ALCOHOL SYNTHESIS OVER Fe/Cu/ZnO CATALYSTS

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INTRODUCTION

In the attempt to produce higher molecular weight oxygenated compounds from synthesis gas (H_2 + CO) for utilization as fuels and intermediate chemicals, an approach to catalytically forming higher alcohols is to combine an alkyl-forming agent with a methanol synthesis catalyst. It is well-known that copper-based catalysts are very selective for the synthesis of methanol (1-3). On the other hand, cobalt- and iron-based catalysts promote the Fischer-Tropsch synthesis (4,5) of hydrocarbons. The Fischer-Tropsch process converts synthesis gas to a mixture of predominantly linear alkanes and alkenes rather non-selectively but in such a manner that the product distribution with respect to carbon chain length displays a recognizable pattern (6-8), commonly referred to as the Schulz-Flory distribution (9,10). This distribution arises from the stepwise catalytic polymerization and hydrogenation of CO by processes whose reaction mechanisms have not been fully established (11-13).

Utilizing mixed copper/cobalt catalysts has led to enhanced selectivities for the synthesis of higher alcohols (14-19). However, the quantity of hydrocarbons formed were greater than the quantity of higher alcohols formed (18,19), methane was the dominant product (15,16), or methanol was the most selectively formed product (14,17,18). It appears that the copper/cobalt catalysts that contain small amounts of cobalt (<8 wt%) are principally methanol synthesis catalysts in which the cobalt has suppressed the catalytic activity while shifting the selectivity toward higher molecular weight products (19). The distribution of products, which are linear, indicates that they are formed by a Fischer-Tropsch mechanism.

Iron-based Fischer-Tropsch catalysts are usually promoted with copper, e.g. 20% Cu relative to Fe (20-23), where the copper increases the activity of the catalysts via its redox properties during the preparation of the catalysts (20,22). Oxygenates are often observed as products over these catalysts, but the yields of these products are inversely proportional to the reactant stream space velocity, e.g. more oxygenates are formed at lower gas hourly space velocities (GHSV) (21). The linear products that are synthesized over these catalyst follow the Schulz-Flory distribution.

The present work has utilized a well-characterized Cu/ZnO = 30/70 mol% methanol synthesis catalyst (2,24-27) into which small amounts of iron have been introduced. It is shown that the incorporation of the latter alkyl-forming agent caused the production of higher molecular weight compounds, both paraffins and olefins, as well as alcohols.

EXPERIMENTAL

The Fe/Cu/ZnO catalysts were coprecipitated from heated nitrate solution by sodium carbonate, calcined, pelletized, and reduced with H_2/N_2 = 2/98 vol% at 250°C according to a procedure previously described in detail for the binary Cu/ZnO catalysts (2,25). A schematic of the catalytic reactor system has been presented (2), but a high pressure unit for pumping liquids into the synthesis gas stream at a reactor pressure of 75 atm has been added at the top of the reactor preheater sec-

tion (28). The exit gas was reduced to ambient pressure and was sampled approximate-every hr using a heated automatic sampling valve and analyzed using an on-line Hewlett-Packard 5730A gas chromatograph coupled with a H-P Model 3388A Integrator/Controller. Condensables (at 0°C) were collected and further analyzed by direct liquid injection into the H-P GC and a Finnigan 4021 GC/MS/Nova system. The analyses resulted in less than 2% error in the carbon atom balance.

The catalysts were characterized by BET surface area determination using argon and by electron microscopy using a Philips 400T electron microscope fitted with a STEM unit and an X-ray energy dispersive spectrometer.

RESULTS

The influence of iron concentration on the catalytic activity of the Fe/Cu/ZnO catalysts was determined for the usual testing conditions employed for methanol synthesis catalysts. The results are given in Table 1, and it is evident that the activities of the catalysts decrease with increasing iron content. These conversions can be compared with the 55 ± 5% carbon conversion observed with the undoped Cu/ZnO = 30/70 methanol catalyst (26). The catalyst containing the lowest iron content produced predominantly methanol, while the catalyst containing 9.0 mol% iron produced an appreciable quantity of waxes. Therefore, the Fe/Cu/ZnO = 1.2/31.8/67.0 catalyst was chosen for further study.

In examining the effect of CO_2 concentration in the synthesis gas on the activity and selectivity of the catalyst, it was observed that the maximum conversion to products (12.0 mol%) and the greatest selectivity to C_2-C_7 hydrocarbons (60.7 C atom %) occurred with a $H_2/CO/CO_2$ = 70/28/2 vol% synthesis gas. However, the highest selectivities toward methanol and methane were produced by the $H_2/CO/CO_2$ = 70/24/6 vol% synthesis gas (see Table 1). On the other hand, the highest selectivity toward the C_2-C_5 alcohols (17.1%) was achieved with CO_2-free H_2/CO = 70/30 synthesis gas to yield a C_2-C_5/C_1 alcohol molar ratio of 0.61.

Using the binary H_2/CO synthesis gas, the effect of the partial pressure of the reactants on the higher alcohol synthesis was investigated. The results are presented in Table 2, and it is evident that as the H_2/CO ratio decreased, the % carbon conversion to products also decreased. However, the water gas shift reaction became more efficient at the same time so that the selectivity of CO conversion to CO_2 increased as the H_2/CO ratio decreased. As the latter ratio decreased, the selectivity toward the higher alcohols relative to methanol increased. Analyses of the condensable liquids collected from the reactions with the low H_2/CO ratio synthesis gases showed that traces of 2-methyl-1-propanol and 2-methyl-1-butanol were present. It was estimated that these trace compounds were each less than 5 wt% of the total C_4 and C_5 alcohol product.

