

Carbon–Carbon Bond Formation Pathways in CO Hydrogenation to Higher Alcohols

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Carbon–carbon bond formation pathways during CO hydrogenation to higher alcohols were studied on alkali-promoted Cu-based catalysts (K–CuMgCeO_x and Cs–Cu/ZnO/Al₂O₃) using ¹³CO/H₂/¹²CH₃OH reactants. C–C bonds in ethanol form via two pathways, direct reactions of ¹³CO and direct coupling of ¹²CH₃OH. On K–Cu_{0.5}Mg₅CeO_x, direct reactions of ¹³CO are the predominant pathway for the initial C–C bond steps. On Cs–Cu/ZnO/Al₂O₃, ethanol is predominantly formed via direct coupling of oxygen-containing C₁ intermediates derived from ¹²CH₃OH. Cs⁺ cations introduce a methanol-coupling pathway unavailable on catalysts without Cs⁺ promoter, leading to higher alcohol synthesis rates. After ethanol formation, additional chain growth occurs via aldol-type coupling pathways using C₁ intermediates derived from ¹²CH₃OH on both K–Cu_{0.5}Mg₅CeO_x and Cs–Cu/ZnO/Al₂O₃ catalysts. © 1999

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Key Words: CO hydrogenation; carbon–carbon bond formation; higher alcohol synthesis; Cu catalysts; isotopic tracers.

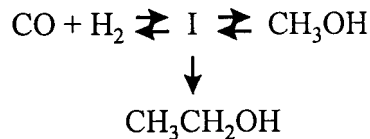
INTRODUCTION

Several studies of the reaction pathways required for the formation of initial carbon–carbon bonds during higher alcohol synthesis from CO/H₂ have been reported on unmodified and alkali-modified low-temperature methanol synthesis catalysts (1–3), but significant details of the mechanism remain unclear. Initial C–C bond formation pathways on these catalysts differ significantly from those on MgO-based Cu catalysts leading to similar higher alcohol products (4). Also, C–C bonds after ethanol synthesis appear to form in steps that follow the structural rules of base-catalyzed aldol condensation reactions on K–CuMgCeO_x catalysts using methanol-derived C₁ species for chain growth (4, 5).

Nunan *et al.* (1) and Elliot and Pennella (2) used isotopic tracers in order to probe the intermediate species involved in the formation of ethanol from CO/H₂ on Cs–Cu/ZnO and

Cu/ZnO/Al₂O₃ catalysts, respectively. ¹³CH₃OH–¹²CO/H₂ reactant mixtures on Cs–Cu/ZnO led to the formation of ethanol molecules with high ¹³C content (1). ¹³C NMR analysis confirmed that a large fraction of the ethanol formed was doubly labeled and that the minority singly labeled ethanol had the ¹³C atom distributed equally between the two carbon positions. Secondary reactions of primary methanol products lead to ethanol synthesis, and the role of CO appears to be limited to the formation of CH₃OH on Cs–Cu/ZnO catalysts. These results and subsequent theoretical studies of activation barriers for possible methanol coupling pathways led these authors to propose that initial C–C bond formation occurs via nucleophilic attack of formaldehyde by a methanol-derived surface formyl species on Cs⁺ (1).

In a similar study by Elliot and Pennella (2) on unpromoted Cu/ZnO/Al₂O₃ catalysts using ¹³CH₃OH/¹²CO/H₂, singly labeled, doubly labeled, and unlabeled ethanol were all detected among the initial reaction products, suggesting that both ¹²CO and ¹³CH₃OH participate in the synthesis of ethanol. The ¹³C content in ethanol (at very short bed residence times) depended on the ¹³CH₃OH partial pressure in the reactant mixture. For example, the ¹³C content in ethanol increased from 31.4 to 55.7% as the ¹³CH₃OH partial pressure in the feed increased from 4.0 to 10.7 kPa at a bed residence time of 0.49 s. Also, the ¹³C content in ethanol decreased with increasing bed residence time. They proposed that a surface bound C₁ species (I), formed from either synthesis gas or methanol, was an intermediate in the formation of ethanol.



Calverley and Smith (3) also found that both methanol and CO are incorporated directly into the ethanol product on Cu/ZnO catalysts. Namely, both methanol and CO are direct precursors to the C₁ species responsible for C–C bond formation in ethanol. The nonbinomial distribution of the

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ethanol ^{13}C isotopomers led the authors to conclude that reactions of two methanol-derived C_1 intermediates to form ethanol were slightly more probable than random combinations of C_1 species formed from CO and methanol with equal probability. They suggested that this may reflect the proximity of catalytic sites that activate CO and methanol.

