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A Chain Growth Scheme for the Higher Alcohols Synthesis

KEVIN J. SMITH AND ROBERT B. ANDERSON

Department of Chemical Engineering and Institute for Materials Research, McMaster University, Hamilton, Ontario

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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. 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.

1. INTRODUCTION

The conversion of synthesis gas to higher alcohols over promoted methanol catalysts was first reported in the 1920's (*7*). Subsequently it has been established that methanol catalysts containing up to three metal oxides and promoted with alkali, produce methanol and higher alcohols particularly 2-methyl-1-propanol (*3, 6, 10*). Recently the use of a Cu/ZnO methanol catalyst, promoted with 0.5% K_2CO_3, operated under moderate conditions (285°C and 10.4 MPa), was reported (*8*). This catalyst gave a range of higher alcohol selectivities depending on the reaction conditions, particularly the H_2/CO feed gas ratio.

Chain growth schemes have proved useful in describing the isomer and carbon number distributions of the Fischer–Tropsch synthesis (*2*). Prior to this development, Graves (*5*) used a similar idea to predict qualitatively the alcohols present in the product from a commercial alcohol production unit. He suggested that the higher alcohols occur via condensation reactions and that these obey certain addition rules. This chain growth scheme has been summarized by Anderson *et al.* (*1*).

The present paper describes a chain growth scheme for the alcohol product distribution obtained on a 0.5% K_2CO_3-promoted Cu/ZnO catalyst. The growth parameters were estimated from experimental data and their physical significance is discussed. Results of experiments with alcohols added to the synthesis gas are also reported and discussed in terms of the chain growth scheme.

2. EXPERIMENTAL

The selectivity data were obtained using a copper-lined, single-pass tubular reactor. The reactor and ancillaries had a maximum operating pressure of 14 MPa, obtained with a Superpressure air-operated, diaphragm compressor which pumped premixed synthesis gas to a storage cylinder rated at 35 MPa. Reactor pressures were controlled with a Grove 91W back-pressure regulator, and feed flows with a Matheson reducing valve and a Whitey needle valve. Product analyses were made by gas chromatography, using both thermal conductivity and flame ionization detectors. Samples were taken on-line with a Carle sampling valve maintained at 190°C. Condensed products were also analyzed. Product gas

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chromatograph peaks were identified by comparison of relative retention times, obtained from test mixtures of the alcohols. Formic acid, acetic acid, and acetone were also included in the mixtures but were never present in the reactor product. At the suggestion of a reviewer methyl and ethyl formates were tried; their retention times differed from adjacent alcohol peaks by about 30 s. Methyl formate evolved at about the time of a very small unknown peak, corresponding to less than 0.005 mol% of the product gas.

Addition of the liquid alcohols to the synthesis gas was achieved with a Gilson 302 high-pressure metering pump. The liquid alcohol was added to the synthesis gas before the reactor entrance. At the point of addition, the feed gas line was at 200°C, and this temperature was maintained to the reactor entrance with a heating tape. The alcohol concentration in the feed was always less than 10% so that none of the alcohol condensed in the feed gas line or reactor. The product gas line was also maintained at 200°C with a heating tape. Additional experimental details are given in (*8, 9*).

The commercial Cu/ZnO catalyst used in the present work was promoted with 0.5% K_2CO_3 and had a BET surface area of 36 m^2/g. The unpromoted catalyst had a composition (expressed as weight percentage) of $46CuO:46ZnO:8Al_2O_3$.

3. CHAIN GROWTH SCHEME DEVELOPMENT

The reaction scheme proposed by Graves (*5*) assumed that the formation of higher alcohols occurred by condensation of two lower alcohols, with hydrogen loss at an α-position or β-position carbon atom, the latter being the faster process. It was also assumed that hydrogen loss from methanol was slower than from a β-carbon and that secondary alcohols react by loss of the hydroxyl group only. These assumptions led to a qualitative description of the higher alcohols produced in the commercial alcohol synthesis (*1, 5*).