In studying the effects of the synthesis gas feed rate on alcohol synthesis, the inlet GHSV was varied in four steps from 2500 to 6250 hr^{-1} (contact time = 1.44 to 0.58 sec, respectively) with the H_2/CO = 50/50 gas mixture. As the contact time increased, the carbon conversion to alcohols and hydrocarbons increased in a directly proportional manner. The carbon atom ratio of higher alcohols to methanol remained relatively constant at 2.1 ± 0.1, while the alcohol/hydrocarbon molar ratio decreased with increasing contact time. Thus, longer contact times favored hydrocarbon synthesis, while shorter contact times shifted the selectivity towards the alcohols. This indicates that both alcohols and hydrocarbons are primary products.

This was further supported by injecting liquid isopropylamine into the inlet synthesis gas stream under the experimental conditions given in Table 3. The small quantity of isopropylamine pumped into the system had little effect on the carbon conversion. However, the production of alcohols was completely suppressed, while the synthesis of hydrocarbons was only partially inhibited, particularly the forma-

TABLE 1

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

Fe/Cu/Zn (mol%)	0.3/32.1/67.6	1.2/31.8/67.0	9.0/31.4/59.6
Catalyst Charge (g)	2.4547	2.4556	2.6971
Total Conversion			
$CO + CO_2$ (mol%)	23.1	10.6	8.3
(mol/kg cat/hr)	17.0	8.0	6.3
Selectivity (C atom%)			
Methanol	95.2	16.0	5.1
Ethanol	0.4	4.2	7.8
1-Propanol	0.0	2.4	2.8
2-Propanol	0.0	0.2	0.2
1-Butanol	0.0	1.4	2.2
1-Pentanol	0.0	0.7	1.2
Methane	1.4	24.3	17.9
Ethane	0.7	9.0	10.2
Ethylene	0.0	1.0	1.0
Propane	0.1	12.4	7.3
Propylene	0.0	1.0	7.6
C_4-C_7 Hydrocarbons	2.2	23.3	24.5
C_5^+ Alcohols and C_8^+ Hydrocarbons	0.0	4.1	11.2
Group Mole Ratios			
C_2-C_5 Alcohols/Methanol	0.002	0.22	1.12
C_1-C_5 Alcohols/C_1-C_7 Hydrocarbons	38.9	0.51	0.31
C_2-C_3 Olefins/C_2-C_3 Paraffins	0.0	0.10	0.47
Yields (g/kg cat/hr)			
Methanol	518	41.0	10.3
C_2-C_5 Alcohols	1.6	15.6	18.3

tion of methane and ethane. Thus, the hydrocarbon distribution was shifted slightly toward longer chain molecules and, as indicated in Table 3, from paraffins to olefins. It is evident from the data for the amines that the injected isopropylamine principally trapped methyl and ethyl groups.

A reduced Fe/Cu/ZnO = 1.2/31.8/67.0 catalyst was examined by electron microscopy after being ultrasonically dispersed from an ethanol suspension onto a carbon-coated titanium grid. Metallic copper crystallites, predominantly with a diameter of about 5.0 nm, were supported on the ZnO matrix. Electron diffraction showed that Cu ($\bar{1}$11) planes. Using a 5 nm electron probe, energy dispersive X-ray analysis of the ZnO phase indicated that it contained about 15% Cu and 0.8% Fe. A few bimetallic Fe-Cu particles were observed that contained more iron than copper. However, in general the iron was homogeneously dispersed over the catalyst.

Analysis of a tested catalyst by Auger spectroscopy indicated that the atomic composition of the surface was Cu/Zn/O/C = 15.0/9.9/6.2/68.9 %. No Fe was detected by Auger or X-ray photoelectron spectroscopy. Thus, it appears that carbon covered the iron and most of the ZnO surface, but much of the copper phase was left exposed. The BET surface area of the used catalyst, as removed from the reactor under a

TABLE 2

Reactant Concentration Effects on Alcohol Synthesis over the 1.2% Iron Catalyst at 250°C, 75 atm, 5000 hr^{-1} and $H_2/CO/CO_2$ = 30/70/0 to 70/30/0. Catalyst Charge = 2.4524g.

$H_2/CO/CO_2$ (vol%)	30/70/0	40/60/0	50/50/0	60/40/0	70/30/0
Conversion					
CO (mol%)	1.5	2.8	4.3	6.5	8.2
(mol/kg cat/hr)	2.7	4.1	5.4	6.5	6.1
Yields (g/kg cat/hr)					
Methanol	4.1	9.2	15.1	18.2	17.7
Ethanol	3.2	6.5	9.4	10.6	9.0
1-Propanol	1.8	3.9	5.4	5.6	4.9
2-Propanol	0.2	0.4	0.5	0.4	0.4
1-Butanol	0.9	2.0	2.9	2.9	2.7
1-Pentanol	0.4	1.0	1.5	1.5	1.3
Selectivity (C atom%)					
Carbon Dioxide	41.5	30.5	23.9	19.6	16.8
Methanol	4.8	6.9	8.7	8.8	8.9
C_2-C_5 Alcohols	11.4	15.9	17.4	15.4	14.2
C_1-C_7 Hydrocarbons	42.3	46.7	50.0	56.2	60.1

nitrogen atmosphere, was 0.4 m^2/g, and this contrasts with the surface area of 37-40 m^2/g for tested binary Cu/ZnO = 30/70 catalysts (25,26). After washing the tested ternary catalyst with cyclohexane, the surface area was found to be 15 m^2/g.

