater section of the reactor. The exit gas stream was continually sampled by means of a heated automated gas sampling valve controlled by the GC integrator/controller unit. GC analyses were carried out using Chromosorb 101, Poropak Q, and 28% Pennwalt 223 columns.

Results

Using the catalysts prepared as described in the previous section, a number of test reactions for the alkylation of amines by intermediates derived from alcohols were run. Monosubstituted amines were utilized as reactants so that the reactions would not be limited to monoalkylations, e.g. as would be the case with disubstituted amine reagents, while at the same time they would allow a disproportionation reaction to proceed if it were promoted. Additional tests are described elsewhere [67].

Reaction of Methylamine with n-Butanol. The reactor containing reduced Cu/ZnO = 30/70 mol% catalyst was pressurized to 26 atm with a $\text{CH}_3\text{NH}_2/\text{N}_2 = 3/97$ mol% gas mixture, the gas hourly space velocity (GHSV) was adjusted to 8870 hr^{-1} (by volume at STP), and the catalyst was heated to 190°C . Using the high pressure pump, liquid n-butanol was injected into the gas stream at the rate of $25 \text{ }\mu\text{l}/\text{min}$. A 57.3% butanol conversion to products occur with a 96% selectivity to methylbutylamine. A small amount of methyl-dibutylamine was formed, as indicated in Table 27, and the quantity of water formed corresponded exactly to the number of moles of n-butanol that had reacted. No ammonia or dimethylamine was detected in the exit stream.

The GHSV of the gas stream was decreased, and this effectively decreased the partial pressure of the monomethylamine in the reactor. Accordingly, the conversion of n-butanol decreased somewhat to 53.6% as shown in Table 27. However, the same high selectivity toward methylbutylamine was observed, even though the GHSV was 17% lower than in the previous test.

The reactant gas stream was changed to $\text{H}_2/\text{CH}_3\text{NH}_2/\text{N}_2 = 21.36/2.36/76.28$ mol%, and the pressure and GHSV were increased as indicated in Table 27. Again, the selectivity remained the same, but the conversion of the reactants to products increased. This is especially significant since the GHSV had been increased about 27% above that in the previous test. Therefore, it appears that the presence of H_2 in the system enhances the alkylation of mono-

TABLE 27

Reaction^a of Methylamine with n-Butanol at 190°C over 2.45 g
of the Cu/ZnO = 30/70 mol% Catalyst

N ₂ (mol/hr)	H ₂ (mol/hr)	CH ₃ NH ₂ (mol/hr)	n-BuOH (mol/hr)	Pressure (atm)	GHSV (hr ⁻¹)	Total n-BuOH Conversion(%)	% Selectivity BuNHCH ₃ Bu ₂ NCH ₃		% Carbon Balance
0.876	0.245	0.0271	0.0164	30	9360	62.2	96	4	99.5
1.055	0	0.0326	0.0164	26	8870	57.3	96	4	100.0
0.876	0	0.0271	0.0164	24	7360	53.6	96	4	100.1

^a ± 0.0002 mol/hr

TABLE 28

Reaction^a of Isopropylamine with Isopropanol and Disproportionation
of Isopropylamine over Cu/ZnO and Pd/SiO₂ Catalysts at 75 atm

Catalyst	Temperature (°C)	Isopropylamine (mol/hr)	Isopropanol (mol/hr)	GHSV ₁ (hr ⁻¹)	Total Amine Conversion(%)	Selectivity to Diisopropylamine	% Carbon Balance
Cu/ZnO	190	0.0064	0.0086	4700	70.3	100	100.7
Cu/ZnO	190	0.0071	0	4700	22.5	54	101.7
Cu/ZnO	159	0.0066	0.0083	4700	54.5	100	102.0
Cu/ZnO	159	0.0071	0	4700	2.8	50	100.0
Pd/SiO ₂	190	0.0057	0.0094	1500	56.1	61	99.3
Pd/SiO ₂	190	0.0071	0	1500	52.8	47	97.2

^a ± 0.0001 mol/hr

methylamine by n-butanol. However, it has been clearly demonstrated that the reaction proceeds with high selectivity in the absence of H_2 . The yields of methylbutylamine were 2.87 mol/l of catalyst/hr in the absence of hydrogen and 3.07 mol/l/hr in the presence of hydrogen.

Reactions of Isopropylamine with Isopropanol. A 2.45 g (3.2 ml) portion of the CuO/ZnO catalyst, after reduction, was pressurized to 75 atm with $H_2/CO/CO_2 = 70/24/6$ vol% synthesis gas, the GHSV was adjusted to 4700 hr^{-1} , and the catalyst was tested for methanol synthesis activity at 250°C . A carbon conversion to methanol of 56% was observed, which is the expected catalytic activity for this reaction at the designated temperature and pressure [16].