By using these ideas, with a few additional assumptions, equations describing the alcohol distributions may be derived. For the simplest case of a one-carbon addition a qualitative description of the alcohol distribution is possible (*8*). It was assumed that α-addition did not occur beyond the first step and no addition occurred on a —CH group. Hence, the predicted prod-

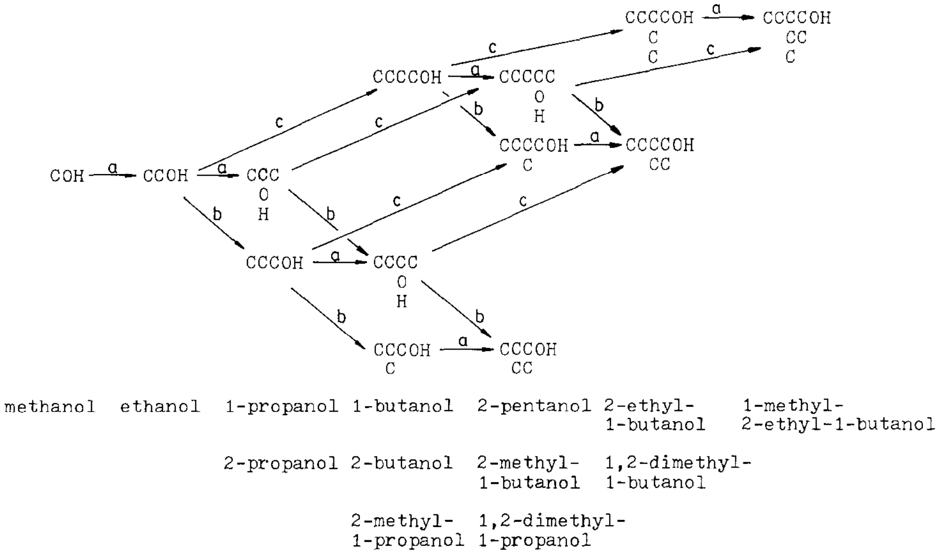


FIG. 1. Higher alcohol chain growth scheme. The species shown, for example, CCOH, are adsorbed intermediates. Desorption steps leading to the products are not shown.

ucts were methanol, ethanol, 1-propanol, and 2-methyl-1-propanol, which contradicts the observed presence of 2-propanol and 2-butanol in the reaction products (Table 2). Furthermore, the presence of 1-butanol suggests that two-carbon additions also occur.

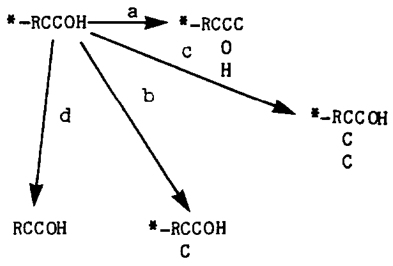
Modifying the simple chain growth scheme to include two carbon additions and α-addition beyond the first step leads to the scheme of Fig. 1, which assumes the following growth rules, required to predict the experimentally observed product distribution:

(1) Higher alcohol formation results from the reaction of two intermediates of lower carbon number. At least one of these has a carbon number of one or two. Thus, growth is by one or two carbon addition only.

(2) Addition occurs at the α- or β-carbon (with respect to the hydroxylated carbon atom) of the reaction intermediate. Addition does not occur on a —CH group. Two-carbon addition does not occur at an α-carbon.

(3) All the reaction rates are assumed to be first order with respect to the concentration of growing intermediate at the surface, including desorption of this intermediate. The rate constants are also assumed independent of carbon number and all steps are irreversible.