Cu/ZnO and $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalysts unpromoted by alkali form small amounts of ethanol from CO/H_2 mixtures (1, 2). The addition of Cs^+ to Cu/ZnO (1, 6) or $\text{Cu}/\text{ZnO}/\text{Cr}_2\text{O}_3$ ($\text{Cu}/\text{Zn}/\text{Cr} = 38/54/8$ at.) (7) markedly increased the rate of formation of ethanol and higher alcohols. For example, at 548 K and 7.6 MPa with a H_2/CO ratio of 0.45, ethanol formation rates increased from 3.0 to 24.6 g/(kg_{cat}·h) with the addition of 4.0 wt% Cs^+ to $\text{Cu}/\text{ZnO}/\text{Cr}_2\text{O}_3$, whereas methanol formation rates increased only from 200 to 271 g/(kg_{cat}·h) (7). Alkali promotes methanol, ethanol, and higher alcohol synthesis reactions on Cu/ZnO ; the effectiveness of the alkali promoter increases in the order $\text{Cs} > \text{Rb} > \text{K} > \text{Na} \sim \text{Li}$ (6, 8). Minahan *et al.* (9) have also reported that Cs^+ is a better promoter than K^+ for higher alcohol synthesis on high-temperature $\text{ZnO}/\text{Cr}_2\text{O}_3$ catalysts. Addition of methanol to CO/H_2 reactant mixtures increased the rate of formation of ethanol and higher alcohols on Cs-promoted $\text{Cu}/\text{ZnO}/\text{Cr}_2\text{O}_3$ (7), but not on K-promoted $\text{Cu}/\text{ZnO}/\text{Cr}_2\text{O}_3$ (10) catalysts at reaction conditions far removed from methanol synthesis equilibrium. The higher ethanol formation rate may reflect a direct coupling reaction of methanol to form ethanol catalyzed by sites modified by the Cs^+ promoter. Alcohol chain growth probability increased with increasing Cs^+ concentration on $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalysts (11).

A recent report described the results of isotopic tracer studies of $^{12}\text{CH}_3\text{OH}/^{13}\text{CO}/\text{H}_2$ mixtures on $\text{K}-\text{Cu}_{0.5}\text{Mg}_5\text{CeO}_x$ catalysts (4). These catalysts are among the best reported catalysts for higher alcohol synthesis at low temperatures and pressures (4, 5, 11–13). Reactions of $^{12}\text{CH}_3\text{OH}/^{13}\text{CO}/\text{H}_2$ mixtures led to the formation of predominantly labeled ethanol at short residence times. Ethanol was formed from the ^{13}CO component in the reactant mixture, without significant involvement of the $^{12}\text{CH}_3\text{OH}$ present in the feed. In effect, $\text{K}-\text{Cu}_{0.5}\text{Mg}_5\text{CeO}_x$ materials do not catalyze direct coupling reactions of methanol that form C–C bonds. The ^{13}C content in ethanol decreases with increasing residence time because of reverse aldol reactions of higher alcohols. This process leads to products with lower isotopic purity because ethanol is formed from higher alcohols, which contain lower ^{13}C contents because of the significant involvement of $^{12}\text{CH}_3\text{OH}$ in the formation of C–C carbon bonds after the formation of the initial C–C bond in ethanol. The observed effects of residence time on the isotopomer distributions and on the rates of formation of ethanol, methyl formate, and methyl acetate are consistent with an intermediate role of methyl formate and methyl acetate in ethanol formation. Nucleophilic attack of surface

methyl formate (or formate) species by surface CH_3OCO^- species, formed by the reaction of CO and surface methoxide, appears to lead to the formation of the initial carbon-carbon bond on $\text{K}-\text{Cu}-\text{Mg}_5\text{CeO}_x$ catalysts (4).

In view of the subtle residence time effects that influence the isotopomer distribution on $\text{K}-\text{Cu}-\text{Mg}_5\text{CeO}_x$ catalysts (4), we have reexamined in this study the reaction pathways for the formation of higher alcohols from CO/H_2 , especially the chain-growth pathways from C_1 to C_2 alcohols, on Cs-modified $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ methanol synthesis catalysts. Our study attempts to resolve different mechanistic conclusions reached on $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$, Cs- Cu/ZnO , and $\text{K}-\text{Cu}_{0.5}\text{Mg}_5\text{CeO}_x$ by a detailed analysis of the chemical and isotopic composition of reaction products as a function of residence time and CO conversion.