The temperature was lowered to 190°C , and the synthesis gas stream was replaced by nitrogen flowing at the same GHSV. Using the high pressure pump, an isopropylamine/isopropanol mixture with a molar ratio of 1.00/1.34 was injected into the N_2 stream at the rate of 20 μl of liquid mixture per min. As shown in Table 28, about 70% of the isopropylamine was alkylated to diisopropylamine (1.35 mol of product/l of catalyst/hr). No ammonia was detected in the exit gas, and the water content corresponded to the production rate of the diisopropylamine. These observations indicate that disproportionation of the isopropylamine was not occurring under these experimental conditions.

However, the isopropylamine/isopropanol mixture was replaced by pure isopropylamine (at 10 $\mu\text{l}/\text{min}$), and about 22% of the isopropylamine disproportionated into ammonia and diisopropylamine. Decreasing the temperature from 190°C to 159°C decreased the degree

of disproportionation to approximately 3%, see Table 28. Replacing the isopropylamine by a 1.00/1.26 isopropylamine/isopropanol feed at twice the flow rate resulted in about 55% of the amine being alkylated with 100% selectivity to diisopropylamine. The yield of the latter compound corresponds to 1.16 mol/l of catalyst/hr. These experiments indicate that the disproportionation reaction is suppressed by the presence of the alcohol in the feed stream. In addition, the disproportionation reaction can be significantly decreased by lowering the temperature.

It should be noted that after five days of continuous testing, the catalyst, when removed from the reactor under a nitrogen atmosphere, was observed to be pitch black. This indicated that the catalyst had not suffered sintering such that metallic copper would agglomerate. Indeed, the black color has been assigned to the presence of highly interdispersed, electronically interacting catalyst components that produce the active state of the catalyst [14].

A Pd/SiO₂ catalyst was also studied for its amine alkylation activity. A 4 g (10 ml) sample of the 4.8 wt% Pd/SiO₂ catalyst, after reduction, was pressurized to 75 atm with a H₂/CO = 70/30 vol% synthesis gas. With the GHSV = 5000 hr⁻¹, the catalyst was heated to 250°C, and the methanol synthesis activity was determined during a 53 hr test. A 3.0% carbon conversion to methanol (0.55 mol/l/hr) was observed. The temperature was lowered to 190°C, the feed gas mixture was replaced by nitrogen, and the reactor system was purged under these conditions for one day.

A 1.65/1.00 molar ratio isopropanol/isopropylamine mixture was injected into the N_2 gas stream by means of the high pressure pump at the rate 20 μ l/min. The observed total amine conversion was about 56%, as given in Table 28, but the selectivity to diisopropylamine was only 61% (at the rate of 0.2 mol/l/hr). The ammonia and water yields, 0.0013 and 0.00068 mol/hr respectively, indicated that approximately two-thirds of the substituted amine product was formed by disproportionation of isopropylamine, while about one-third arose by alkylation of the amine reactant with isopropanol. Replacing the injected liquid mixture by pure isopropylamine flowing at 10 μ l/min led to nearly the same degree of amine conversion as observed in the previous test (Table 28). Therefore, the disproportionation reaction was proceeding at a faster rate in the absence of the alcohol than it was in the presence of a small excess of the alcohol.

Reaction of Isopropylamine with Ethanol. A 2.45 g (2.9 ml) sample of the Cu/ZnO, after reduction, was subjected to an alkylation study utilizing ethanol. However, the reactor system was first pressurized to 75 atm with $H_2/CO/CO_2 = 70/24/6$ vol% synthesis gas flowing at GHSV = 5200 hr^{-1} and then heated to 225°C . A 17.9% carbon conversion to methanol, with a yield of 10.4 mol/l/hr, was observed. The reactor temperature was lowered to 190°C (carbon conversion to methanol = 2.0%), and the synthesis gas was replaced by nitrogen flowing at the same rate (0.612 mol N_2 /hr). Under these experimental conditions, a 1/1 molar ratio mixture of ethanol and isopropylamine was injected into the N_2 stream at the rate of

20 μ l/min. The results are shown in Table 29. The selectivity to the desired product, ethylisopropylamine, was 86% and no diethylisopropylamine was observed in the exit gas.

Ammonia, usually a product of disproportionation, was detected in the product stream. However, no diisopropylamine was found, but, unexpectedly, diethylamine was observed, as was isopropanol. These observations indicate that trans-alkylation might be occurring, as represented by equation 21, followed by disproportionation

of the ethylamine (equation 22). These equations indicate that the isopropanol, ammonia, diethylamine product proportions should be 2/1/1. Indeed, the observed production rates were 0.00063/0.00027/0.00022 mol/hr ($\pm$ 0.00010), respectively.