DISCUSSION

The composition of the synthesis gas mixture has a pronounced effect on the selectivity observed over the Fe/Cu/ZnO catalyst. The presence of CO_2 in the synthesis gas tends to favor the formation of low molecular weight products, i.e. methanol and methane. When CO_2 is removed from the reactant stream, carbon chain growth is promoted, apparently due to exposure of sites active in the transfer of alkyl groups. In the absence of CO_2, the percentage of CO converted to carbon dioxide, alcohols, and hydrocarbons increased as the H_2/CO ratio was increased from 0.43 to 2.33. Similar behavior has been observed with other iron catalysts, for which the rate of synthesis increased as the hydrogen content of the feed increased (6).

The carbon chain growth reactions that occurred over these iron-containing catalysts can be treated as a polymerization process in which the molecular weight distribution of products is determined by the chain propagation and chain transfer steps. The Schulz-Flory molecular weight distribution can be derived to give the following equation:

$$N_x = N_o(1-\alpha)^2\alpha^{x-1}, \qquad 1)$$

where N_x is the total number of molecules containing x carbon atoms, N_o is the total number of monomer units ($-CH_2-$) in the system, and α is the probability of chain growth (28). Equatiion 1 can be expressed in logarithmic form as

TABLE 3

Effects of Isopropylamine on Product Distributions over a 1.2% Fe Containing Cu/ZnO Catalyst at 235°C, 75 atm, 5000 hr^{-1}, and $H_2/CO/CO_2$ = 70/30/0 vol%. Catalyst Charge = 2.414 g. (R = isopropyl).

Isopropylamine in Feed (μl/min)	0	20
$H_2/CO/RNH_2$ (molar ratio)	2.33/1.00/0	2.33/1.00/0.08
CO Conversion (mol%)	4.45	4.38
(mol/kg/hr)	3.4	3.3
Products ($x10^{+4}$ 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_2H_5	0	0.70
R-N-(CH_3,C_2H_5)	0	7.71
R-N-$(C_2H_5)_2$	0	0.35
R-NH-(n-C_3H_7)	0	0.38
Certain Molar Ratios		
Alcohols/Hydrocarbons	0.2	0
Olefins/Paraffins	0.1	1.4

$$\log (N_x/N_o) = \log [(1-\alpha)^2/\alpha] + x\log\alpha. \qquad 2)$$

If the graphical representation of log (N_x/N_o) vs x gives a straight line, and the values of α determined from the intercept and the slope are in good agreement, then the molecular weight distribution follows the Schulz-Flory law.

Figure 1 demonstrates that both the alcohols and the hydrocarbons produced over the Fe/Cu/ZnO catalyst follow the Schulz-Flory law. The propagation constant (α) is 0.32 for the alcohols, while it is equal to 0.55 for the hydrocarbons. This distinct difference in α values again suggests that the alcohols and the hydrocarbons are formed by different pathways over this catalyst. In the absence of CO_2 and at a lower temperature of 235°C, the distributions for alcohols and hydrocarbons yield α values of 0.47 and 0.53, respectively. Upon addition of isopropylamine to the reactor feed gas (Table 3), the production of alcohols was stopped, while the hydrocarbon distribution was shifted toward longer chain products to give α = 0.58. The distribution of alkyl groups on the product amines (excluding the isopropyl group) yielded a non-linear plot, showing that the formation of these alkyl groups do not follow the Schulz-Flory distribution. This indicates that the amines primarily attack the alcohol precursor. If the amines had reacted with the alcohols after they formed, the Schulz-Flory distribution of the alkyl groups would have produced the same distribution as that of the alcohols with α = 0.47.

The yield of C_2 substituted amines lies above the expected value found for the alcohol distribution, while the quantities of C_1 and C_3 alkylated amines fall below the expected values. This could be due to a methyl transfer reaction, as reported previously (29), to form a C_2 oxygenated species that is readily attacked by the amine. The results of the present amine trapping experiments are in contrast to those obtained with ammonia and synthesis gas over other iron catalysts (30). In the latter work, exclusively primary amines were formed that obeyed the Schulz-Flory distribution to give α = 0.69. It was proposed that ammonia attacked ($-CH_x$) inter-

mediates. However, in the presence work, it is evident that the amines reacted with the oxygenated intermediates and that the hydrocarbon intermediate was left essentially undisturbed.

CONCLUSIONS

While a complete mechanistic reaction scheme has not been verified for this catalyst system, the following conclusions have been deduced from the experimental data:

(a) both alcohols and hydrocarbons are primary products formed over the Fe/Cu/ZnO catalysts,

(b) two polymerization processes are indicated, one with short carbon chain length for alcohols and one with the usual chain length for hydrocarbons,

(c) the alcohols are formed by interaction of methanol precursors and iron-bound intermediates, with the methanol precursor behaving as a monomer in the alcohol synthesis,

(d) the optimum catalysts for the synthesis of C_2-C_5 alcohols contain small amounts of iron (~1%), which is homogeneously dispersed throughout the catalyst, and

(e) hydrocarbon growth appears to occur very actively over Fe-Cu intermetallic particles.

