Journal of Catalysis **188,** 125–131 (1999)
Article ID jcat.1999.2650, available online at http://www.idealibrary.com on

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

Mingting Xu[1] and Enrique Iglesia[2]

Department of Chemical Engineering, University of California at Berkeley, Berkeley, California 94720

Received March 16, 1999; revised July 30, 1999; accepted July 30, 1999

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/Al$_2$O$_3$) using ^{13}CO/H$_2$/^{12}CH$_3$OH reactants. C–C bonds in ethanol form via two pathways, direct reactions of ^{13}CO and direct coupling of ^{12}CH$_3$OH. On K-Cu$_{0.5}$Mg$_5$CeO$_x$, direct reactions of ^{13}CO are the predominant pathway for the initial C–C bond steps. On Cs-Cu/ZnO/Al$_2$O$_3$, ethanol is predominantly formed via direct coupling of oxygen-containing C$_1$ intermediates derived from ^{12}CH$_3$OH. 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 C$_1$ intermediates derived from ^{12}CH$_3$OH on both K-Cu$_{0.5}$Mg$_5$CeO$_x$ and Cs-Cu/ZnO/Al$_2$O$_3$ catalysts. © 1999 **Academic Press**

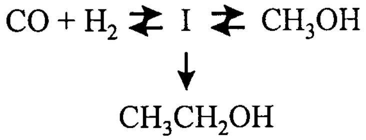
Key Words: **CO hydrogenation; carbon–carbon bond formation; higher alcohol synthesis; Cu catalysts; isotopic tracers.**

INTRODUCTION

Several studies of the reaction pathways required for the formation of initial carbon–carbon bonds during higher alcohol synthesis from CO/H$_2$ 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 C$_1$ 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/H$_2$ on Cs-Cu/ZnO and Cu/ZnO/Al$_2$O$_3$ catalysts, respectively. ^{13}CH$_3$OH–^{12}CO/H$_2$ reactant mixtures on Cs-Cu/ZnO led to the formation of ethanol molecules with high ^{13}C content (1). ^{13}C NMR analysis confirmed that a large fraction of the ethanol formed was doubly labeled and that the minority singly labeled ethanol had the ^{13}C 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 CH$_3$OH 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/Al$_2$O$_3$ catalysts using ^{13}CH$_3$OH/^{12}CO/H$_2$, singly labeled, doubly labeled, and unlabeled ethanol were all detected among the initial reaction products, suggesting that both ^{12}CO and ^{13}CH$_3$OH participate in the synthesis of ethanol. The ^{13}C content in ethanol (at very short bed residence times) depended on the ^{13}CH$_3$OH partial pressure in the reactant mixture. For example, the ^{13}C content in ethanol increased from 31.4 to 55.7% as the ^{13}CH$_3$OH partial pressure in the feed increased from 4.0 to 10.7 kPa at a bed residence time of 0.49 s. Also, the ^{13}C content in ethanol decreased with increasing bed residence time. They proposed that a surface bound C$_1$ species (I), formed from either synthesis gas or methanol, was an intermediate in the formation of ethanol.



$$\begin{array}{c} CO + H_2 \rightleftharpoons I \rightleftharpoons CH_3OH \\ \downarrow \\ CH_3CH_2OH \end{array}$$

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 C$_1$ species responsible for C–C bond formation in ethanol. The nonbinomial distribution of the

---

[1] Current address: Engelhard Corporation, Research Center, 101 Wood Avenue, Iselin, NJ 08830.

[2] To whom correspondence should be addressed. E-mail: iglesia@cchem.berkeley.edu. Fax: 1-510-642-4778.

0021-9517/99 $30.00

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 $Cu/ZnO/Al_2O_3$ 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 $Cu/ZnO/Cr_2O_3$ (Cu/Zn/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 $g/(kg_{cat} \cdot h)$ with the addition of 4.0 wt% Cs^+ to $Cu/ZnO/Cr_2O_3$, whereas methanol formation rates increased only from 200 to 271 $g/(kg_{cat} \cdot h)$ (7). Alkali promotes methanol, ethanol, and higher alcohol synthesis reactions on Cu/ZnO; the effectiveness of the alkali promoter increases in the order $Cs > Rb > K > Na \sim Li$ (6, 8). Minahan *et al.* (9) have also reported that Cs^+ is a better promoter than K^+ for higher alcohol synthesis on high-temperature ZnO/Cr_2O_3 catalysts. Addition of methanol to CO/H_2 reactant mixtures increased the rate of formation of ethanol and higher alcohols on Cs-promoted $Cu/ZnO/Cr_2O_3$ (7), but not on K-promoted $Cu/ZnO/Cr_2O_3$ (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 $Cu/ZnO/Al_2O_3$ catalysts (11).