EXPERIMENTAL METHODS

Isotopic tracer studies of alcohol synthesis pathways on Cs-promoted $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ were carried out using an equimolar mixture of ^{13}CO and H_2 . $^{12}\text{CH}_3\text{OH}$ was added in order to probe the respective roles of ^{13}CO and $^{12}\text{CH}_3\text{OH}$ in chain-growth pathways leading to the formation of ethanol and of higher alcohols from CO/H_2 mixtures. ^{13}CO depleted of ^{18}O (^{13}C : 99%, $^{18}\text{O} < 1\%$, Cambridge Isotope) was used as the labeled reactant because ^{18}O impurities in ^{13}C -labeled methanol normally interfere with the isotopic analyses of oxygen-containing reaction products. The catalysts were prepared by coprecipitation of Cu, Zn, and Al mixed nitrate solutions with an aqueous solution of KOH and K_2CO_3 at 338 K and constant pH of 9, as described in detail elsewhere (5, 12). The resulting material was filtered, thoroughly washed with deionized water, dried, and treated in flowing dry air at 623 K, followed by impregnation to incipient wetness of dried powders with an aqueous solution of cesium acetate. Copper surface areas were measured by N_2O decomposition on prerduced samples. Characterization data for Cs- $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ and $\text{K}-\text{Cu}_{0.5}\text{Mg}_5\text{CeO}_x$ are shown in Table 1. The preparation of the $\text{K}-\text{Cu}_{0.5}\text{Mg}_5\text{CeO}_x$ sample has been described previously (5).

TABLE 1

Catalyst Composition and BET and Copper Surface Areas

Sample	$K(\text{Cs})^a$	Cu (wt%)	BET area (m ² /g-cat)	Cu surface area (m ² /g-cat)	Cu ^b dispersion
$\text{Cu}_{0.5}\text{Mg}_5\text{CeO}_x$	1.0	7.7	147	11.4	0.14
$\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$	(2.9)	44	62	23.5	0.05

^aBulk composition measured by atomic absorption. Values in parentheses are for catalysts promoted with Cs instead of K.

^bDispersion calculated from the ratio of surface Cu (determined by N_2O decomposition at 363 K) to the total number of Cu atoms in the catalyst.

Isotopic tracer experiments were carried out at low temperatures (538 K) and low CO conversions (<1%). Reaction rates were first measured at 2.0 MPa at several space velocities [6000–24,000 cm³(¹³CO + H₂)/g-cat-h] using an equimolar mixture of ¹³CO and H₂ and 0.1 g catalyst. After these steady-state rate measurements, the H₂/¹³CO reactant mixture was routed through a saturator containing liquid ¹²CH₃OH at 294 K, and the chemical and isotopic compositions of reaction products were measured by gas chromatography and mass spectrometry at several space velocities and CO conversion levels. All inlet and outlet lines were heated to 363 K in order to prevent condensation of reactants and products. A syringe sample of the effluent stream was analyzed using a capillary column and mass spectrometric detection (Hewlett–Packard, Model 5890 II Plus GC; Hewlett–Packard, Model 5972 Mass Selective Detector). Reaction products were also condensed using a liquid nitrogen trap in order to accumulate the larger amounts required for accurate isotopic content measurements. Several aliquots from these samples were injected into the GC-MS system. The isotopic content in reactants and products was calculated from the measured mass spectra using a matrix deconvolution method that accounts for natural abundance ¹³C and for ion fragmentation kinetics (14).

RESULTS AND DISCUSSION

Under the conditions of our study (538 K, 2.0 MPa, and H₂/¹³CO = 1), the methanol equilibrium partial pressure was 86.6 kPa (15). The ¹²CH₃OH partial pressure present in the reactant mixture was 13.3 kPa, corresponding to a ¹²CH₃OH to ¹³CO molar ratio of 1:75. Isotopic tracer studies were carried out at CO conversions below 1%. Ethanol, 1-propanol, isobutanol (2-methyl-1-propanol), methyl formate, methyl acetate, and CO₂ were detected among the products formed from ¹²CH₃OH/¹³CO/H₂ mixtures on Cs-Cu/ZnO/Al₂O₃. Selectivities to methyl formate and methyl acetate were lower on Cs-Cu/ZnO/Al₂O₃ than those previously reported on K-Cu_{0.5}Mg₅CeO_x (4). On K-Cu_{0.5}Mg₅CeO_x, methyl acetate intermediates appear to be the initial products of C–C bond formation steps and the precursors to ethanol. Table 2 shows alcohol synthesis rates on 2.9 wt% Cs-Cu/ZnO/Al₂O₃ and 1.0 wt% K-Cu_{0.5}Mg₅CeO_x catalysts at 538 K and 2.0 MPa. Ethanol synthesis rates are much higher on 2.9 wt% Cs-Cu/ZnO/Al₂O₃ than on 1.0 wt% K-Cu_{0.5}Mg₅CeO_x catalysts, even though the rate of methanol formation is only 40% lower on the latter. The methanol concentration (including methanol added at a rate of 9.9×10^{-7} mol/g-s) in the effluent is about 12.5% lower on 1.0 wt% K-Cu_{0.5}Mg₅CeO_x than on 2.9 wt% Cs-Cu/ZnO/Al₂O₃ catalysts. The higher ethanol synthesis rates on Cs-Cu/ZnO/Al₂O₃ may reflect faster C–C bond formation rates or a slower rate of subsequent chain growth reactions. 1-Propanol and 2-methyl-1-propanol