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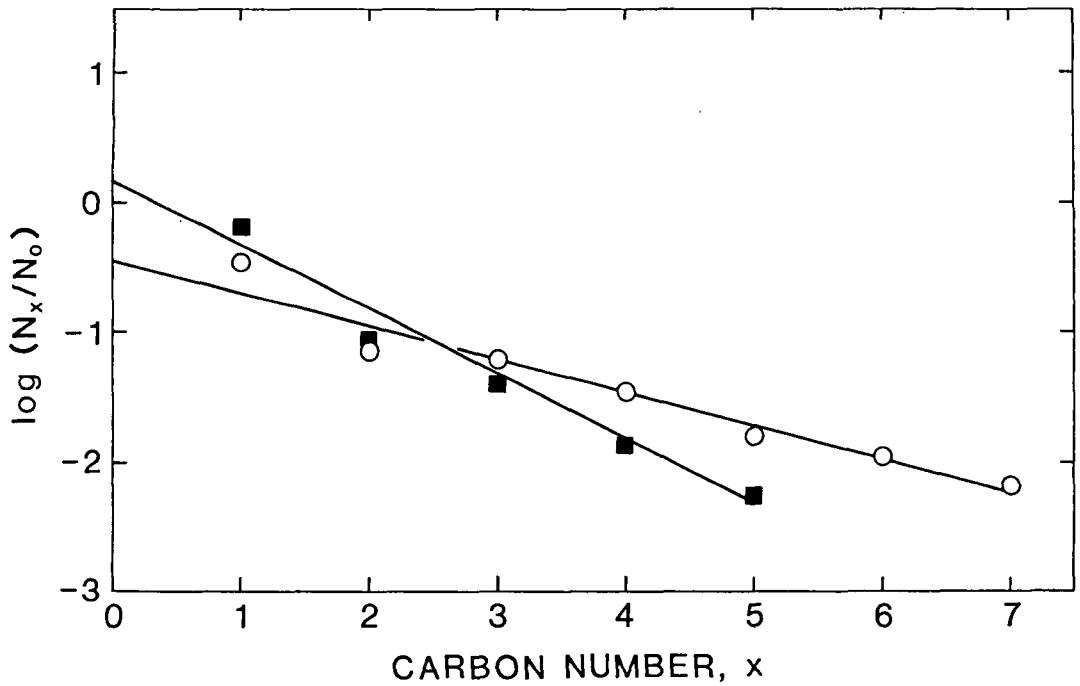

FIGURE 1. The Schulz-Flory Distribution of Alcohols (■) and Hydrocarbons (O) Produced over the Fe/Cu/ZnO = 1.2/31.8/67.0 mol% Catalyst from $H_2/CO/CO_2$ = 70/24/6 vol% Synthesis Gas at 75 atm, GHSV = 5000 hr^{-1}, and 250°C.

THE SYNTHESIS OF HIGHER ALCOHOLS ON Cu/ZnO CATALYSTS PROMOTED WITH K_2CO_3

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Alkali oxides added to methanol catalysts increase the formation of ethanol, n-propanol and isobutyl alcohol. This result has been known for many years, yet few quantitative studies have been reported in the literature. Data obtained on a commercial copper-zinc oxide catalyst promoted with K_2CO_3 are presented and compared with published work. Catalyst particles with a mean diameter of about 0.9 mm were used. The catalyst was initially reduced in $2H_2$ + 1CO gas at 300°C and atmospheric pressure for 12-15 hours. Most of the synthesis tests were made at 285°C and 13.2 MPa of $1H_2$ + 2CO gas. The alkali concentration varied from 0-10 wt % K_2CO_3; the optimum amount was about 0.5% by weight, as shown in Table 1. The H_2 to CO feed ratio was important in determining the higher alcohol selectivity. The rate of production of isobutyl alcohol varied as $p_{H2}^{-0.7}\ p_{CO}^{2.2}$ while for methanol, ethanol and n-propanol both exponents were positive and less than 1.6. Decreasing the hydrogen to carbon monoxide ratio from 2 to 0.5 more than doubled the isobutyl alcohol selectivity.

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TABLE 1: PROMOTER CONCENTRATION EFFECTS

Pressure = 13.2 MPa. Temperature = 285°C

Wt.% K_2CO_3	0	0.5	1.0	2.0	3.0	10.0
Inlet space velocity (h^{-1})	4300	3300	3800	4300	4600	2900
H_2:CO in feed	0.44	0.47	0.52	0.49	0.48	0.44
Alcohol selectivities(1)						
methanol	65.8	48.6	61.4	75.7	82.4	81.8
ethanol	6.4	4.8	4.8	3.7	2.6	1.6
2-propanol	1.7	0.8	1.8	1.8	1.4	0.3
1-propanol	5.3	6.7	9.2	8.1	7.0	5.2
1-butanol	2.1	4.0	2.5	1.3	1.1	2.2
2-butanol	0.8	1.5	1.7	1.0	1.3	0.9
2-methyl-1-propanol	10.1	18.8	13.8	7.1	3.8	4.6
pentanols	8.0	14.8	4.8	1.2	0.5	3.4
(H_2+CO) consumption						
$mmol.g^{-1}.h^{-1}$	50.5	58.5	68.5	41.5	54.3	16.0
$mmol.m^{-2}.h^{-1}$	1.19	1.61	1.76	1.18	1.66	0.89

(1) selectivity = $\frac{\text{C atoms in alcohol i}}{\text{total C atoms in alcohols}} \times 100\%$