Thus, for a general intermediate, the possible reactions are



where *-ROH implies an adsorbed surface species, a and b are first-order rate constants for one carbon addition at the α- and β-position, respectively, c is the first-order rate constant for two carbon-addition at the β-position, and d is the desorption rate constant. If the primary alcohol has a branch at the β-position, however, only one-carbon addition at the α-position can occur. Growth at a secondary alcohol can only occur at the β-position. The above scheme is similar to that of Graves except that secondary alcohols are assumed to grow by hydrogen loss, and only one or two carbons may be added to the intermediate for each growth step. Starting at methanol and following these rules, leads to the chain growth scheme of Fig. 1, which does not show the desorption step of each intermediate.

To obtain the distribution equations, a steady state mass balance is written for each adsorbed intermediate. For example, a balance on the intermediate leading to 1-propanol may be written as

$$b \cdot A_2 = (a + b + c + d) \cdot A_{n3}$$

where A_2 is the concentration of the adsorbed intermediate leading to ethanol and A_{n3} is the concentration of the adsorbed intermediate leading to 1-propanol. Hence

$$A_{n3}/A_2 = b/(a + b + c + d)$$

By reporting these rate constants relative to the desorption rate, and assuming, as Graves did, that one-carbon β-addition and the desorption rate are faster than α-addition or two-carbon β-addition, this equation may be simplified to

$$A_{n3}/A_2 = \beta/(1 + \beta) = C_{n3}/C_2$$

where $\beta = b/d$, C_{n3} and C_2 are the 1-propanol and ethanol gas phase concentrations, respectively. In a similar manner the equations of Table 1 may be derived. In all cases it is assumed that $a,c \ll b$ and $a \ll d$, to simplify the distribution equations. The approximations are valid in the present work, but are not essential to the growth scheme development. Note that in Table 1 the distribution equations have been simplified by using variables A, B, C as defined in Table 1.

Also shown in Table 1 are product concentration ratios written in terms of chain

TABLE 1

Alcohol Product Distribution Equations

Alcohol, mole fraction relative to methanol	Distribution equation in terms of	
	Rate constants[a]	Probabilities
Ethanol	A	$h(1-k)$
1-Propanol	A^2B	$hk(1-k)$
2-Propanol	A^2	$h^2(1-k)^2$
1-Butanol	A^3C	$hl(1-k)$
2-Butanol	$2A^3B$	$2kh^2(1-k)^2$
2-Methyl-1-propanol	$A^3B^2/(1-AB)$	hk^2
2-Pentanol	A^3C	$hl(1-k)$
2-Methyl-1-butanol	$2A^4BC/(1-AB)$	$2hkl$
1,2-Dimethyl-1-propanol	$2A^4B^2/(1-AB) + A^4B^2/(1-AB)^2$	$2h^2k^2(1-k) + h^2k^2$

[a] Where: $A = \alpha/(1+\beta) = h(1-k)$, $AB = \beta/(1+\beta) = k$, and $A^2C = \gamma/(1+\beta) = l$.

growth probabilities. For this growth scheme the probability of chain growth depends on which species is growing. The following growth probabilities may be defined:

$$h = a/(a + d) = \alpha$$

where $\alpha = a/d$ and h is the probability of growth when only α-addition can occur;

$$k = (a + b + c)/(a + b + c + d) = \beta/(1 + \beta)$$

which is the probability of growth for the general case. With the approximations for the rate constants, k is also equal to the probability of growth when only β-addition can occur.

An additional parameter is required to distinguish between one- and two-carbon addition when β-addition occurs. Hence

$$l = c/(a + b + c + d) = \gamma/(1 + \beta)$$

where $\gamma = c/d$. Using these equations the carbon number distribution in terms of rate constants may be rewritten in terms of probabilities as shown in Table 1.

