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The Effects of Carbon Dioxide, Methanol, and Alkali Promoter Concentration on the Higher Alcohol Synthesis over a $Cu/ZnO/Cr_2O_3$ Catalyst

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The behavior of the methanol and higher alcohol (HAS) syntheses as a function of catalyst promoter concentration, CO_2 feed gas concentration, and methanol feed gas concentration has been investigated over a $Cu/ZnO/Cr_2O_3$ catalyst at 10 MPa and 285–315°C. In the presence of CO_2 in the feed gas, the methanol and HAS yields are greater for the unpromoted catalyst than the 0.5% K_2CO_3-promoted catalyst. The methanol and HAS yields also reach a maximum as the CO_2 concentration increases for both catalysts. In the absence of CO_2, both the methanol and HAS yields reach a maximum as the K_2CO_3 promoter concentration increases. The complex behavior results from the ability of these catalysts to incorporate CO, CO_2, and methanol into higher alcohols, on at least two different types of catalytic sites. It is suggested that CO_2 participates directly in HAS on copper sites while alkali/copper interfacial sites are involved in converting CO. Higher alcohol production is therefore very sensitive to the feed gas composition and the components and composition of the catalyst.

INTRODUCTION

The synthesis of higher alcohols over alkali-promoted methanol catalysts has been studied since about 1930 (*1*). Earlier studies were performed using the high-temperature Zn–Cr oxide catalysts that were typical for methanol synthesis until the 1960's. More recently, higher alcohol production over the low-temperature Cu-containing methanol catalysts has been reported by Smith and Anderson (*2*) and by Klier and co-workers (*3*).

Promotion of the methanol synthesis catalysts by alkali metals and operation at temperatures and CO/H_2 ratios higher than are typical for the methanol synthesis enhances the yields of higher alcohols (*1*, *2*). The product distribution modeling studies of Smith and Anderson (*4*) showed that ethanol production is the slow step in the series of reactions that lead to 1-propanol and 2-methyl-1-propanol, the dominant higher alcohol products.

Alkali Promoter Effects

Smith and Anderson (*2*) found that higher alcohol yields passed through a maximum as the K_2CO_3 promoter concentration was increased on their $Cu/ZnO/Al_2O_3$ catalyst. Vedage *et al.* (*5*) have shown that alkali promotion enhances the rate of methanol production as well as the yields of higher alcohols with CO + H_2 feeds over a CsOH-promoted Cu/ZnO catalyst. However, when the feed contained CO_2, methanol synthesis was not enhanced by alkali promotion. Sheffer and King (*6*) also observed enhanced methanol yields from a CO + H_2 feed when their copper catalyst was promoted with alkali.

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Effect of Carbon Dioxide

Very little data have been presented showing the effects of CO_2 on the higher alcohol synthesis (HAS). Tronconi *et al.* (*7*) observed decreased yields of higher alcohols when CO_2 was added to the CO/H_2 feed over a Zn–Cr–K–oxide catalyst at 400°C. These workers proposed that active sites were poisoned by water, produced in the reverse water gas shift (WGS) reaction when CO_2 was present in the feed. Ramaroson and coworkers (*8*) found that HAS yields were drastically reduced when $CO_2/H_2 = 1/3$ feed gas was substituted for a $CO/H_2 = 1/2$ feed over their Cu-containing catalysts. These workers suggested that unlike CO, CO_2 is not a favorable reactant in the chain growth reactions that produce higher alcohols. Elliot (*9*) has made the contrary observation that higher alcohol yields are enhanced by addition of CO_2 to the feed gas over a Cu/ZnO catalyst. A satisfactory explanation of these various effects is not easily made since none of these studies explored the effects of a wide range of CO_2 concentrations on the rates of higher alcohol formation.

The most recent information regarding the methanol synthesis indicates that both CO and CO_2 participate directly in methanol formation (*10, 11*) and recent ^{13}C labeling studies show that methanol and higher alcohol syntheses are intimately related (*12–15*). Clearly, the effect of CO_2 on the higher alcohol synthesis over alkali-promoted Cu/ZnO catalysts should be investigated further to clarify some of the observations described.

Effect of Methanol

Recent ^{13}C labeling studies have confirmed that methanol is incorporated directly into higher alcohol products (*12–15*). However, very little data have been presented on the effects of methanol concentration on higher alcohol synthesis yields. In most studies of the HAS, the methanol synthesis reaction is at equilibrium and the methanol concentration is not treated as an independent variable because it is not added to the feed. Smith and Anderson (*2*) reported that addition of methanol to the reactor feed enhanced the yield of ethanol while Chernobrivets *et al.* (*16*) observed no such increase. However, both groups found that the yield of 2-methyl-1-propanol was enhanced when 1-propanol was added to the feed. In order to clarify the effects of methanol on the HAS, the methanol concentration in the reactor must be manipulated by adding various amounts of methanol to the feed. In addition, performing these experiments with various amounts of CO_2 in the feed and/or with various amounts of promoter on the catalyst will give insight into some of the features of the HAS which have not been previously studied.