A chain growth scheme for the synthesis of alcohols from carbon monoxide and hydrogen is proposed. The scheme describes the alcohol product distribution, assuming one or two carbon addition at the α- or β-carbon atom of the growing alcohol. Estimates of the distribution parameters were obtained from selectivities measured for a range of operating conditions on a Cu/ZnO catalyst promoted with 0.5% K_2CO_3. Typical data showing the values of growth parameters and the comparison of observed and predicted alcohol yields are given in Table 2. The α-addition is a slow step with a large activation energy (140 kJ/mol) while β-addition is faster and has a smaller activation energy (66 kJ/mol). Large methanol selectivities result from the slow initial α-addition, and large 2-methyl-1-propanol selectivities from α-addition being the only growth step of the 2-methyl-1-propanol intermediate. The rate of chain growth is approximately proportional to the CO partial pressure and the rate of chain termination proportional to the H_2 partial pressure. Addition of alcohols to the synthesis gas resulted in significant increases in the yields of some of the alcohols, consistent with the chain growth scheme.

Two papers have been published on this work, Can. J. Chem. Eng., 61, 40 (1983) and J. Catal., 85, 428 (1984).

Table 2: Predicted and Measured Product Distributions

Pressure 10.4 MPa Temperature 285°C

Feed H_2/CO		0.49		0.93		2.01
Space Velocity (h^{-1})		2900		8200		32000
Conversion %						
(H_2+CO)		39		41		23
CO		28		34		27
Alcohols(1)	measured	predicted	measured	predicted	measured	predicted
methanol	0.6177	0.6313	0.8530	0.8572	0.9610	0.9649
ethanol	0.0536	0.0575	0.0505	0.0512	0.0227	0.0227
2-propanol	0.0046	0.0040	0.0022	0.0022	0.0021	0.0003
1-propanol	0.0643	0.0574	0.0378	0.0357	0.0076	0.0071
1-butanol	0.0224	0.0077	0.0062	0.0007	0.0027	0.0008
2-butanol	0.0111	0.0065	0.0043	0.0029	0.0027	0.0004
2-methyl-1-propanol	0.1484	0.1519	0.0402	0.0414	0.0012	0.0024
pentanols	0.0780	0.0838	0.0059	0.0086	0	0.0015

Estimated growth scheme parameters:

Rate constants:

α	0.136	0.056	0.015
β	1.986	0.870	0.254
γ	0.170	0.013	0.022

Probabilities:

h	0.136	0.056	0.015
k	0.665	0.465	0.203
ℓ	0.057	0.007	0.018

(1) selectivity = $\frac{\text{C atoms in alcohol i}}{\text{total C atoms in alcohols}}$

DIRECT SYNTHESIS OF 2-METHYL-1-PROPANOL

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INTRODUCTION

The hydrogenation of carbon monoxide to aliphatic alcohols follows the general equations

$$2nH_2 + nCO \longrightarrow C_nH_{2n+1}OH + (n-1)H_2O \qquad 1)$$

and

$$(n+1)H_2 + (2n-1)CO \longrightarrow C_nH_{2n+1}OH + (n-1)CO_2 \qquad 2)$$

The isomer distribution in the $C_nH_{2n+1}OH$ involves linear primary, branched primary, or branched secondary alcohols depending on the catalysts used. It is well known that linear alcohols are co-products of hydrocarbon synthesis over Group VIII metals, primarily iron (1), while both linear and branched alcohols are products of CO hydrogenation over methanol synthesis catalysts modified with alkali promoters (2). It is this second class of catalysts that has been shown to produce 2-methyl-1-propanol in relatively high yields. The conditions utilized in the early work (3-7) were rather severe, however, exemplified by the pressure range 300-400 atm and temperatures above 400°C. The catalysts were in general alkali-promoted oxides of zinc and manganese with structural promoters such as chromia or alumina. Only recently Smith and Anderson (8) have demonstrated that the low pressure copper-zinc oxide-alumina methanol synthesis catalysts could be promoted by potassium carbonate to enhance the yields of higher alcohols, optimized the K_2CO_3 concentration, and developed a mathematical model for the chain growth that accounted for high degree of branching. The synthesis was carried out at temperatures below 300°C and pressures 100 - 130 atm over the $K_2CO_3/Cu/ZnO/Al_2O_3$ catalysts. Further study of alkali and alkaline earth promoted copper-based catalysts demonstrated that alkali hydroxide promotion enhances higher alcohol yields at pressures as low as 75 atm in the temperature range 250-310°C (9). Cesium was found to be the most effective promoter and its surface concentration optimized in the binary Cu/ZnO catalysts.

In the present work we report an investigation of the effect of reaction conditions on the yields of higher alcohols, particularly 2-methyl-1-propanol (isobutanol), over the Cs/Cu/ZnO = 0.4/30/70 catalyst (9). High selectivities for direct synthesis of isobutanol are demonstrated herein.

RESULTS AND DISCUSSION

The selectivity patterns have been studied at 75 atm, temperature range 288-325°C, H_2/CO = 0.45, and contact time range 1-5 sec in an apparatus described earlier (10). The catalyst preparation was that of ref. 9 with the cesium compound being CsOH. The products of the synthesis were, in the order of abundance, alcohols, esters, ketones, and aldehydes.