A recent report described the results of isotopic tracer studies of $^{12}CH_3OH/^{13}CO/H_2$ mixtures on K-$Cu_{0.5}Mg_5CeO_x$ 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 $^{12}CH_3OH/^{13}CO/H_2$ 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 $^{12}CH_3OH$ present in the feed. In effect, K-$Cu_{0.5}Mg_5CeO_x$ 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 $^{12}CH_3OH$ 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 K-Cu-Mg_5CeO_x catalysts (4).

In view of the subtle residence time effects that influence the isotopomer distribution on K-Cu-Mg_5CeO_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 $Cu/ZnO/Al_2O_3$ methanol synthesis catalysts. Our study attempts to resolve different mechanistic conclusions reached on $Cu/ZnO/Al_2O_3$, Cs-Cu/ZnO, and K-$Cu_{0.5}Mg_5CeO_x$ 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 $Cu/ZnO/Al_2O_3$ were carried out using an equimolar mixture of ^{13}CO and H_2. $^{12}CH_3OH$ was added in order to probe the respective roles of ^{13}CO and $^{12}CH_3OH$ 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%, $^{18}O < 1\%$, 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 prereduced samples. Characterization data for Cs-$Cu/ZnO/Al_2O_3$ and K-$Cu_{0.5}Mg_5CeO_x$ are shown in Table 1. The preparation of the K-$Cu_{0.5}Mg_5CeO_x$ sample has been described previously (5).

TABLE 1

Catalyst Composition and BET and Copper Surface Areas

Sample	$K(Cs)^a$	Cu (wt%)	BET area (m^2/g-cat)	Cu surface area (m^2/g-cat)	Cu^b dispersion
$Cu_{0.5}Mg_5CeO_x$	1.0	7.7	147	11.4	0.14
$Cu/ZnO/Al_2O_3$	(2.9)	44	62	23.5	0.05

[a] Bulk composition measured by atomic absorption. Values in parentheses are for catalysts promoted with Cs instead of K.

[b] Dispersion 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 $cm^3(^{13}CO + H_2)$/g-cat-h] using an equimolar mixture of ^{13}CO and H_2 and 0.1 g catalyst. After these steady-state rate measurements, the $H_2/^{13}CO$ reactant mixture was routed through a saturator containing liquid $^{12}CH_3OH$ 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 ^{13}C and for ion fragmentation kinetics (14).

RESULTS AND DISCUSSION

Under the conditions of our study (538 K, 2.0 MPa, and $H_2/^{13}CO = 1$), the methanol equilibrium partial pressure was 86.6 kPa (15). The $^{12}CH_3OH$ partial pressure present in the reactant mixture was 13.3 kPa, corresponding to a $^{12}CH_3OH$ to ^{13}CO 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 CO_2 were detected among the products formed from $^{12}CH_3OH/^{13}CO/H_2$ mixtures on Cs-Cu/ZnO/Al_2O_3. Selectivities to methyl formate and methyl acetate were lower on Cs-Cu/ZnO/Al_2O_3 than those previously reported on K-$Cu_{0.5}Mg_5CeO_x$ (4). On K-$Cu_{0.5}Mg_5CeO_x$, 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/Al_2O_3 and 1.0 wt% K-$Cu_{0.5}Mg_5CeO_x$ catalysts at 538 K and 2.0 MPa. Ethanol synthesis rates are much higher on 2.9 wt% Cs-Cu/ZnO/Al_2O_3 than on 1.0 wt% K-$Cu_{0.5}Mg_5CeO_x$ 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-$Cu_{0.5}Mg_5CeO_x$ than on 2.9 wt% Cs-Cu/ZnO/Al_2O_3 catalysts. The higher ethanol synthesis rates on Cs-Cu/ZnO/Al_2O_3 may reflect faster C–C bond formation rates or a slower rate of subsequent chain growth reactions. 1-Propanol and 2-methyl-1-propanol (isobutanol) synthesis rates, however, are also higher on Cs-Cu/ZnO/Al_2O_3 than on K-$Cu_{0.5}Mg_5CeO_x$ 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/Al_2O_3 than on K-$Cu_{0.5}Mg_5CeO_x$. Thus, it appears that Cs-Cu/ZnO/Al_2O_3 catalysts provide an alternate and more effective pathway for the formation of the initial C–C bond.

