DIRECT SYNTHESIS OF 2-METHYL-1-PROPANOL

K. Klier, R. G. Herman, and C. W. Young

Department of Chemistry and Center for Surface
and Coatings Research, Lehigh University, Bethlehem, PA 18015

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.

ACKNOWLEDGEMENT

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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

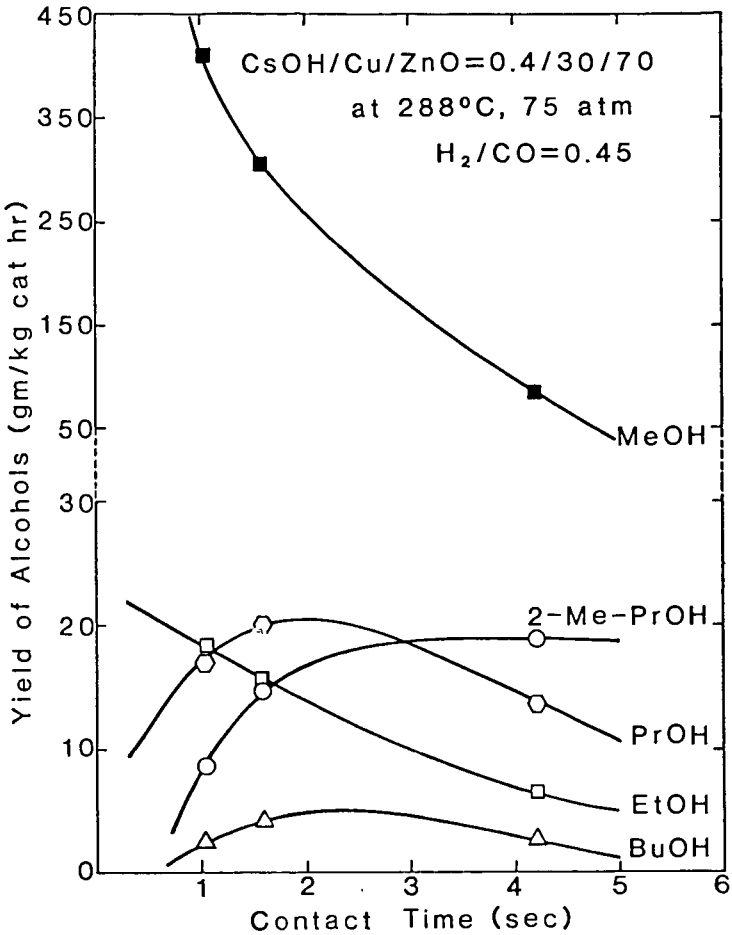

Figure 1. The contact time dependence of alcohol yields at 75 atm, 288°C, H_2/CO = 0.45 over the CsOH /Cu/ZnO = 0.4/30/70 catalyst.

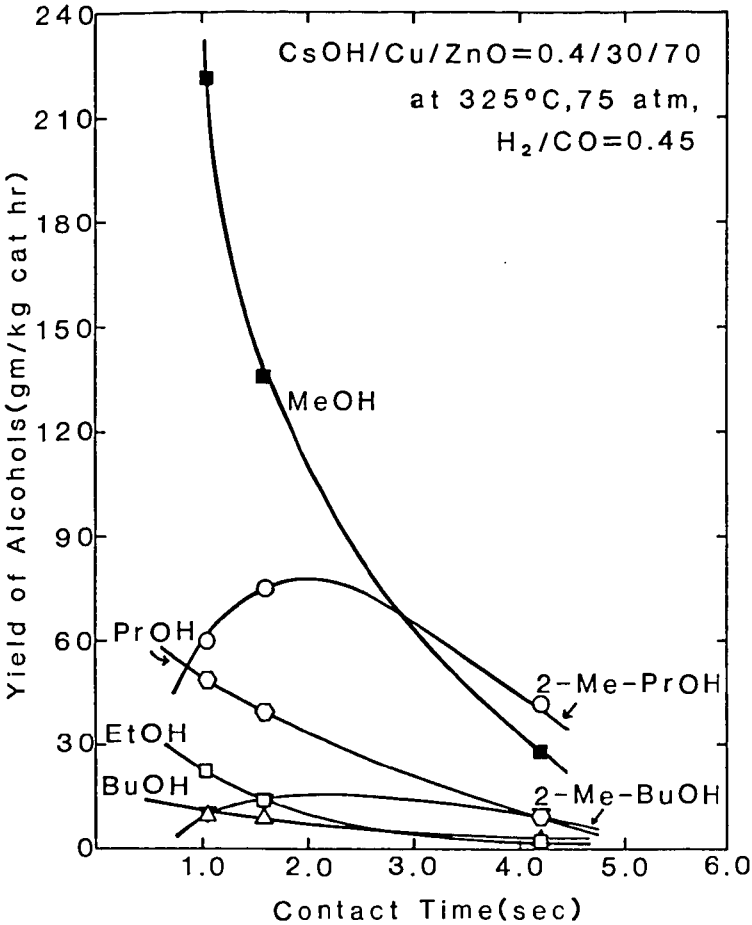

Figure 2. The contact time dependence of alcohol yields at 75 atm, 325°C, H_2/CO = 0.45 over the CsOH/Cu/ZnO = 0.4/30/70 catalyst.