TABLE 2

Rates of Alcohol Formation from ¹³CO/H₂/¹²CH₃OH Reactants on 2.9 wt% Cs-Cu/ZnO/Al₂O₃ and 1.0 wt% K-Cu_{0.5}Mg₅CeO_x Catalysts at a Bed Residence Time of 3.0 s (538 K, 2.0 MPa, ¹³CO/H₂/¹²CH₃OH = 100/100/1.3)

	2.9 wt% Cs-Cu/ZnO/Al ₂ O ₃		1.0 wt% K-Cu _{0.5} Mg ₅ CeO _x	
	r_1^a	r_2^b	r_1^a	r_2^b
Methanol	4.6×10^{-7} (2.0×10^{-8})		2.8×10^{-7} (2.4×10^{-8})	
Ethanol	1.1×10^{-7} (4.7×10^{-9})	1.6×10^{-7} (6.8×10^{-9})	7.0×10^{-9} (6.1×10^{-10})	1.0×10^{-8} (8.8×10^{-10})
1-Propanol	3.4×10^{-8} (1.4×10^{-9})		3.2×10^{-9} (2.8×10^{-10})	
Isobutanol	1.6×10^{-8} (6.8×10^{-10})		ND ^c	

^a Here, r_1 is the net rate of alcohol formation as mol/g-s. Values in parenthesis are in units of mol/m² Cu-s.

^b Here, r_2 is the overall rate of ethanol formation found by taking into account ethanol consumed in 1-propanol and isobutanol formation.

^c Not detected.

(isobutanol) synthesis rates, however, are also higher on Cs-Cu/ZnO/Al₂O₃ than on K-Cu_{0.5}Mg₅CeO_x at the low conversions of our study. Total rates of formation of ethanol (r_2 , in Table 2) are also much higher on Cs-Cu/ZnO/Al₂O₃ than on K-Cu_{0.5}Mg₅CeO_x. Thus, it appears that Cs-Cu/ZnO/Al₂O₃ catalysts provide an alternate and more effective pathway for the formation of the initial C–C bond.

Figure 1 shows the concentration of alcohol products as a function of bed residence time on 2.9 wt% Cs-Cu/ZnO/Al₂O₃. The bed residence time was calculated from the gas flow rate at reaction temperature and pressure and the total catalyst bed volume. The methanol concentration in the effluent, which includes any methanol added, increases with increasing bed residence time, because methanol synthesis equilibrium is not reached rapidly on 2.9 wt% Cs-Cu/ZnO/Al₂O₃ under these conditions. Ethanol concentrations increase linearly with residence time initially and then more slowly at longer bed residence times. This is consistent with a decrease in ethanol synthesis rates as bed residence time increases, as expected from an intermediate product that can undergo secondary reactions. 1-Propanol concentrations increase almost linearly with bed residence time. Isobutanol concentrations show a sigmoidal shape with an initial zero slope typical of a secondary reaction product formed by reactions of earlier intermediates, in this case by C₁ addition to ethanol and 1-propanol, as proposed earlier on Cs-Cu/ZnO/Al₂O₃ (11) and on K-Cu_{0.5}Mg₅CeO_x (4). Subsequent aldol condensation reactions of isobutanol are very slow because of steric effects and because isobutanol lacks the two α -hydrogens required for aldol-type chain-growth steps (5, 16).