Figures 1-4 and Tables 1-2 describe the product composition under various conditions used. These results can be summarized as follows:

1. The general Smith-Anderson pattern for alcohols (8) is confirmed. However, secondary alcohols are very minor products over the Cs/Cu/ZnO catalyst. This is a result that differs from all previous reports (2-8) and is interpreted as due to the absence of an acid component in the Cs/Cu/ZnO catalyst.
2. The selectivity to isobutanol increases with increasing temperature and contact time.
3. Esters are minor products with methyl esters of C_1-C_3 carboxylic acids dominating. The selectivity to esters decreases with increasing temperature and goes through a maximum with increasing contact time. This is consistent with the ability of the Cs/Cu/ZnO catalyst to hydrogenate esters to the corresponding alcohols (11).

The mechanism of the alcohol and ester forming reactions has been discussed elsewhere (9). We point out that the selectivity pattern is such that the formation of isobutanol can be maximized and that of esters suppressed by the choice of conditions and of recycling schemes. The utility of isobutanol rests in its high energy density compared to methanol, in its high octane number (12), and in its being a convenient source of isobutene via catalytic dehydration.

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Table I

Product distribution over Cu/ZnO = 30/70 catalysts with varying concentrations of cesium salts at 288°C, 75 atm, H_2/CO = 0.45
Total flow rate = 8 l/hr Yield in gm/kg cat/hr,
Selectivity in carbon atom percent

	Cu/ZnO		CsOH/Cu/ZnO (0.4/30/70)		CsOH/Cu/ZnO (0.8/30/70)		CsOOCH/Cu/ZnO (0.4/30/70)	
	Yield	Selec-tivity	Yield	Selec-tivity	Yield	Selec-tivity	Yield	Selec-tivity
CO	2136.65	-	1757.35	-	2110.69	-	2015.85	-
CO_2	124.38	-	96.17	-	78.83	-	97.67	-
H_2O	-	-	-	-	-	-	0.32	-
CH_4	3.93	2.06	3.46	1.54	3.89	1.92	3.47	1.72
C_2H_6	1.90	1.06	0.54	0.26	0.37	0.19	0.57	0.30
CH_3OH	283.73	74.31	322.11	71.88	318.66	78.86	303.58	75.31
$HCOOCH_3$	6.16	1.72	7.94	1.89	8.74	2.31	8.04	2.13
C_2H_5OH	20.83	7.59	17.90	5.56	12.92	4.45	15.01	5.18
CH_3COOCH_3	11.13	3.78	8.04	2.33	4.45	1.43	6.68	2.15
C_3H_7OH	12.11	5.07	24.29	8.67	14.95	5.92	17.55	6.97
$(CH_3)_2CHCH_2OH$	5.33	2.41	14.82	5.72	9.01	3.86	12.11	5.20
C_4H_9OH	3.67	1.66	5.59	2.16	2.47	1.06	2.44	1.05
$C_2H_5COOCH_3$	0.55	0.21	-	-	-	-	-	-
$CH_3COOC_2H_5$	0.30	0.12	-	-	-	-	-	-
CO conversion %	14.11		17.54		14.27		14.89	

Table II

Product distribution over the 0.4% CsOH doped Cu/ZnO (=30/70) catalyst at 325°C, 75 atm H_2/CO = 0.45, 0.75, 1, and 2.33 Yield in gm/kg cat/hr

H_2/CO ratio =	2.33	1			0.75			0.45		
Flow Rate =	15 l/hr	3 l/hr	2 l/hr	1 l/hr	3 l/hr	2 l/hr	1 l/hr	12 l/hr	8 l/hr	3 l/hr
CO	1284.28	391.79	245.62	119.43	513.94	315.33	141.92	3281.8	1991.57	640.53
CO_2	152.86	175.76	134.22	75.26	163.35	132.76	82.39	316.42	327.48	217.17
H_2O	3.44	1.47	1.03	0.44	1.02	0.75	0.47	1.02	1.08	0.68
CH_4	9.81	7.49	5.83	3.79	6.70	5.52	3.60	13.42	11.47	6.80
C_2H_6	1.59	1.55	1.12	0.56	1.31	1.05	0.62	3.73	3.52	2.25
CH_3OH	683.53	62.18	33.47	9.74	53.42	29.17	10.24	211.73	135.69	27.91
$HCOOCH_3$	3.36	0.73	0.49	0.29	0.61	0.43	0.31	3.01	1.90	0.74
C_2H_5OH	33.53	5.59	2.97	0.84	4.84	2.52	0.90	22.07	14.19	2.60
C_2H_5CHO	-	0.36	0.23	0.075	0.50	0.25	0.094	1.58	1.32	0.33
CH_3COOCH_3	2.91	1.18	0.68	0.31	1.24	0.75	0.37	5.46	3.97	0.85
C_3H_7OH	36.31	17.82	10.21	3.12	16.90	9.21	3.51	48.55	39.39	8.92
$(CH_3)_2CHCHO$	-	1.05	1.02	0.81	2.23	2.27	1.15	1.93	3.70	2.40
$C_2H_5(CO)CH_3$	-	1.28	0.60	0.54	1.90	1.74	0.80	4.03	4.47	1.46
$C_2H_5CHOHCH_3$	3.47	1.71	1.56	0.80	2.02	2.46	1.25	4.10	3.57	1.50
$(CH_3)_2CHCH_2OH$	18.13	41.45	27.92	14.51	41.02	29.85	16.18	60.22	75.15	42.07
C_4H_9OH	4.78	3.90	2.45	0.91	3.53	2.20	0.94	9.41	9.27	2.78
$C_3H_7(CO)CH_3$	-	0.15	0.30	0.32	0.58	0.98	0.24	0.91	1.25	0.56
$C_2H_5(CH_3)CHCH_2OH$	3.35	6.91	4.73	3.15	7.32	5.61	3.28	9.31	12.88	9.30
$C_5H_{11}OH$	-	1.18	0.67	0.45	1.43	2.17	0.47	3.19	2.63	0.59
C_5^+	-	9.71	8.21	6.25	14.50	12.31	6.93	6.99	13.95	15.11
CO Conversion %	35.32	29.05	29.86	29.30	23.64	25.82	28.10	11.86	15.62	20.25