TABLE 2

Rates of Alcohol Formation from $^{13}CO/H_2/^{12}CH_3OH$ Reactants on 2.9 wt% Cs-Cu/ZnO/Al_2O_3 and 1.0 wt% K-$Cu_{0.5}Mg_5CeO_x$ Catalysts at a Bed Residence Time of 3.0 s (538 K, 2.0 MPa, $^{13}CO/H_2/^{12}CH_3OH = 100/100/1.3$)

	2.9 wt% Cs-Cu/ZnO/Al_2O_3		1.0 wt% K-$Cu_{0.5}Mg_5CeO_x$	
	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/m^2 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.

Figure 1 shows the concentration of alcohol products as a function of bed residence time on 2.9 wt% Cs-Cu/ZnO/Al_2O_3. 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/Al_2O_3 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 C_1 addition to ethanol and 1-propanol, as proposed earlier on Cs-Cu/ZnO/Al_2O_3 (11) and on K-$Cu_{0.5}Mg_5CeO_x$ (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).

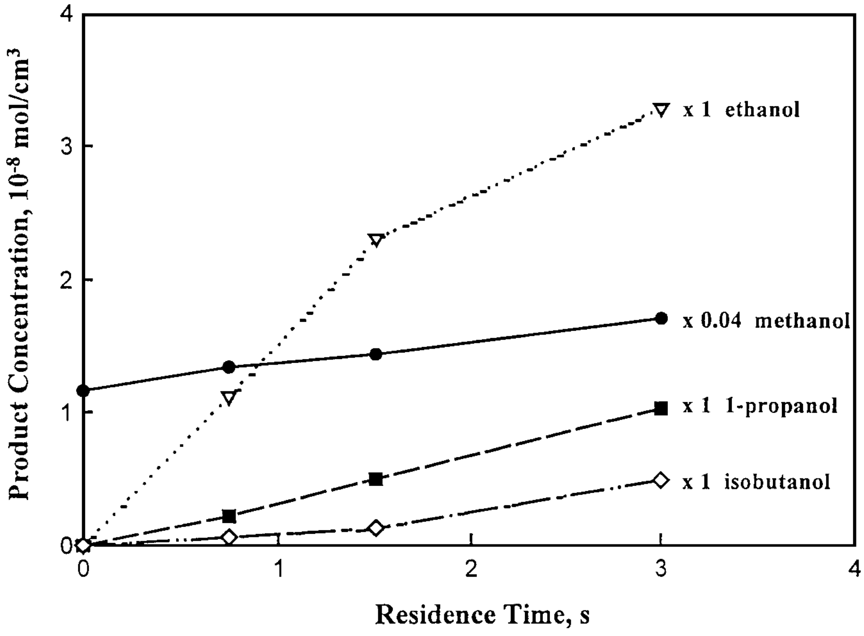


FIG. 1. Effect of bed residence time on product concentration for 2.9 wt% Cs-Cu/ZnO/Al_2O_3 (538 K, 2.0 MPa, $^{13}CO/H_2/^{12}CH_3OH = 100/100/1.3$).

The ^{13}C contents in CO, methanol, ethanol, and 1-propanol are shown in Fig. 2 as a function of bed residence time. The ^{13}C distribution in the ethanol formed from $^{13}CO/H_2/^{12}CH_3OH$ mixtures is shown in Table 3. The ^{13}C content in methanol increases with increasing bed residence time because hydrogenation of ^{13}CO dilutes the initially unlabeled methanol with the $^{13}CH_3OH$ formed. The ^{13}C content in ethanol also increases with increasing bed residence. Extrapolation of these data to zero bed residence time shows that the initial ethanol products contain about 14% ^{13}C. Thus, ethanol is formed predominantly from two initially unlabeled methanol molecules on 2.9 wt% Cs-Cu/ZnO/Al_2O_3.

This behavior differs markedly from that of K-$Cu_{0.5}Mg_5CeO_x$ (4) and Cu/ZnO/Al_2O_3 (2) catalysts, but it resembles that reported on Cs-promoted Cu/ZnO (1). On