The growth rules predict alcohols up to a maximum carbon number of seven. In Graves' work, octanols were detected although in most other work, alcohols above pentanols occurred in insignificant quantities (*7*). Limiting the addition to a maximum of two carbon atoms per step, implies that the largest normal alcohol has a carbon number of four. Furthermore, carbon addition to an adsorbed species stops following β-addition to an α-substituted intermediate or α-addition to a β-substituted intermediate. The latter case, together with the assumption that $b \gg a, c$, allows the prediction of relatively large amounts of 2-methyl-1-propanol. The large methanol yields follow since it is assumed that $a \ll d$. Hence, these observations are consistent with published data (*4, 7*) where the measured components were highly branched, with low carbon number and few normal alcohols.

4. RESULTS AND DISCUSSION

4.1 Parameter Estimates

Estimates of the parameters of the distribution equations were obtained by nonlinear least-square estimation, applied to the observed alcohol distribution at each operating condition. The pentanols were included in the data used to estimate the parameters; however, for the pentanols, only the total mole fraction was considered, since not all the pentanol-branched species were identified. Thus, seven data points (being the mole fractions of ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-

methyl-1-propanol, and pentanols divided by the methanol mole fraction) were used to estimate the three parameters at each operating condition. Table 2 gives predicted and measured values for a representative set of measured distributions. The predicted values are those obtained using the nonlinear least-square parameter estimates shown.

The data of Table 2 show that this model predicts the distributions successfully. For the major components, ethanol, 1-propanol, 2-methyl-1-propanol, and total pentanols, the predicted versus measured values agree within 10%. The largest errors occur for 1-butanol and 2-butanol where the predictions are sometimes twice the measured values; however, these components are a small fraction of the other alcohols and their concentrations are close to the experimental error.

Theoretical alcohol selectivities may be calculated using the growth probability equations of Table 1. These results are illustrated in Figs. 2 and 3, where typical values obtained from experimental data were assumed for the two probabilities remaining constant. These figures show that the probability *h* has the most significant effect on the alcohol selectivity. In the present work, however, *h* was always less than 0.2, while *k* reached a maximum of about 0.75. For large higher alcohol selectivities, the probability of growth in the initial step, α, must be large. Thus, the high probability of desorption of the methanol precursor for the

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	
Alcohol[a]	Measured	Predicted	Measured	Predicted	Measured	Predicted
Ethanol	0.0434	0.0455	0.0296	0.0299	0.0118	0.0118
2-Propanol	0.0025	0.0021	0.0008	0.0009	0.0007	0.0001
1-Propanol	0.0348	0.0303	0.0148	0.0139	0.0026	0.0024
1-Butanol	0.0091	0.0026	0.0018	0.0002	0.0007	0.0002
2-Butanol	0.0045	0.0028	0.0013	0.0008	0.0007	0.0001
2-Methyl-1-propanol	0.0601	0.0601	0.0118	0.0121	0.0003	0.0006
Pentanols	0.0253	0.0266	0.0014	0.0020	—	0.0003
	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	

[a] Ratio of alcohols to methanol on a molar basis.

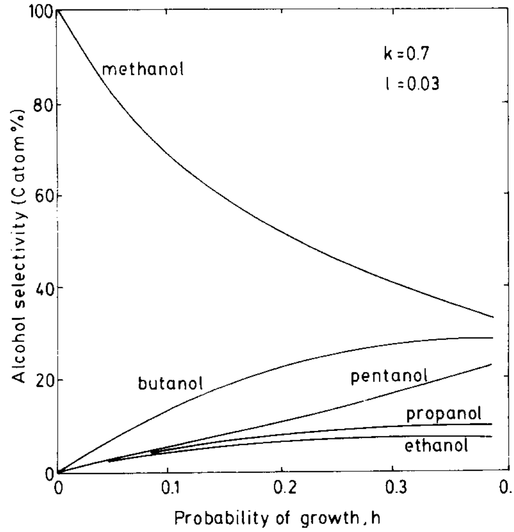


FIG. 2. Alcohol selectivities predicted from growth scheme probabilities.

experimental conditions investigated here, limits the attainable butanol selectivity.