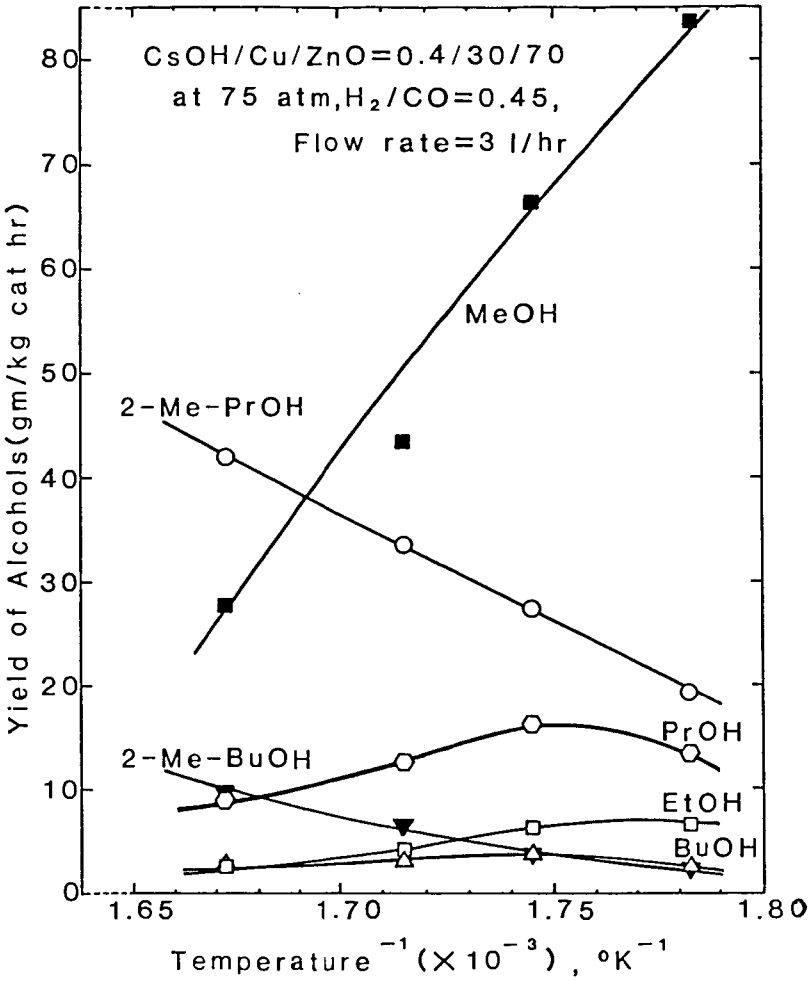

Figure 3. The temperature dependence of alcohol yields at 75 atm, H_2/CO = 0.45 at GHSV = 1200 over the CsOH /Cu/ZnO = 0.4/30/70 catalyst.

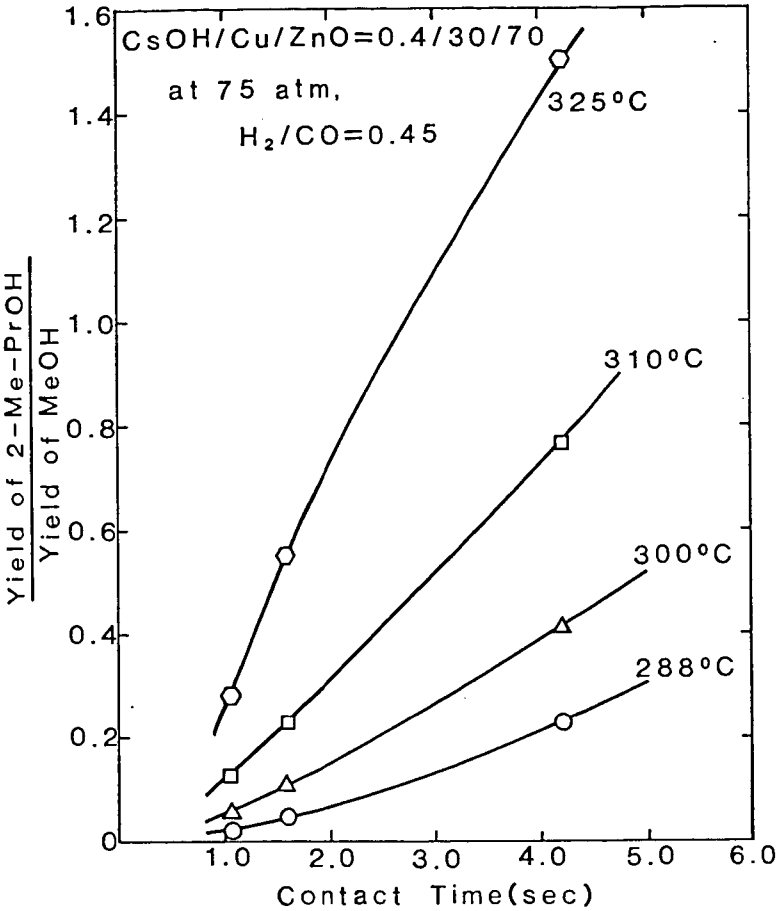

Figure 4. Selectivity to 2-methyl-1-propanol expressed as the ratio of yields of 2-methyl-1-propanol and methanol at 75 atm, H_2/CO = 0.45, as a function of contact time and temperature.