In view of the discussion presented above, the purpose of the present investigation is to address the following issues:

(1) Carbon dioxide is indirectly important to the HAS because of its well-documented importance in methanol synthesis. However, knowledge of direct effects of CO_2 on the HAS is extremely limited. Since CO_2 is present in any realistic reactor configuration for production of higher alcohols, its effects on the HAS must be elucidated.

(2) Recent studies have shown that methanol is a direct precursor to intermediates involved in higher alcohol production. Therefore, it may be possible to optimize the yields of higher alcohols by manipulating the methanol concentration in the reactor. However, data showing the kinetic effects of methanol on the HAS are lacking and so must be generated.

The data generated as a result of this investigation have also been used to develop a kinetic model of the methanol and higher alcohol synthesis that will be presented in a subsequent paper (*17*).

EXPERIMENTAL

Catalyst Preparation

The $CuO/ZnO/Cr_2O_3 = 30/60/10$ (metal atom percent) catalyst was prepared by coprecipitation from 1 *N* metal nitrate solu-

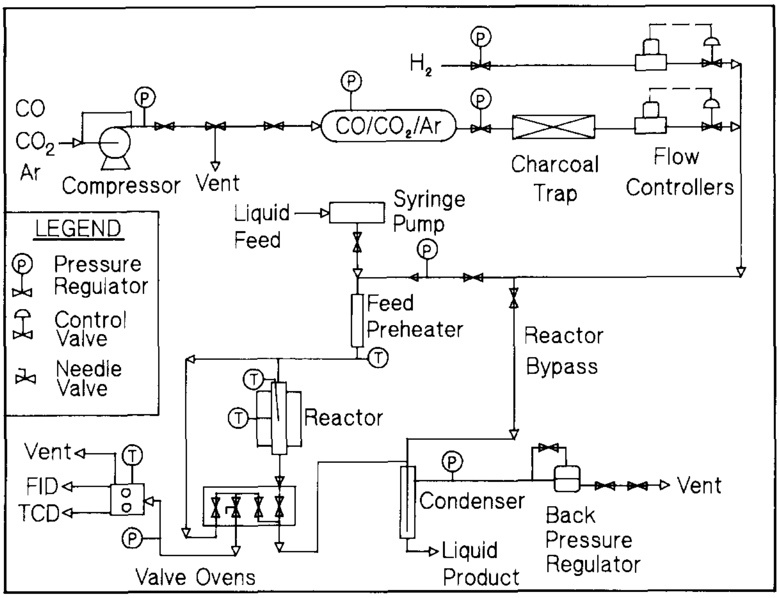

FIG. 1. Schematic of reactor and flow system.

tions by rapid addition of 1 *N* sodium carbonate at 50 to 60°C. The washed precipitate was dried for 20 h at 110°C, broken into pieces, and calcined in air at 350°C for 4 h. Calcined catalysts were promoted with various amounts of K_2CO_3 by the incipient wetness method, and dried overnight at 120°C. The catalyst powder was pelleted, crushed, and sieved to 16–25 mesh, producing particles with an average diameter of about 0.94 mm. The catalyst particle size was chosen to minimize internal diffusion effects. The same rate of methanol synthesis was measured for particles of average size 0.94 and 0.64 mm, which, together with mass transfer calculations that estimated the catalyst effectiveness factor, indicated the absence of internal mass transfer limitations in the system (*12*). Prior to testing the catalysts were heated to 300°C in flowing H_2 (35 mL/min) for at least 5 h.

Reactor and Flow System

The reactor unit is shown schematically in Fig. 1. Mixtures of CO, CO_2, and Ar were prepared in an 8.5-liter high-pressure storage tank using a Superpressure air-operated compressor. A rupture disc and purge line were included between the compressor and the storage tank and a charcoal trap downstream of the storage tank effectively removed iron carbonyls from the CO feed gas. Hydrogen was used directly from a cylinder and feed gas flows were regulated using Brooks model 5810B/5835D1 flowmeter-controllers. Reactor exit gases passed through a high-pressure condenser maintained at 0°C before exiting through a Grove 91W back pressure regulator to vent. Tubing and fittings were made of 304 and 316 stainless steel.

The fixed-bed tubular reactor, lined with a tight fitting 1.0-cm-i.d. copper tube, was operated in the integral mode in the present work. Typically about 1.6 g of catalyst was placed on top of glass wool supported on a wire mesh support. The catalyst was covered with more glass wool and glass beads, intended to serve as a feed preheating zone. The reactor was situated coaxially inside a heated aluminum block and a thermocouple, placed in the center of the catalyst bed, was used as the sensing element for an Omega 2001 temperature controller.