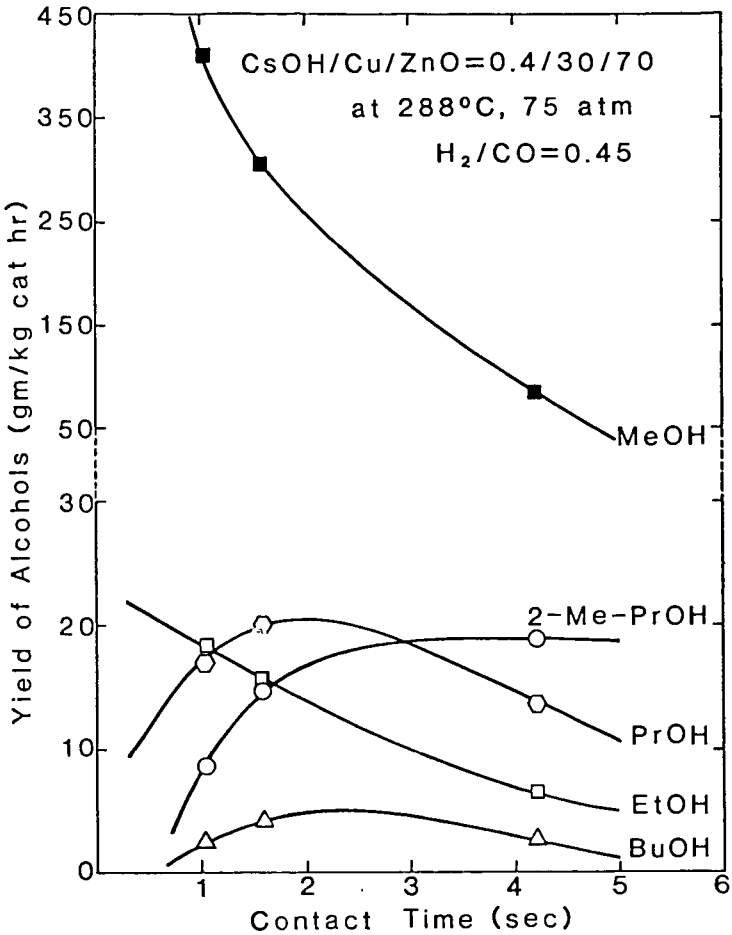

Figure 1. The contact time dependence of alcohol yields at 75 atm, 288°C, H_2/CO = 0.45 over the CsOH /Cu/ZnO = 0.4/30/70 catalyst.

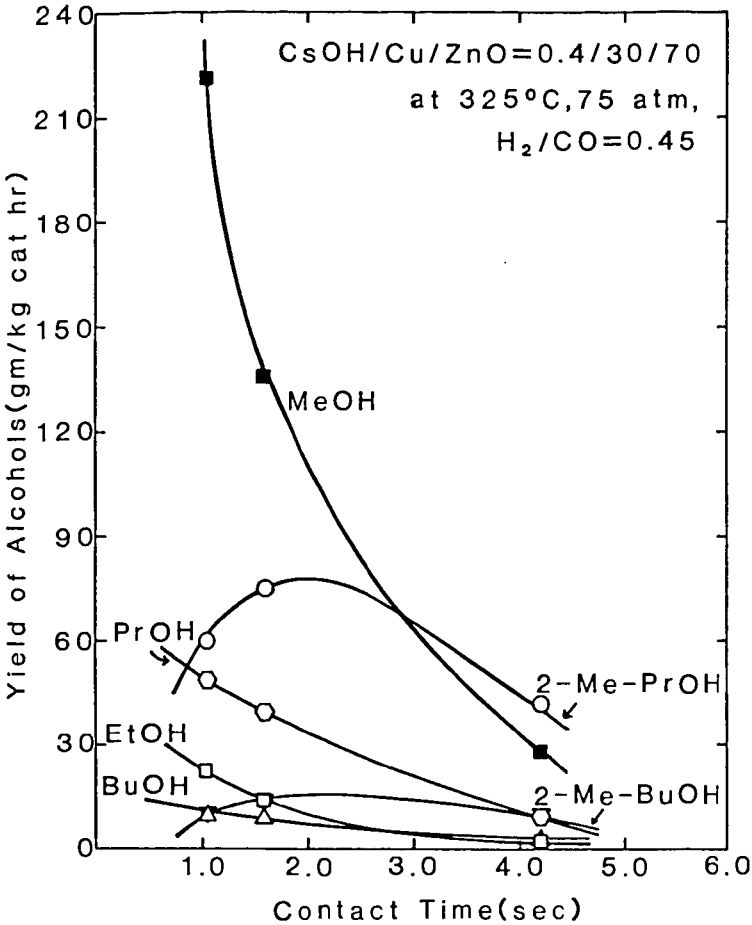

Figure 2. The contact time dependence of alcohol yields at 75 atm, 325°C, H_2/CO = 0.45 over the CsOH/Cu/ZnO = 0.4/30/70 catalyst.