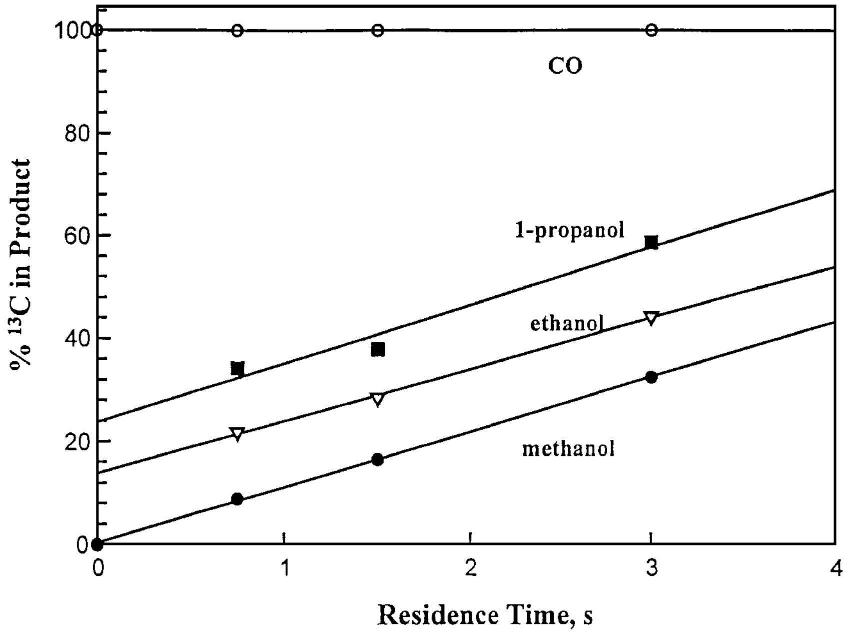


FIG. 2. Effect of bed residence time on product carbon-13 distribution for 2.9 wt% Cs-Cu/ZnO/Al_2O_3 (538 K, 2.0 MPa, $^{13}CO/H_2/^{12}CH_3OH =$ 100/100/1.3).

TABLE 3

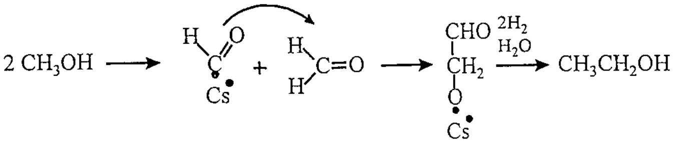
Isotopic Composition of Ethanol Formed from $^{13}CO/H_2/^{12}CH_3OH$ Reactants on 2.9 wt% Cs-Cu/ZnO/Al_2O_3 at Several Bed Residence Times (538 K, 2.0 MPa, $^{13}CO/H_2/^{12}CH_3OH$ = 100/100/1.3) (Isotopomer Distributions in mol%)

Contact time (s):	0^a	0.75	1.5	3.0
$^{13}CH_3$–$^{13}CH_2OH$	1.8	7.6	11.0	22.6
$^{13}CH_3$–$^{12}CH_2OH$	8.0	9.6	12.8	15.9
$^{12}CH_3$–$^{13}CH_2OH$	16.5	18.8	22.6	27.2
$^{12}CH_3$–$^{12}CH_2OH$	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-$Cu_{0.5}Mg_5CeO_x$, the ^{13}C content in the ethanol formed from the $^{13}CO/H_2/^{12}CH_3OH$ 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-$Cu_{0.5}Mg_5CeO_x$, ethanol was formed predominantly by direct reactions of ^{13}CO leading initially to methyl acetate containing a methyl group from $^{12}CH_3OH$ and an acetate group from ^{13}CO. The hydrolysis of methyl acetate then leads to $^{12}CH_3OH$ and $^{13}CH_3{}^{13}CH_2OH$. On Cs-containing Cu/ZnO/Al_2O_3 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^-, Zn^{+2}, and Cu surface atoms are not able to stabilize the intermediates required for direct methanol-coupling pathways. Cs^+ addition to Cu/ZnO/Al_2O_3 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/Al_2O_3 (2) and K-$Cu_{0.5}Mg_5CeO_x$ (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/Al_2O_3, and it forms via coupling reactions of methanol-derived C_1 species (Fig. 2), but it contains detectable amounts of ^{13}C (14%). A small fraction of the ethanol isotopomers (1.8% at zero residence time) contain two ^{13}C-atoms, suggesting that they formed directly from ^{13}CO on Cs-Cu/ZnO/Al_2O_3, possibly via reaction pathways involving methyl acetate intermediates, as suggested earlier on K-$Cu_{0.5}Mg_5CeO_x$ (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.