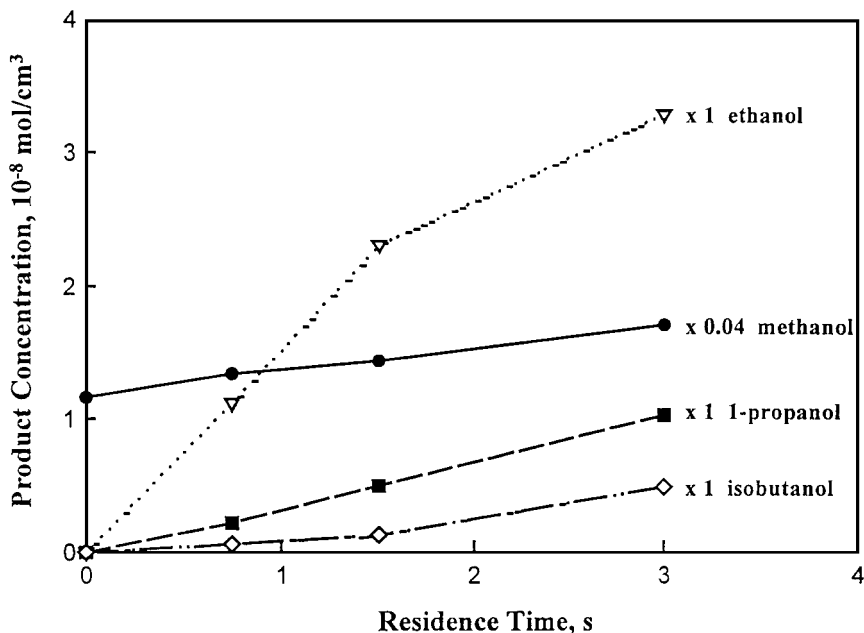


FIG. 1. Effect of bed residence time on product concentration for 2.9 wt% Cs-Cu/ZnO/Al₂O₃ (538 K, 2.0 MPa, ¹³CO/H₂/¹²CH₃OH = 100/100/1.3).

The ¹³C contents in CO, methanol, ethanol, and 1-propanol are shown in Fig. 2 as a function of bed residence time. The ¹³C distribution in the ethanol formed from ¹³CO/H₂/¹²CH₃OH mixtures is shown in Table 3. The ¹³C content in methanol increases with increasing bed residence time because hydrogenation of ¹³CO dilutes the initially unlabeled methanol with the ¹³CH₃OH formed. The ¹³C content in ethanol also increases with increasing bed res-

idence. Extrapolation of these data to zero bed residence time shows that the initial ethanol products contain about 14% ¹³C. Thus, ethanol is formed predominantly from two initially unlabeled methanol molecules on 2.9 wt% Cs-Cu/ZnO/Al₂O₃.

This behavior differs markedly from that of K-Cu_{0.5}Mg₅CeO_x (4) and Cu/ZnO/Al₂O₃ (2) catalysts, but it resembles that reported on Cs-promoted Cu/ZnO (1). On

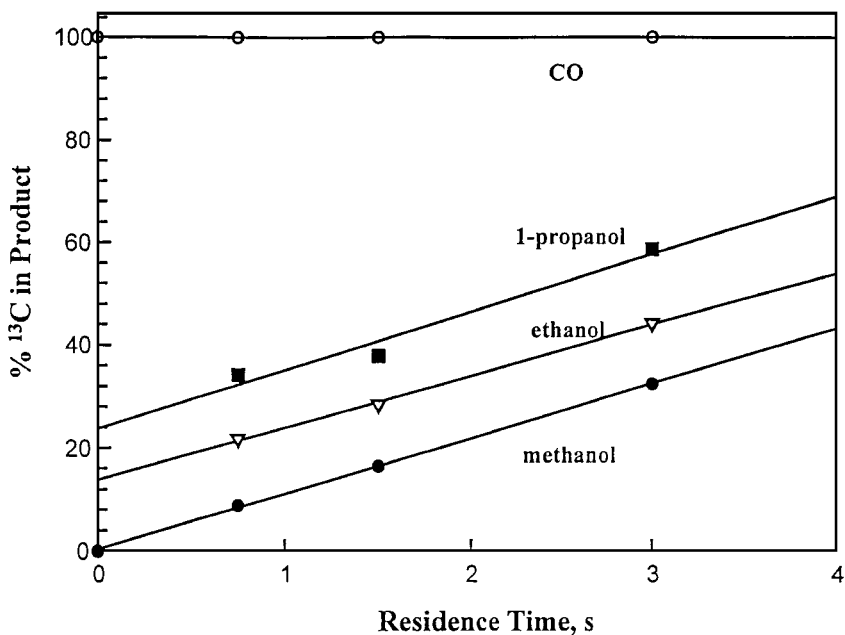


FIG. 2. Effect of bed residence time on product carbon-13 distribution for 2.9 wt% Cs-Cu/ZnO/Al₂O₃ (538 K, 2.0 MPa, ¹³CO/H₂/¹²CH₃OH = 100/100/1.3).