Numerous precautions were taken to ensure that methanol and other alcohols did not condense upstream of the condenser. Methanol, added to the feed using a Gilson model 302 pump, entered the flow system immediately upstream of the feed preheater. A thermocouple placed in the center of the feed stream, downstream of the preheater, showed that addition of methanol caused the feed temperature to decrease by only 1 or 2°C (for example from 125 to 123°C: well above the dew point of the methanol in the feed stream). Feed and product sampling lines were heated with electrical tracing, and a layer of fiberglass pipe wrap was added as insulation. Thermocouples, fixed to the outside wall of the sampling and reactor exit lines were the sensing elements for a United Electric Controls temperature controller. The input heating voltage was set so that the maximum attainable tubing temperature was 200°C, and the tubing temperature was normally maintained at 180°C. Valves on the high pressure side of the sampling system presented a problem for the heating system. A special valve oven was designed in which the valves and associated tubing were imbedded in an aluminum block, heated by two 250 W cartridge heaters and maintained at 165°C.

Analytical Methods

Feed and product analyses were performed using two gas chromatographs. A charcoal column and thermal conductivity detector were used to quantify H_2, Ar, CO, and CO_2. Methanol and trace hydrocarbons were analyzed on-line and the liquid product was analyzed off-line using a Chromosorb 101 column and a flame ionization detector. Alcohols normally detected in the products were methanol, ethanol, 1-propanol, 2-butanol, 2-methyl-1-propanol, 1-butanol, and 1-pentanol but small amounts of other species were detected in some runs including methyl formate, 2-propanol, and methyl acetate. The predominance of low carbon number alcohols was the result of the relatively high space velocities (low conversions), typically $> 20000\ h^{-1}$, used in the present work.

Choice of Experimental Conditions

Initial experiments were based on a full 2^4 factorial experimental design to explore the effects of temperature, catalyst promoter concentration, CO_2 feed concentration, and methanol feed concentration. Considerations in the choice of experimental conditions were as follows:

(1) Higher alcohol synthesis rates are low below about 285°C (*2*), so this was chosen as the lowest temperature of the study. Although catalyst deactivation due to sintering is normally a concern above 300°C for copper catalysts, the present $CuO/ZnO/Cr_2O_3$ catalyst has been shown to have good thermal stability during a 60-h run at 325°C (*18*). Therefore, the high-temperature setting of 315°C was chosen to ensure that catalyst deactivation was avoided.

(2) In previous work (*18*), a promoter concentration of 0.5 wt% K_2CO_3 was used and this was chosen as the low promoter level in the present study. In order to determine the effect of large promoter concentrations in the presence of methanol and CO_2 a catalyst promoted with 4% K_2CO_3 was also tested.

(3) It was desired to effect significant changes in the methanol concentration in the reactor without approaching equilibrium, or causing condensation in the reactor. A feed concentration of 1.8 mol% methanol was achievable with the Gilson liquid pump and satisfied this criterion. Furthermore, high space velocities (20000 mL feed/mL catalyst/h) helped prevent the methanol synthesis from reaching equilibrium.

(4) The carbon/hydrogen ratio was set at the optimum of 2/1 determined by Smith and Anderson (*2*) and also used by Vedage *et al.* (*5*) for CO_2 free feed mixtures. In the present work, the $(CO + CO_2)/H_2$ ratio was maintained at 2/1 and CO_2/CO ratios of zero and 1/5 were chosen as the low and high levels of CO_2 concentration, respectively. The in-

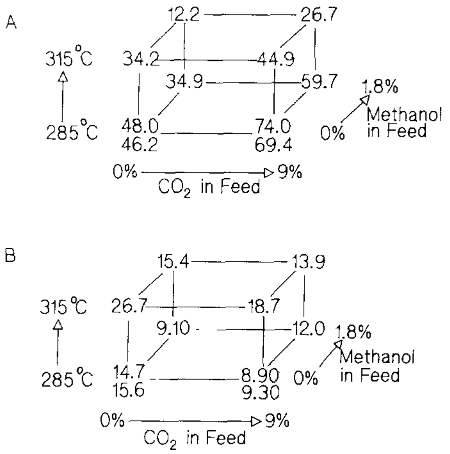

FIG. 2. Space–time yields of methanol at conditions of interest in the present study (yields in mmol/h/gram of catalyst, $(CO_2 + CO)/H_2 = 2/1$, space velocity = 20000 h^{-1}, P = 10MPa). (A) 0.5% K_2CO_3 promoted catalyst. (B) 4.0% K_2CO_3 promoted catalyst.

ert Ar concentration was typically about 10%.