The same reactants were used with a 4 g (10 ml) portion of the Pd/SiO₂ catalyst at 190°C in flowing nitrogen. The molar ratio of the ethanol/isopropylamine reactants was 1.45/1.00, and the liquid injection rate was again 20 μ l/min. Table 29 shows that the isopropylamine was transformed into a number of products, with a 34% selectivity to the ethylisopropylamine alkylation product and a 34% selectivity toward the disproportionation product, diisopropylamine. Although the carbon balance was satisfactory, the nitrogen balance was only 89% that of the determined inlet feed. This appears to be caused by a low determination of the ammonia content in the exit gas and would reduce the above reported selectivities

TABLE 29
Reaction^a of Isopropylamine with Ethanol at 190°C and 75 atm
over Cu/ZnO and Pd/SiO₂ Catalysts

Catalyst	Isopropylamine (mol/hr)	Ethanol (mol/hr)	GHSV (hr ⁻¹)	Total Amine Conversion(%)	% Selectivity			% Carbon Balance
					i-PrNH ₂ ^b	(i-Pr) ₂ NH ^c	Et ₂ NH ^d	
Cu/ZnO	0.0034	0.0084	5200	41.7	86	0	6.5	103.3
Pd/SiO ₂	0.0071	0.0103	1500	73.2	34	34	4.8	101.8

^a ± 0.0001 mol/hr

^b i-PrNH₂ = ethylisopropylamine

^c (i-Pr)₂NH = diisopropylamine

^d Et₂NH = diethylamine

somewhat. In any case, it seems that the trans-alkylation/disproportionation sequence is also occurring to a small extent over this catalyst. However, the disproportionation of isopropylamine is clearly the significant side-reaction pathway over the Pd/SiO₂ catalyst.

Summary

The experiments described here demonstrate that the alcohols adsorb onto the Cu/ZnO and Pd/SiO₂ catalysts to form a surface intermediate that reacts with amines. The resultant alkylamines are analogous to the methylamines obtained when synthesis gas, rather than alcohols, is utilized as the carbon-containing reactant. This further indicates that the kinetically important surface species is an *aldehydic* or *hydroxycarbenoic* intermediate. No hydrocarbons derived from the alcohols were observed in the reactor exit stream.

Under comparable experimental conditions, the selectivity of the Cu/ZnO catalyst is appreciably higher than that observed for the Pd/SiO₂ catalyst (Tables 28 and 29). The principal side-reaction occurring over the latter catalyst is disproportionation of the reactant substituted amine, e.g. similar to equation 22, and this reaction can be monitored by the yield of ammonia. It was shown that the disproportionation reaction over Pd/SiO₂ was somewhat suppressed by the presence of alcohols in the reactant stream, while the reaction was inhibited over the Cu/ZnO catalyst under the same conditions. This might reflect the degree of competition between the alcohol and the primary amine for reactive surface sites on the materials. The experimental results indicate that

alcohols are more successful competitors over the Cu/ZnO catalyst than they are over the Pd/SiO₂, and this parallels the methanol synthesis activity of these catalysts.

The amine alkylation reactions readily proceed under mild conditions over these catalysts. Tables 27 and 28 show that alcohols are efficient amine alkylating agents over the Cu/ZnO catalyst at 190°C and pressures of 24-75 atm. The selectivities and activities are appreciably higher than those typically observed for analogous reactions over hydrogenation-type catalysts [68]. Therefore, the efficiency in forming the reactive intermediate from alcohol displayed by the Cu/ZnO catalyst is reflected in its high amine alkylation activity.

These experiments show that catalysts that can be utilized for the low temperature/pressure formation of methanol from synthesis gas can also be used for the alkylation of amines with alcohols. In addition, the following features have been established:

- (1) Unsupported Cu/ZnO can be successfully utilized as an amine alkylation catalyst,
- (2) Alkylation of a primary amine by a primary or secondary alcohol occurs at fast rates, high selectivities, and mild conditions over the Cu/ZnO catalyst,
- (3) Alkylation of a primary amine by a primary or secondary alcohol occurs at slower rates and with poorer selectivities over the Pd/SiO₂ catalyst than were obtainable with the Cu/ZnO,

- (4) Disproportionation of the primary amine occurs to a greater extent over the Pd/SiO₂ catalyst than over the Cu/ZnO catalyst, and, in fact, this reaction is inhibited over the latter catalyst by the presence of alcohols,
- (5) The extent to which the disproportionation reaction proceeds can be suppressed by lowering the temperature,
- (6) Hydrogen is not a necessary component of the reactant stream, but its presence can enhance the net yield of alkylated amine, and
- (7) An appreciable excess of the reactant amine is not necessary for high selectivity toward the monoalkylated product to be achieved.