TABLE 3

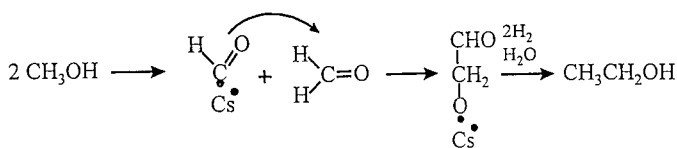
Isotopic Composition of Ethanol Formed from $^{13}\text{CO}/\text{H}_2/^{12}\text{CH}_3\text{OH}$ Reactants on 2.9 wt% Cs-Cu/ZnO/Al₂O₃ at Several Bed Residence Times (538 K, 2.0 MPa, $^{13}\text{CO}/\text{H}_2/^{12}\text{CH}_3\text{OH} = 100/100/1.3$) (Isotopomer Distributions in mol%)

Contact time (s):	0 ^a	0.75	1.5	3.0
$^{13}\text{CH}_3\text{-}^{13}\text{CH}_2\text{OH}$	1.8	7.6	11.0	22.6
$^{13}\text{CH}_3\text{-}^{12}\text{CH}_2\text{OH}$	8.0	9.6	12.8	15.9
$^{12}\text{CH}_3\text{-}^{13}\text{CH}_2\text{OH}$	16.5	18.8	22.6	27.2
$^{12}\text{CH}_3\text{-}^{12}\text{CH}_2\text{OH}$	73.7	64.0	53.6	34.2
Total ^{13}C content	14.0	21.8	28.7	44.1

^a Values were determined by extrapolating to zero bed residence time.

K-Cu_{0.5}Mg₅CeO_x, the ^{13}C content in the ethanol formed from the $^{13}\text{CO}/\text{H}_2/^{12}\text{CH}_3\text{OH}$ mixture was initially very high (90%) showing that ethanol was formed predominantly from ^{13}CO . The ^{13}C content in ethanol decreased with increasing bed residence time because of reverse aldol reactions of higher alcohols with lower ^{13}C content (4). On 1.0 wt% K-Cu_{0.5}Mg₅CeO_x, ethanol was formed predominantly by direct reactions of ^{13}CO leading initially to methyl acetate containing a methyl group from $^{12}\text{CH}_3\text{OH}$ and an acetate group from ^{13}CO . The hydrolysis of methyl acetate then leads to $^{12}\text{CH}_3\text{OH}$ and $^{13}\text{CH}_3^{13}\text{CH}_2\text{OH}$. On Cs-containing Cu/ZnO/Al₂O₃ catalysts, however, ethanol was formed predominantly via direct methanol coupling reactions, as proposed earlier on Cs-promoted Cu/ZnO (1, 8). These pathways involve nucleophilic attack of formaldehyde by adsorbed formyl species, with both species formed preferentially from methanol (Scheme 1). Cs⁺ is required to stabilize the required formyl species. K⁺, Zn²⁺, and Cu surface atoms are not able to stabilize the intermediates required for direct methanol-coupling pathways. Cs⁺ addition to Cu/ZnO/Al₂O₃ increases ethanol synthesis rates by introducing a direct methanol-coupling reaction pathway that is not available on catalysts without Cs⁺ promoters. Direct methanol-coupling pathways become less important on Cu/ZnO/Al₂O₃ (2) and K-Cu_{0.5}Mg₅CeO_x (4) and the slower pathways proceeding directly from ^{13}CO become detectable on these catalysts.

Ethanol is predominantly unlabeled (86% ^{12}C) at zero bed residence times on Cs-Cu/ZnO/Al₂O₃, and it forms via coupling reactions of methanol-derived C₁ species (Fig. 2), but it contains detectable amounts of ^{13}C (14%). A small fraction of the ethanol isotopomers (1.8% at zero residence



SCHEME 1

time) contain two ^{13}C -atoms, suggesting that they formed directly from ^{13}CO on Cs-Cu/ZnO/Al₂O₃, possibly via reaction pathways involving methyl acetate intermediates, as suggested earlier on K-Cu_{0.5}Mg₅CeO_x (4). The amount of singly labeled ethanol is about 24.5% at zero residence time (Table 3). The ^{13}C content is significantly higher at the 1-carbon position in ethanol than in the methyl group, suggesting that some of the singly labeled ethanol can form via direct carbonylation of methanol by ^{13}CO .