RESULTS AND DISCUSSION

The methanol and higher alcohol space–time yields (STY, defined as the mmol of methanol or higher alcohols in the product/g catalyst/h), which are average synthesis rates for the integral reactor, determined from the set of factorial experiments are presented in Figs. 2 and 3. Repeat experiments shown in the figures demonstrated that the data were reproduceable. Subsequent experiments at intermediate levels of the variables investigated in the factorial design were also completed and are discussed together with the factorial design experiments in the following sections.

Temperature Effects

The methanol yield increases with temperature over the 4% K_2CO_3-promoted catalyst as expected. For the 0.5% promoted catalyst the methanol yield decreases with increasing temperature due to the high methanol activity of this catalyst that results in a significant reverse reaction as the methanol synthesis approaches equilibrium. Since equilibrium conversion to methanol is lower at 315°C than at 285°C, the methanol yield decreases with increasing temperature over the 0.5% K_2CO_3 catalyst.

The higher alcohol synthesis never approaches equilibrium under conditions used in the present work, and so yields increase with temperature, as expected.

K_2CO_3 Promoter Effects

The 0.5% promoted catalyst is substantially more active than the 4% promoted catalyst for both methanol and higher alcohols synthesis at both temperatures of the factorial design experiments. An excessive amount of promoter apparently blocks or otherwise alters active sites. The effect of promoter at intermediate promoter concentrations is presented in Fig. 4. Both the methanol and higher alcohol yields exhibit a maximum with respect to promoter concentration, consistent with the observations reported by others (*2*, *15*). Two possible explanations for this observation can be readily advanced:

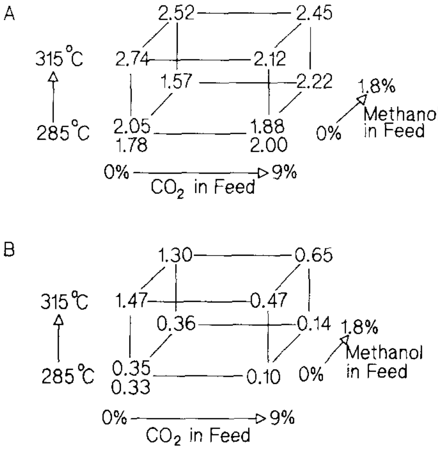

FIG. 3. Space–time yields of higher alcohols at conditions of interest in the present study (yields in mmol/h/gram of catalyst, $(CO_2 + CO)/H_2 = 2/1$, space velocity = 20000 h^{-1}, P = 10 MPa). (A) 0.5% K_2CO_3 promoted catalyst. (B) 4.0% K_2CO_3 promoted catalyst.

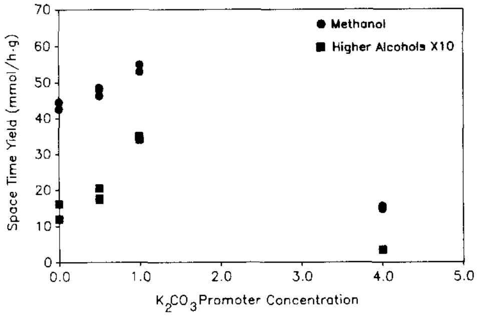

FIG. 4. Effect of K_2CO_3 promoter concentration on methanol and higher alcohol yields (285°C, CO/H_2 = 2/1, 10 MPa).

(1) Methanol synthesis requires copper sites while HAS requires alkali sites. Consequently, a balance of methanol-producing and higher alcohol-producing sites is required for optimum HAS yields. At large promoter concentrations, methanol production declines, which reduces the driving force for higher alcohol production.

(2) Higher alcohols are produced at copper–alkali interfaces. The copper–alkali interfacial area and hence the higher alcohol yields pass through a maximum as the promoter concentration is increased. This explanation is analogous to that suggested by Nunan *et al.* (*15*) to explain the effects of Cs loading on a Cu/ZnO alcohol synthesis catalyst in terms of bifunctional catalyst activity.

The surface areas of the unpromoted and promoted catalysts, before pretreatment, are presented in Table 1. Earlier work showed that the promoted $CuO/ZnO/Cr_2O_3$ catalyst lost very little surface area upon reduction in H_2/CO synthesis gas (*18*). Therefore, the surface ares in Table 1 indicate that the differences in the performance of the various catalysts are not the result of gross changes in total surface area upon promotion with alkali, but rather of changes in the character of the catalytic surface.