The three parameters α, β, and γ are ratios of a growth constant and a desorption constant. For application to data from an integral reactor, these constants should be relatively independent of reactant concentrations. These parameters may also change with temperature, following the Arrhenius Law.

The apparent activation energy for the chain growth parameters α, β, and γ were estimated from data measured at 10.4 MPa, a H_2/CO feed ratio of 0.9, and a space velocity of 2000 h^{-1}. The parameter values are shown as a function of temperature in Fig. 4, from which the apparent activation energies were estimated as 66 kJ/mol for β, while for α and γ the activation energies were approximately 140 kJ/mol. The lower activation energy for β is consistent with the previous observation that reaction of the methanol precursor is the major barrier in the synthesis of higher alcohols. For the operating conditions and catalyst investigated here, this reaction was always slow.

Figure 5 shows the dependence of the parameters α and β on the average H_2/CO ratio (i.e., the average of the inlet and exit conditions), obtained at 285°C and 10.4 MPa. From the slopes of these plots the parameters α and β vary approximately as P_{CO}/P_{H_2}. Hence, as a first approximation the rate of growth (at both the α or β carbon) varies as the CO partial pressure, while the desorption rate varies as the H_2 partial pressure. The data scatter of Fig. 5 are partly a result of the approximations associated with the chain growth scheme derivation, when the parameters are a function of reactant concentration.

4.2 Effect of Alcohols Added to Feed Gas

The proposed chain growth scheme assumes that the higher alcohol synthesis occurs sequentially. The alcohol growth and desorption rates were assumed to be first order and irreversible. With the addition of alcohols to the reactant, however, it is probable that the surface concentration of the precursor of the particular alcohol would increase, which would increase the yield of alcohols produced by growth of the particular precursor. These observations may yield a technique for determining if the chain growth steps of this work are consistent, and may also have some practical advantage.

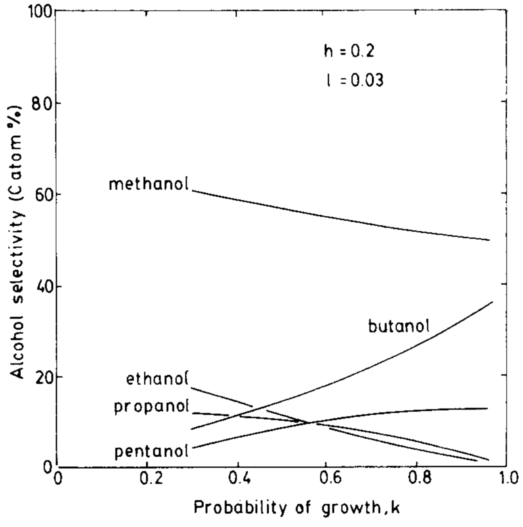


FIG. 3. Alcohol selectivities predicted from growth scheme probabilities.