Direct coupling of methanol is the predominant ethanol synthesis pathway on Cs-Cu/ZnO/Al₂O₃, but some ethanol can also form directly from CO as proposed for 1.0 wt% K-Cu_{0.5}Mg₅CeO_x catalysts and from carbonylation of methanol by ^{13}CO . The ^{13}C content in methanol increases linearly with increasing bed residence time because ^{13}CO hydrogenation leads to the formation of labeled methanol (Fig. 2). The ^{13}C content in ethanol also increases linearly with increasing residence time. The *net* increase in ^{13}C content in ethanol with increasing bed residence time is very similar to that in methanol (Table 4), suggesting that ethanol forms directly from methanol or that both ethanol and methanol form from a common C₁ intermediate species. As discussed earlier, the latter has been ruled out by the predominant formation of unlabeled ethanol at zero bed residence time. Therefore, the *increased* ^{13}C content in ethanol with increasing bed residence time is a result of the direct reactions of methanol.

The observed differences in reaction pathways for initial C-C bond formation on Cs-promoted Cu/ZnO/Al₂O₃ and K-Cu_{0.5}Mg₅CeO_x may reflect the different basicity of the Cs and K oxides used as promoters. As mentioned earlier, Cs⁺ is a better promoter than K⁺ for higher alcohol synthesis (9). The addition of methanol to CO/H₂ reactants at conditions far removed from methanol synthesis equilibrium increased the synthesis rates of ethanol and of higher alcohols on Cs-Cu/ZnO/Cr₂O₃ (7) but not on K-Cu/ZnO/Cr₂O₃ (9). Cs⁺-O²⁻ cation-anion pairs appear to activate C-H bonds in formaldehyde to form surface

TABLE 4

Effect of Bed Residence Time on Product Carbon-13 Content on 2.9 wt% Cs-Cu/ZnO/Al₂O₃ at Several Bed Residence Times (538 K, 2.0 MPa, $^{13}\text{CO}/\text{H}_2/^{12}\text{CH}_3\text{OH} = 100/100/1.3$)

Contact time (s):	0 ^a	0.75	1.5	3.0
Methanol	0	8.8	16.4	32.5
Ethanol	14.0 (0)	21.7 (7.7)	28.4 (14.4)	44.2 (30.2)
1-Propanol	24.0 (0)	34.1 (10.1)	37.9 (13.9)	58.7 (34.7)

Note. Values in parentheses are the net increase in ^{13}C content with increasing bed residence time.

^a Values at zero bed residence time were determined by extrapolation (see Fig. 2).

Cs⁺(CHO⁻) species, as proposed earlier (1, 8), and these Cs-stabilized species form C–C bonds via nucleophilic reactions with formaldehyde formed in methanol dehydrogenation steps. In contrast, K⁺-O²⁻ and Zn²⁺-O²⁻ species may lack sufficiently basic anions (O²⁻) or acidic cations (K⁺) to cleave the strong C–H bonds in formaldehyde to form and stabilize surface K⁺(CHO⁻). An alternate possibility is that higher density of Cu surface sites on Cs-Cu/ZnO/Al₂O₃ (23.5 m² Cu/g, in Table 1) compared with that on K-Cu_{0.5}Mg₅CeO_x (11.4 m² Cu/g, in Table 1) leads to higher local concentrations of highly reactive and thermodynamically disfavored formaldehyde intermediates near the alkali oxides that can catalyze the formation of C–C bonds from two formaldehyde molecules.

The low ¹³C-content in the ethanol formed on Cs-Cu/ZnO/Al₂O₃ shows that methanol coupling proceeds much faster than on K-Cu_{0.5}Mg₅CeO_x, which forms C–C bonds via alternate and less effective pathways. As a result, overall ethanol synthesis rates are higher on Cs-Cu/ZnO/Al₂O₃ than on K-Cu_{0.5}Mg₅CeO_x. As discussed below, the synthesis of 1-propanol and isobutanol proceeds via sequential C₁ additions using ethanol on both types of catalysts (11, 17). Thus, the total rate of ethanol synthesis is best represented by the sum of the rates of formation of all higher alcohols. As shown in Table 2, the calculated rate of ethanol formation at a residence time of 3.0 s is about an order of magnitude greater on 2.9 wt% Cs-Cu/ZnO/Al₂O₃ (1.6 × 10⁻⁷ mol/g-s or 6.8 × 10⁻⁹ mol/m² Cu-s) than on 1.0 wt% K-Cu_{0.5}Mg₅CeO_x (1.0 × 10⁻⁸ mol/g-s or 8.8 × 10⁻¹⁰ mol/m² Cu-s).