If methanol is converted to higher alcohols on alkali sites, addition of methanol to the CO + H_2 feed over the alkali-promoted catalyst would result in increased yields of higher alcohols and the effect would be exaggerated when high alkali loadings are used. This is not observed (Fig. 3), suggesting that the synthesis of both methanol and higher alcohols requires the same type of sites. The shapes of the promoter versus yield curves for methanol and higher alcohol synthesis in Fig. 4 are also very similar, showing maxima at the same promoter concentration. This is further evidence that the activity for CO conversion to both methanol and higher alcohols resides at alkali/copper interfaces.

Effects of Carbon Dioxide

The results presented in Fig. 2 show that addition of CO_2 to the feed enhances the yield of methanol substantially for the 0.5% K_2CO_3-promoted catalyst while depressing the yield of methanol over the 4% promoted catalyst. Subsequent experiments were conducted with different CO_2 concentrations over the unpromoted and the 0.5% promoted catalyst and the results are presented in Fig. 5. In the absence of CO_2 the methanol yield is higher for the 0.5% promoted catalyst than for the unpromoted catalyst. In the presence of CO_2, however, the trend is dramatically reversed. Although the difference for the 0% CO_2 data is small, a *t* test of these data comparing the mean methanol STYs for the unpromoted (average STY = 43.5 mmol/g/h and standard error, *s* = 1.4) and 0.5% promoted catalysts (average STY

TABLE 1

Surface Areas of K_2CO_3-Promoted $Cu/ZnO/Cr_2O_3$ Catalysts

K_2CO_3 Promoter concentration (wt%)	BET Surface area[a] (m^2/g)
0.0	62.7
0.5	71.5
1.0	77.5
4.0	74.8

[a] Unreduced catalyst.

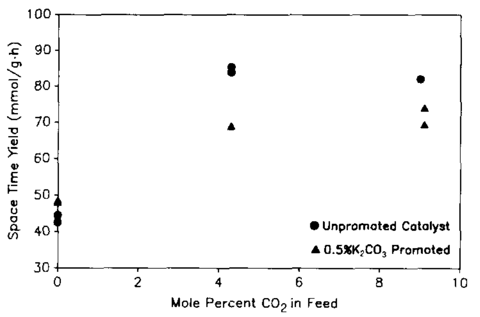

FIG. 5. Effect of CO_2 on yields of methanol over promoted and unpromoted catalysts (285°C, $(CO_2 + CO)/H_2 = 2/1$, 10 MPa).

= 47.6 mmol/g/h and s = 1.2) at 0% CO_2, confirmed the significance of the difference.

Liu and co-workers (*10, 19*) have suggested that both CO and CO_2 are converted to methanol, on different sites, and Jackson (*20*) has found evidence that CO and CO_2 are strongly adsorbed on different sites. With these studies in mind, the present results may indicate that alkali/copper interfacial sites are important in CO conversion while unpromoted copper is implicated in CO_2 hydrogenation. This view helps to reconcile a variety of apparently contradictory results reported in the literature. Catalysts with high copper loadings and no alkali promotion appear to favor CO_2 hydrogenation (*21–24*), while highly dispersed copper catalysts, or those promoted with alkali, are active for CO conversion (*5, 6*).

The results in Fig. 5 show that CO_2 addition results in a large increase in methanol yield over the unpromoted catalyst, presumably because there are a large number of copper sites active for CO_2 hydrogenation. The promoted catalyst is more active in the absence of CO_2 because alkali promotion increases the number of CO hydrogenation sites, i.e., copper/alkali interfaces. Addition of CO_2 results in only a modest increase in methanol yield over promoted catalysts because there are few alkali free sites to take advantage of the increased CO_2 concentration. In the extreme case of the 4% promoted catalyst, the promoter concentration is so large that the number of interfacial sites may be less than for the 1% or 0.5% promoted catalysts. Addition of CO_2 serves only to decrease the partial pressure of CO, thereby reducing the methanol yield. The activity of unpromoted catalyst for CO conversion is probably related to the basic properties of the ZnO phase. Klier *et al.* (*25*) have pointed out that the presence of surface hydroxyl, which is expected to be present on alkali or oxide surfaces, may assist in the production of the important formate intermediate from CO.

The effects of CO_2 on higher alcohol yields appear to be complicated, given the data of Fig. 3. Addition of CO_2 enhances the yield of higher alcohols in some cases and inhibits their formation in others. As with the methanol synthesis, however, CO_2 is clearly undesirable for the 4% K_2CO_3 catalyst. The results of further experiments, performed to determine the effect of a range of CO_2 concentrations on HAS yields over unpromoted and 0.5% promoted catalysts, are presented in Fig. 6. The most striking observation is that the higher alcohol yields pass through a distinct maximum over both catalysts as the CO_2 feed concentration is increased: an observation that has not been previously reported and bears a strong resemblance to the behavior of the methanol synthesis under the same operating conditions. These results may explain the apparent contradiction in the observations of

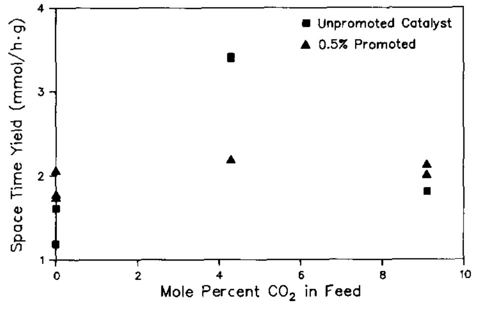

FIG. 6. Effect of CO_2 on yields of higher alcohols over promoted and unpromoted catalyst (285°C, $(CO_2 + CO)/H_2 = 2/1$, 10 MPa).