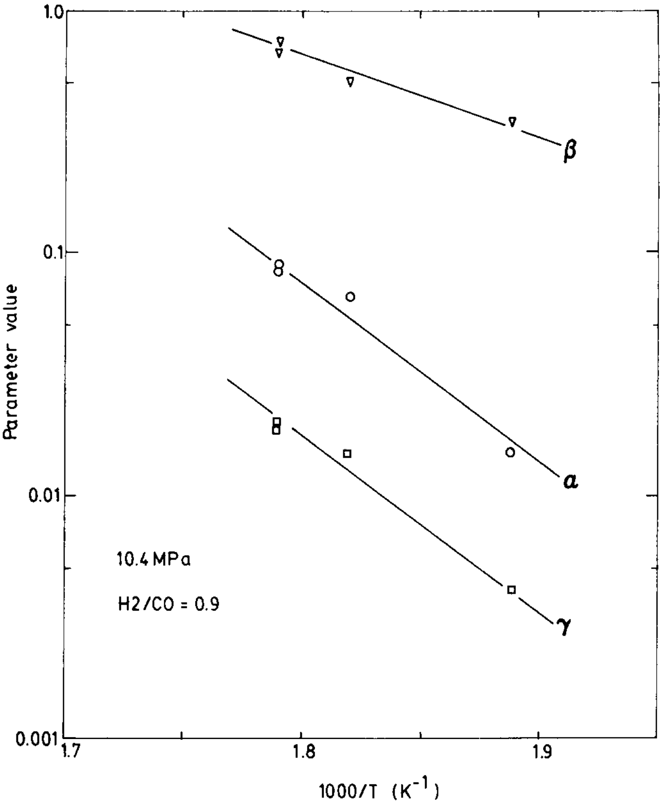


FIG. 4. Arrhenius diagram for chain growth parameters at 10.4 MPa and H_2/CO = 0.9.

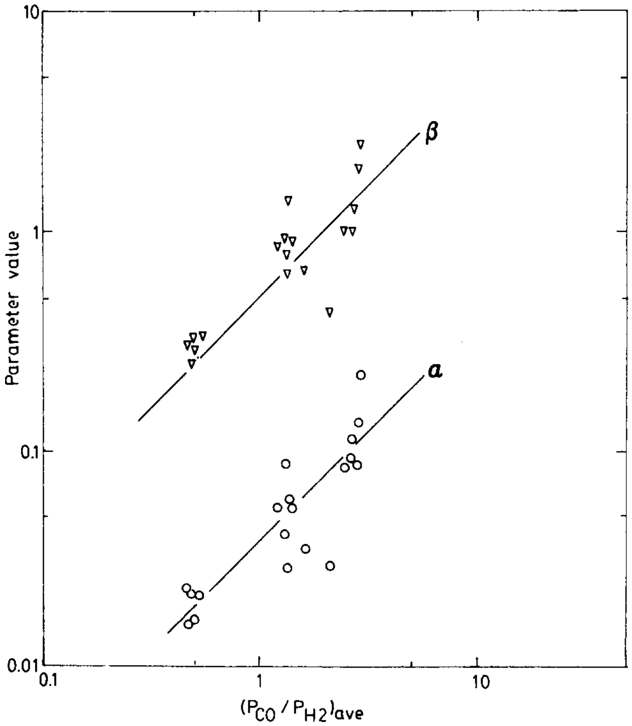


FIG. 5. Chain growth parameters as a function of average CO/H_2 ratio at 10.4 MPa and 285°C.

Addition of alcohols to the feed has been reported by Chernobrivets *et al.* (*3*) on a promoted Cr_2O_3/ZnO catalyst. They found an increase in the 2-methyl-1-propanol yield, upon the addition of 1-propanol, while the addition of methanol had no effect on the propanol or the 2-methyl-1-propanol yield. From these observations, they concluded that 1-propanol is a probable intermediate in the 2-methyl-1-propanol formation, which is consistent with the chain growth scheme proposed here.

In the present work, the alcohol yields were measured for the 0.5% K_2CO_3 promoted Cu/ZnO catalyst at 285°C, 10.4 MPa, and space velocities of approximately 2500 h^{-1}. The feed gas had a H_2/CO ratio of 0.9 with various alcohols added to this reactant. These data are summarized in Table 3. As with the work of Chernobrivets *et al.*, addition of 1-propanol increased the 2-methyl-1-propanol yield. However, additional observations may be made from these data.

Compared to the case of no alcohol added to the feed gas, addition of methanol doubled the ethanol and 1-propanol yields. The yields of all other alcohols were approximately the same as for the case of no alcohol addition. Ethanol addition increased the propanol and butanol yields, while addition of 2-propanol increased the 1-butanol and 2-butanol, but not the 2-methyl-1-propanol. The largest increase occurred with the addition of 1-propanol, increasing the 2-butanol and the 2-methyl-1-propanol, but not the 1-butanol. The pentanols were also increased significantly, as observed for the case of 1-butanol addition.