V. CONCLUSIONS

The two quaternary Cu/Co/Cr/K catalysts that were prepared according to patent instructions showed similar, but markedly low, catalytic activities. The selectivities were poor, and in each case the major product was methane. Water was also a product, and the water-gas shift reaction occurred over these catalysts to produce CO_2 . The catalytic data indicate that the selectivity to alcohols can be increased by increasing the pressure, decreasing the gas hourly space velocity, and decreasing the CO_2 content of the synthesis gas, although the latter effect is mainly due to enhanced yields of methanol rather than ethanol. The binary and ternary Co catalysts are good methanation catalysts but exhibit poor alcohol synthesis activity. Testing of $\text{CuO/ZnO} = 30/70$ wt% catalysts impregnated with KOH demonstrated that, under the described reaction conditions, the potassium functioned as a catalytic retardant and hardly promoted the methanation, Fischer-Tropsch, or higher alcohol synthesis.

Kinetic modelling of methanol synthesis from ternary $\text{H}_2/\text{CO}/\text{CO}_2$ gas mixtures over Cu/ZnO catalysts showed that the maximum rate of the reaction is determined by the balance between the promoting effect of CO_2 , which maintains the catalyst in an active state through its oxidizing power, and the retarding effect stemming from strong adsorption of CO_2 when present in high concentrations. A general rate equation was derived that

can be used in its integral form to calculate the carbon conversion to methanol in an integral isothermal flow reactor.

Adding water to the $H_2/CO = 70/30$ vol% synthesis gas stream over the Cu/ZnO catalyst demonstrated that the water gas shift reaction readily proceeded to yield CO_2 . At the same time, the methanol synthesis rate was directly affected by the presence of water in the synthesis gas. A pronounced maximum in the methanol yield was observed at low water concentrations, while at higher concentrations of water the methanol yield was severely retarded. A comparison of the water addition experiments with the data for the CO_2 effect on methanol synthesis clearly showed that water behaves as a more effective promoter at low concentrations and a more severe retardant at high concentrations than does equimolar carbon dioxide at the same experimental conditions.

A study of competitive hydrogenation reactions over the Cu/ZnO catalyst showed that CO was hydrogenated to methanol faster than aromatics were hydrogenated to cycloparaffins. On the other hand, oxygenates, such as propionic acid and propanaldehyde, and olefins were hydrogenated to alcohols and paraffins, respectively, at a faster rate than CO was converted to methanol. With mixtures of CO and aromatics, oxygenates, or olefins, the same trends were observed. However, the presence of CO inhibited the hydrogenation of the aromatics, while the addition of small amounts of oxygenates or olefins to the synthesis gas suppressed to the hydrogenation of CO to methanol. Thus, this demonstrates

that the same surface sites are involved in the activation of all of these molecules for hydrogenation. This data is consistent with the surface sites being surface cations, e.g. copper ions, on the zinc oxide, as suggested previously [1,12-16].

Chemical trapping of a surface intermediate on the Cu/ZnO catalyst was successfully carried out by utilizing amines as the trapping agent. In all cases, the products were methylamines. This indicated that the intermediate that was trapped was a surface formyl or hydroxycarbene species because these moieties undergo specific coupling reactions with amines to form a C-N bond, which in the presence of hydrogen yields methylamine. The aldehydic intermediate was common to both methylamine formation and to methanol synthesis, since it was shown that these were competing surface reactions. Over a 1.2% Fe/Cu/ZnO catalyst, isopropylamine trapped the alcohol precursor but allowed the hydrocarbon synthesis to proceed. However, the presence of the amine altered the hydrocarbon selectivity from predominantly paraffins to principally olefins.

Further studies of the amine trapping reactions were carried out. Analysis of the Schulz-Flory distribution of products formed over the Fe/Cu/ZnO catalyst indicated that the isopropylamine attacked the alcohol precursor and not the completely formed alcohol. Over the Cu/ZnO catalyst, it was shown that mono-substituted amines can react with a variety of alcohols added to the reactor inlet gas stream to actively and selectively

form di-substituted amines, Although a Pd/SiO_2 catalyst also promotes the amine alkylation reaction, it is less active than the Cu/ZnO catalyst. In addition, the former catalyst is less selective because it tends to promote the disproportionation of the reactant amine.

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