Tronconi *et al.* (*7*) and Elliot (*9*) regarding the retarding/promoting effects of CO_2 on the HAS. Furthermore, the superiority of alkali-promoted catalyst in the absence of CO_2, and the reversal of this trend at small concentrations of CO_2 are also strongly analogous to the behavior of methanol synthesis under the same conditions. The strong similarities between the behavior of the methanol and higher alcohol syntheses is taken as evidence for the participation of CO_2 in the HAS (since CO_2 is known to participate in the methanol synthesis). While copper/alkali interfacial sites convert CO to both methanol and higher alcohols, copper sites produce both products from CO_2. The suggestion that the synthesis of methanol and higher alcohols are related by common intermediates and/or catalytic sites has also been made by Elliot (*9*).

The cause of declining yields of methanol and higher alcohols at high concentrations of CO_2 is uncertain. Liu *et al.* (*19*) showed that water had a strong inhibiting effect on methanol production from $CO/CO_2/H_2$ feed while Vedage *et al.* (*26*) observed enhanced methanol yields when small amounts of water were added to a CO/H_2 feed. Vedage further showed that significant incorporation of deuterium into methanol occurred when D_2O was added to the feed. This was taken as evidence for the incorporation of D_2O-derived hydroxyl into the methanol product. It had earlier been suggested by Klier *et al.* (*27*) that strong CO_2 adsorption at sites active for CO conversion caused declining methanol yields at high CO_2 concentrations. Chinchen *et al.* (*28*) have shown that surface oxygen, produced by reaction of CO_2 with clean copper surfaces, enhances CO_2 adsorption capacity. However, this indicates that significant surface oxidation may occur in the presence of large CO_2 concentrations. Thus it appears that a small oxidizing potential in the gas phase is essential for optimum methanol activity. However, large oxidizing potential, manifested as surface oxygen, strongly adsorbed CO_2, or water has a deleterious effect on methanol yields. Since these species necessarily accompany one another, it is very difficult to distinguish which manifestation of oxygen actually produces the inhibiting effect. It is clear, however, that the HAS is inhibited under the same conditions which inhibit methanol production, the expected result if common sites and/or intermediates are involved in the two syntheses.

Effects of Methanol

When methanol is added to the feed gas the net yields of this species decrease because of the approach of methanol synthesis to equilibrium and the increased importance of the reverse reaction. This effect is quite marked as evidenced by the data in Fig. 2 and product inhibition, in addition to equilibrium constraints, has been proposed as an explanation of this phenomenon (*29*).

In CO_2 free synthesis gas, the addition of methanol to the feed did not increase HAS yields for conditions used to produce Fig. 3. This result is surprising in light of the findings of several workers that methanol is a direct precursor to intermediates involved in higher alcohol synthesis (*12–15*). Most studies of the HAS have been performed at relatively high conversions to maximize the selectivity to higher alcohols (*2, 4, 5, 8*). Under such conditions the methanol synthesis is typically close to equilibrium, so the methanol concentration cannot be manipulated as an independent variable.

Further experiments were performed with CO_2-free synthesis gas at high space velocities, and the results of these experiments are presented in Table 2. The results in Table 2A show the same trend of HAS yields decreasing as methanol concentration in the reactor increases. Two possible explanations of this behavior can be advanced:

(1) Methanol competes with other important intermediates for adsorption sites, thus acting as an inhibitor at high concentrations. For example, it is easy to derive a two-site Langmuir–Hinshelwood kinetic expression for production of higher alcohols from methanol which contains a term such as

TABLE 2

Effect of Methanol on Higher Alcohol Yields

GHSV (h^{-1})	Methanol		Higher alcohol STY (mmol/h/g)
	Feed (mol%)	Product (mol%)	
A. Catalyst: 0.5% K_2CO_3 promoted $Cu/ZnO/Cr_2O_3$, CO/H_2 = 2/1, pressure = 10.1 MPa, temperature = 285°C			
30000	0.0	2.93	1.72
30000	2.56	4.44	0.97
30000	5.26	6.59	0.88
20000	0.0	4.14	2.05
20000	1.88	4.92	1.57
B. Catalyst: 1.0% K_2CO_3 promoted $Cu/ZnO/Cr_2O_3$, CO/H_2 + 2/1, pressure = 10.1 MPa, temperature = 315°C			
30000	0.	2.14	3.18
30000	0.65	2.27	3.30
30000	2.26	3.24	3.45

$$P_M/(1 + AP_M)^2,$$

where P_M is the partial pressure of methanol and A is an adsorption equilibrium constant. This expression displays a maximum, the position of which is governed by the magnitude of the adsorption constant A. If A is large, the maximum occurs at a small value of P_M and the effect of adding methanol to the feed is depression of the HAS rate at all but very low methanol concentrations.