On Cs-Cu/ZnO/Al₂O₃, the majority of ethanol forms via direct coupling of methanol and the rest from direct CO reactions and from methanol carbonylation by CO. Based on ¹³C contents in methanol and in ethanol isotopomers at a bed residence time of 3.0 s, the calculated rate of ethanol formation from direct methanol coupling (1.2 × 10⁻⁷ mol/g-s) is much greater than those from methanol carbonylation (2.5 × 10⁻⁸ mol/g-s) and from direct CO reactions (1.5 × 10⁻⁸ mol/g-s). On K-Cu_{0.5}Mg₅CeO_x, the rate of ethanol formation directly from CO, the major pathway, is about 7.5 × 10⁻⁹ mol/g-s. The rate of ethanol formation directly from ¹³CO per Cu surface area is similar on Cs-promoted Cu/ZnO/Al₂O₃ and K-Cu_{0.5}Mg₅CeO_x (6.4 × 10⁻¹⁰ mol/m² Cu-s vs 6.6 × 10⁻¹⁰ mol/m² Cu-s), suggesting that this pathway does not require the acid–base site pairs provided by Cs⁺-O²⁻ in Cs-containing catalysts and required for direct methanol coupling reactions. Since the presence of Cs⁺ enhances the rate of ethanol formation by introducing a methanol-coupling pathway, it is not surprising to observe the lower rate of ethanol formation and the decreased contribution of the methanol-coupling pathway on catalysts free of Cs⁺ (2, 6).

The ¹³C distribution in the 1-propanol formed from ¹³CO/H₂/¹²CH₃OH is shown in Table 5. As also found

TABLE 5

Isotopic Composition of 1-Propanol Formed from ¹³CO/H₂/¹²CH₃OH Reactants on 2.9 wt% Cs-Cu/ZnO/Al₂O₃ at Several Bed Residence Times (538 K, 2.0 MPa, ¹³CO/H₂/¹²CH₃OH = 100/100/1.3)

Contact time (s):	0.75	1.5	3.0
Number of ¹³ C	¹³ C (%)	¹³ C (%)	¹³ C (%)
0	37.5	30.6	10.8
1	35.5	37.1	30.9
2	12.9	21.0	29.2
3	14.1	11.4	29.1
Total ¹³ C content, experimental	34.5	37.8	58.9

for ethanol, 1-propanol products are predominantly unlabeled (76% ¹²C) at zero bed residence time (Fig. 2), suggesting that initial 1-propanol forms predominantly from methanol. The extent of the involvement of ¹³CO, however, is greater in 1-propanol formation (24% ¹³C in 1-propanol) than that in ethanol formation (14% ¹³C) because the ¹³C content in the required ethanol precursor is higher than in the other required reactant. Interestingly, the *net* increase in ¹³C content in 1-propanol with increasing bed residence time is similar to those in methanol and ethanol (Table 4), consistent with the mechanism in which 1-propanol forms via aldol-condensation reactions of methanol and ethanol (11, 17). The aldol condensation reactions between methanol and ethanol do not occur at zero bed residence time because they are secondary reactions. The increase in ¹³C content with increasing bed residence time results from the increased contribution from secondary aldol-condensation reactions. Carbonylation of C₂H₅OH by ¹³CO, which is also a secondary reaction, could also lead to an increase in ¹³C content in 1-propanol with increasing bed residence time. This reaction, if it occurs, is expected to give a higher net increase in ¹³C content in 1-propanol than in ethanol, inconsistent with the similar increase in ¹³C contents in 1-propanol and ethanol with increasing residence time (Table 4).

CONCLUSIONS

Two parallel pathways—reactions of CO to form methylacetate and coupling of methanol-derived C₁ intermediates—lead to the formation of the initial C–C bond in ethanol during reactions of CO/H₂ on alkali-promoted Cu-based catalysts for higher alcohol synthesis. Direct reaction of CO is the predominant pathway for ethanol formation on K-Cu_{0.5}Mg₅CeO_x, but the formation of C–C bonds in 1-propanol and isobutanol proceeds also via aldol condensation of ethanol-derived species with methanol-derived C₁ species. In contrast, C–C bonds in ethanol are

formed predominantly via a faster route involving the coupling of two methanol-derived C_1 species on Cs-promoted Cu/ZnO/Al₂O₃. The addition of Cs⁺ to Cu/ZnO/Al₂O₃ catalysts increases the rate of these synthesis pathways and the rate of formation of ethanol and of higher alcohols. On Cs-Cu/ZnO/Al₂O₃, subsequent chain growth from C₂ to C₃+ alcohols occurs predominantly via aldol condensation reactions involving methanol-derived C₁ intermediates and higher alcohols.

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