Some of these observations support the proposed chain growth scheme. Addition of the 2-propanol should not increase the 2-methyl-1-propanol yield as has been observed. This supports the proposal that 2-propanol can react by addition at the β-carbon alone, to form 2-butanol (Fig. 1). Addition of 1-propanol should not increase the 1-butanol yield but should increase the yields of 2-butanol and 2-methyl-1-propanol. The increase for the latter component should be greater since this occurs via β-addition. These postulates are confirmed by the data of Table 3.

The results of Table 3 also have practical implications. Synthesis of higher alcohols is presently achieved by hydration (ethanol from ethylene, 2-propanol from propylene,

TABLE 3

Effect of Alcohols in Feed Gas

Temperature 285°C, Pressure 10.4 MPa,
Feed H_2/CO = 0.9

Space velocity (h^{-1})	2300	2800	2500	2700	2500	2400
Alcohol added	None	Methanol	Ethanol	2-Propanol	1-Propanol	1-Butanol
Mol% in feed	0	8.6	6.7	4.7	5.2	4.5
	Yields (g · kg^{-1} · h^{-1})					
Methanol	118 ± 18[a]	—	131	127	105 ± 16	87
Ethanol	8 ± 2	16 ± 2	—	3	3 ± 1	2
2-Propanol	1 ± 0	1 ± 0	4	—	<1	<1
1-Propanol	5 ± 1	10 ± 1	27	3	—	1
1-Butanol	2 ± 0	1 ± 1	5	6	2 ± 1	—
2-Butanol	1 ± 0	1 ± 0	10	5	5 ± 1	<1
2-Methyl-1-propanol	4 ± 1	4 ± 0	12	3	33 ± 9	<1
Pentanol	—	—	<1	2	26 ± 9	16

[a] Standard deviations from repeated observations.

and 2-butanol from butylene) or carbonylation (1-propanol or 1-butanol from synthesis gas and ethylene or propylene, respectively). In the short term, it is likely that alcohol production will continue to use olefinic feedstocks (*6*). In the long term, however, alcohol production from synthesis gas may become important. Known technologies by which this may be achieved include the Fischer–Tropsch synthesis, where alcohols are usually produced as minor products, the process developed by Sugier and Freund (*10*) which yields primary alcohols up to butanols, or by the "isobutyl alcohol" process.

The present work shows that the latter process may also be achieved at operating conditions significantly less severe than those reported for zinc–chromite catalysts. Use of a promoted Cu/ZnO catalyst operated at 285°C, 10 MPa, and a feed gas H_2/CO ratio of 0.5 leads to 2-methyl-1-propanol selectivities of 20%. Table 3 shows that addition of alcohols in the feed can increase the alcohol yields significantly. This observation affords a possible route for the production of alcohols, with greater yields than those achieved with either the Fischer–Tropsch synthesis, the traditional "isobutyl alcohol" process or with the promoted Cu/ZnO catalyst of the present work. It is possible that the lower alcohols produced with the promoted Cu/ZnO catalyst, could be recycled in an industrial situation, thereby improving the 2-methyl-1-propanol yield.

5. CONCLUSIONS

The proposed scheme for chain growth describes the higher alcohol product distribution measured for a range of operating conditions. Growth can occur at the α- or β-carbon atom, with the latter the faster step. Large methanol selectivities are a result of a slow initial growth step, while large 2-methyl-1-propanol selectivities are a result of α-addition being the only growth step of the 2-methyl-1-propanol intermediate.

The rate of growth was shown to increase with increasing partial pressure of CO, and the termination rate varied as the H_2 partial pressure, implying that the higher alcohols are favored by CO-rich feeds. In addition, the apparent activation energies for α- and β-addition were estimated as 140 and 66 kJ/mol, respectively.

Addition of alcohols to the feed gas significantly increased the yields of some of the alcohols, this was consistent with the proposed growth scheme.

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