(2) If higher alcohols are formed from both methanol and CO in parallel paths (or methanol, CO, and CO_2), the relative abundance of sites active for these two species will determine the optimum feed composition. Strong adsorption of methanol at sites active for CO hydrogenation (as proposed in Natta's kinetic model of the methanol synthesis (*29*)) could cause an overall inhibition of higher alcohol synthesis rates at high methanol concentrations.

Both of these explanations would result in a complicated relationship between methanol concentrations and HAS yields, which underscores the need to explore the effects of a range of methanol concentrations. Very high concentrations of methanol were unattainable in the present work because of condensation problems in the reactor, but very low methanol concentrations were explored in a series of experiments performed at 315°C over a 1% K_2CO_3-promoted catalyst. The results of these experiments, presented in Table 2B, show that under some conditions modest enhancement of HAS rates are realized by adding methanol to the reactor feed. Adding methanol to CO_2-containing feeds appears to result in an enhancement of HAS yields under the conditions used to generate the data in Fig. 3. Further experiments produced the results shown in Table 3. At 285°C the effect of adding methanol to the feed is small for CO_2 containing gas (Table 3A) while at higher temperatures and low methanol concentrations, the HAS yields are enhanced by methanol addition.

Effects of Ethanol

The effect of adding ethanol to the feed on the rate of C_3^+ formation was also determined. Three runs were performed in sequence in which ethanol was added to the

TABLE 3

Effect of Methanol on Higher Alcohol Yield in $CO/CO_2/H_2$ Synthesis Gas over 0.5% K_2CO_3 Promoted $Cu/ZnO/Cr_2O_3$ Catalyst

GHSV (h^{-1})	Methanol		Higher alcohol STY (mmol/h/g)
	Feed (mol%)	Product (mol%)	
A. $(CO_2 + CO)/H_2$ = 0.58/0.32, pressure = 10.1 MPa, temperature = 285°C			
20000[a]	0.	6.56	2.12
20000[a]	1.92	7.25	2.22
20000[b]	0.0	6.07	2.18
20000[b]	1.81	6.73	2.20
B. $CO/CO_2/H_2$ = 0.399/0.055/0.490, pressure = 10.1 MPa, temperature = 315°C			
38000	0.	1.57	0.38
38000	0.92	1.92	0.42
38000	3.42	3.19	0.69

[a] CO/CO_2 = 0.49/0.09

[b] CO/CO_2 = 0.54/0.04

TABLE 4

Effect of Ethanol on Yield of C_3^+ Alcohols

Ethanol in feed (mol%)	Yield of C_3^+ alcohols (mmol/h/g)
0.48	1.97
0.0	0.80
0.50	1.95

Note. $CO/H_2 = 2/1$, GHSV = 20000 h^{-1}, pressure = 10.1 MPa, temperature = 285°C.

feed, removed, and then added again, and the higher alcohol yield (C_3^+) measured during each experiment. The results, presented in Table 4, show that higher alcohol production is significantly enhanced by addition of ethanol to the feed. This result supports the conclusions of other workers (*1*, *4*) that production of ethanol is the slow step in the series of events leading to higher alcohols and that subsequent conversion of ethanol to higher alcohols is kinetically favorable.

CONCLUSIONS

One of the most striking trends in the results presented in the present work is the analogous behavior of the methanol and higher alcohol syntheses. The observation that alkali promotes both methanol and higher alcohol production from $CO + H_2$ is consistent with the existence of common intermediates in the synthesis of methanol and higher alcohols from CO, on common copper/alkali interfacial sites.

The effects of CO_2 addition to the feed and the alkali–CO_2 interactions in the methanol and higher alcohol syntheses are very similar. This is taken as indirect evidence for the participation of CO_2 in the HAS, which has not been previously reported. It is therefore proposed that CO is converted to intermediates involved in both the methanol and higher alcohol syntheses at copper/alkali interfacial sites, while CO_2 is converted to intermediates involved with both methanol and higher alcohol synthesis on copper sites.