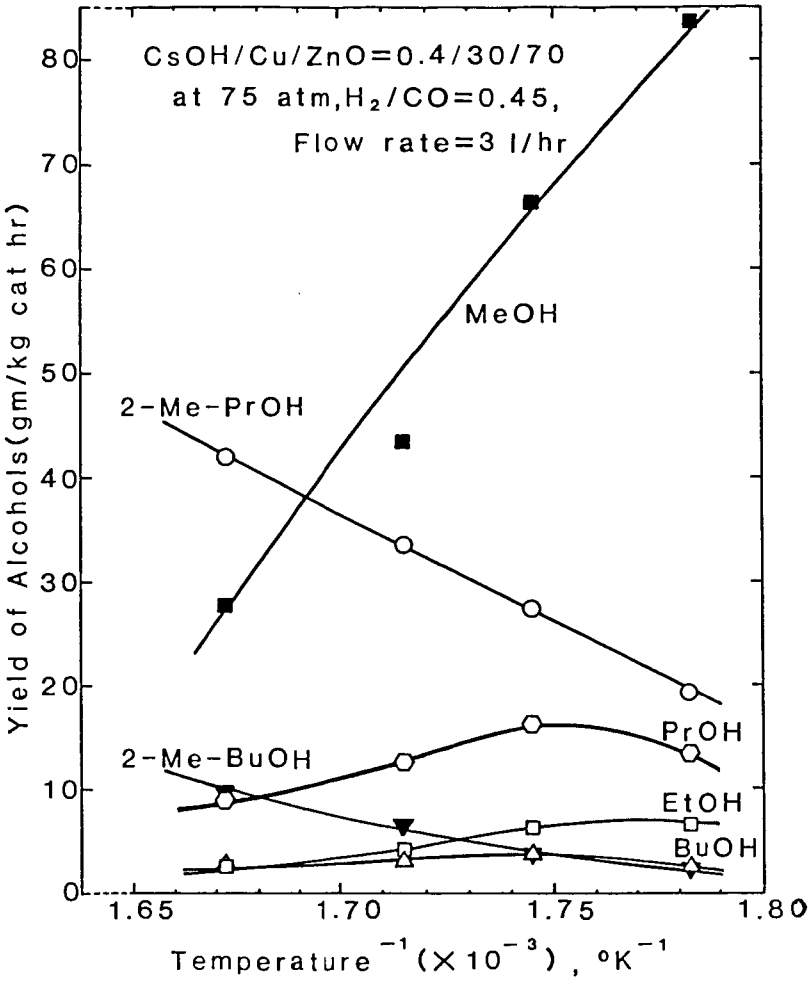

Figure 3. The temperature dependence of alcohol yields at 75 atm, H_2/CO = 0.45 at GHSV = 1200 over the CsOH /Cu/ZnO = 0.4/30/70 catalyst.

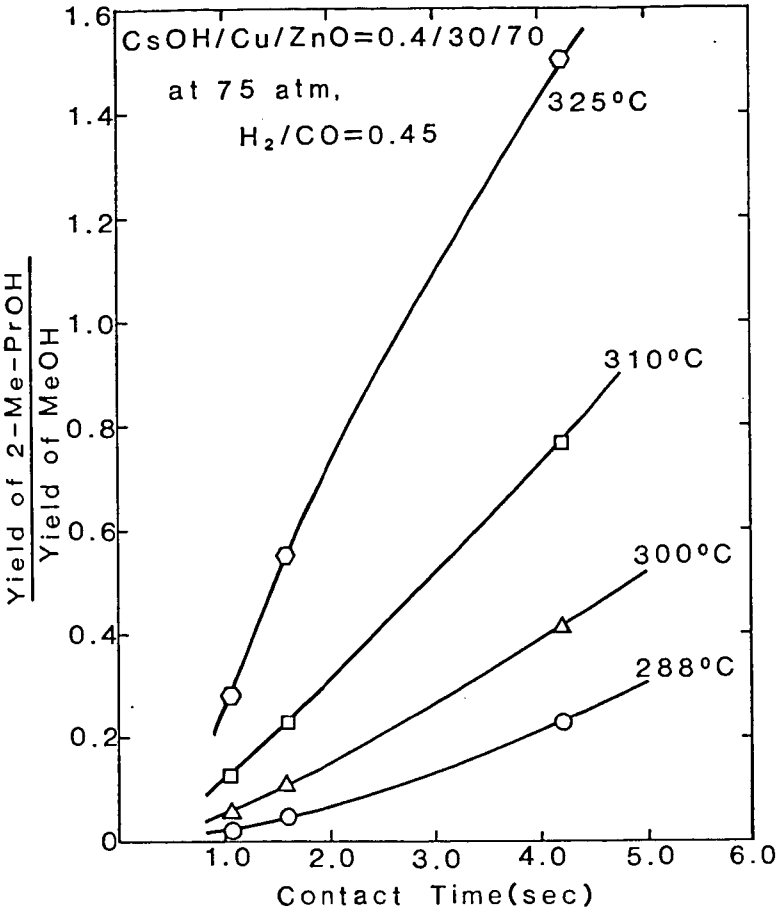

Figure 4. Selectivity to 2-methyl-1-propanol expressed as the ratio of yields of 2-methyl-1-propanol and methanol at 75 atm, H_2/CO = 0.45, as a function of contact time and temperature.