There is now direct evidence that both methanol (*12–15*) and CO (*13*, *14*) participate in higher alcohol formation. However, the kinetic effect of methanol on HAS yields is not straightforward, as evidenced by the methanol addition results presented here. Direct evidence has been presented by Liu *et al.* (*10*) that suggests that methanol is produced from both CO and CO_2 on different catalytic site. Indirect evidence from the present work indicates that CO_2 may also participate in the higher alcohol synthesis. If this is the case, higher alcohol production proceeds from three different carbon sources, on at least two different catalytic sites, which explains the apparent complexity of the kinetic observations of the present work.

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REFERENCES

1. Frolich, P. K., and Cryder, D. S., *Ind. Eng. Chem.* **22**(10), 1051 (1930).
2. Smith, K. J., and Anderson, R. B., *Can. J. Chem. Eng.* **61**, 40 (1983).
3. Vedage, G. A., Himelfarb, P., Simmons, G. W., and Klier, K., *Prepr. Div. Pet. Chem., ACS* **28**(5), 1261 (1983).
4. Smith, K. J., and Anderson, R. B., *J. Catal.* **85**, 428 (1984).
5. Vedage, G. A., Himmelfarb, P. B., Simmons, G. W., and Klier, K., "Solid State Chemistry in Catalysis," Vol. 279, p. 295. ACS Symp. Ser., 1985.
6. Sheffer, G. R., and King, T. S., *J. Catal.* **115**, 376 (1989).
7. Tronconi, E., Ferlazzo, N., Forzatti, P., and Pasquon, I., *Ind. Eng. Chem. Res.* **26**, 2122 (1987).
8. Ramaroson, E., Keiffer, R., and Kiennemann, A., *Appl. Catal.* **4**, 281 (1982).
9. Elliot, D. J., *J. Catal.* **111**, 445 (1988).
10. Liu, G., Willcox, D., Garland, M., and Kung, H. H., *J. Catal.* **96**, 251 (1985).
11. Brown Bourzutschky, J. A., Homs, N. and Bell, A. T., *J. Catal.* **124**, 73 (1990).
12. Calverley, E. M., Ph.D. thesis, McMaster University, 1990.
13. Calverley, E. M., Smith, K. J., to be submitted, J. Catal. 1991.

14. Elliot, D. J., and Pennella, F., *J. Catal.* **114,** 90 (1988).

15. Nunan, J. G., Bogdan, C. E., Klier, K., Smith K. J., Young, C. W., and Herman, R. G., *J. Catal.* **113,** 410 (1988).

16. Chernobrivets, V. L., Rusov, M. T., and Vlasenko, V. M., *Ukr. Khim. Zh.* **35**(6), 604 (1969).

17. Calverley, E. M. and Smith, K. J., *Ind. Eng. Chem. Res.*, submitted, 1991.

18. Calverley, E. M., and Anderson, R. B., *J. Catal.* **104,** 434 (1987).

19. Liu, G., Willcox, D., Garland, M., and Kung, H. H., *J. Catal.* **90,** 139 (1984).

20. Jackson, S. D., *J. Catal.* **115,** 247 (1989).

21. Chinchen, G. C., Denny, P. J., Parker, D. G., Short, G. D., Spencer, M. S., Waugh, K. C., Whan, D. A., *Prepr. Am. Chem. Soc. Div. Fuel Chem.* **29,** 178 (1974).

22. Chinchen, G. C., Denny, P. J., Parker, D. G., Spencer, and Whan, D. A., *Appl. Catal.* **30,** 333 (1987).

23. Friedrich, J. B., Young, D. J., and Wainwright, M. S., *J. Catal.* **80,** 1 (1983).

24. Friedrich, J. B., Young, D. J., and Wainwright, M. S., *J. Catal.* **80,** 14 (1983).

25. Klier, K., Herman, R. G., Nunan, J. G., Smith, K., J., Bogdan, C. E., Young, C. W., and Santiesteban, J. G., *in* "Methane Conversion" (D. M. Bibby, C. D. Chang, C. D., and S. Yuchak, Eds.). Elsevier, Amsterdam, 1988.

26. Vedage, G. A., Pitchai, R., Herman, R. G., and Klier, K., *in* "Proceedings, 8th International Congress on Catalysis Berlin, 1984" Vol. II, p. 47. Dechema, Frankfurt-am-Main, 1984.

27. Klier, K., Chatikavanij, V., Herman, R. G., and Simmons, G. W., *J. Catal.* **74,** 343 (1982).

28. Chinchen, G. C., Spencer, M. S., Waugh, K. C., and Whan, D. A., *J. Chem. Soc. Faraday Trans. I* **83,** 2193 (1987).

29. Natta, G., *in* "Catalysis (P. H. Emmett, Ed.), Vol. 3, Chap. 8. Reinhold, New York, 1955.