SCHEME 1

Direct coupling of methanol is the predominant ethanol synthesis pathway on Cs-Cu/ZnO/Al_2O_3, but some ethanol can also form directly from CO as proposed for 1.0 wt% K-$Cu_{0.5}Mg_5CeO_x$ 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 C_1 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/Al_2O_3 and K-$Cu_{0.5}Mg_5CeO_x$ 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/H_2 reactants at conditions far removed from methanol synthesis equilibrium increased the synthesis rates of ethanol and of higher alcohols on Cs-Cu/ZnO/Cr_2O_3 (7) but not on K-Cu/ZnO/Cr_2O_3 (9). Cs^+–O^{2-} 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/Al_2O_3 at Several Bed Residence Times (538 K, 2.0 MPa, $^{13}CO/H_2/^{12}CH_3OH$ = 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	21.7	28.4	44.2
	(0)	(7.7)	(14.4)	(30.2)
1-Propanol	24.0	34.1	37.9	58.7
	(0)	(10.1)	(13.9)	(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^+–O^{2-} and Zn^{2+}–O^{2-} species may lack sufficiently basic anions (O^{2-}) 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/Al_2O_3 (23.5 m^2 Cu/g, in Table 1) compared with that on K-$Cu_{0.5}Mg_5CeO_x$ (11.4 m^2 Cu/g, in Table 1) leads to higher local concentrations of highly reactive and thermodynamically unfavored formaldehyde intermediates near the alkali oxides that can catalyze the formation of C–C bonds from two formaldehyde molecules.

The low ^{13}C-content in the ethanol formed on Cs-Cu/ZnO/Al_2O_3 shows that methanol coupling proceeds much faster than on K-$Cu_{0.5}Mg_5CeO_x$, which forms C–C bonds via alternate and less effective pathways. As a result, overall ethanol synthesis rates are higher on Cs-Cu/ZnO/Al_2O_3 than on K-$Cu_{0.5}Mg_5CeO_x$. As discussed below, the synthesis of 1-propanol and isobutanol proceeds via sequential C_1 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/Al_2O_3 (1.6×10^{-7} mol/g-s or 6.8×10^{-9} mol/m^2 Cu-s) than on 1.0 wt% K-$Cu_{0.5}Mg_5CeO_x$ (1.0×10^{-8} mol/g-s or 8.8×10^{-10} mol/m^2 Cu-s).

On Cs-Cu/ZnO/Al_2O_3, 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 ^{13}C 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-$Cu_{0.5}Mg_5CeO_x$, 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 ^{13}CO per Cu surface area is similar on Cs-promoted Cu/ZnO/Al_2O_3 and K-$Cu_{0.5}Mg_5CeO_x$ (6.4×10^{-10} mol/m^2 Cu-s vs 6.6×10^{-10} mol/m^2 Cu-s), suggesting that this pathway does not require the acid–base site pairs provided by Cs^+–O^{2-} 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).

TABLE 5

Isotopic Composition of 1-Propanol Formed from $^{13}CO/H_2/^{12}CH_3OH$ Reactants on 2.9 wt% Cs-Cu/ZnO/Al_2O_3 at Several Bed Residence Times (538 K, 2.0 MPa, $^{13}CO/H_2/^{12}CH_3OH = 100/100/1.3$)

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

The ^{13}C distribution in the 1-propanol formed from $^{13}CO/H_2/^{12}CH_3OH$ is shown in Table 5. As also found for ethanol, 1-propanol products are predominantly unlabeled (76% ^{12}C) at zero bed residence time (Fig. 2), suggesting that initial 1-propanol forms predominantly from methanol. The extent of the involvement of ^{13}CO, however, is greater in 1-propanol formation (24% ^{13}C in 1-propanol) than that in ethanol formation (14% ^{13}C) because the ^{13}C content in the required ethanol precursor is higher than in the other required reactant. Interestingly, the *net* increase in ^{13}C 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 ^{13}C content with increasing bed residence time results from the increased contribution from secondary aldol-condensation reactions. Carbonylation of C_2H_5OH by ^{13}CO, which is also a secondary reaction, could also lead to an increase in ^{13}C content in 1-propanol with increasing bed residence time. This reaction, if it occurs, is expected to give a higher net increase in ^{13}C content in 1-propanol than in ethanol, inconsistent with the similar increase in ^{13}C 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 C_1 intermediates—lead to the formation of the initial C–C bond in ethanol during reactions of CO/H_2 on alkali-promoted Cu-based catalysts for higher alcohol synthesis. Direct reaction of CO is the predominant pathway for ethanol formation on K-$Cu_{0.5}Mg_5CeO_x$, but the formation of C–C bonds in 1-propanol and isobutanol proceeds also via aldol condensation of ethanol-derived species with methanol-derived C_1 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 $Cu/ZnO/Al_2O_3$. The addition of Cs^+ to $Cu/ZnO/Al_2O_3$ catalysts increases the rate of these synthesis pathways and the rate of formation of ethanol and of higher alcohols. On $Cs\text{-}Cu/ZnO/Al_2O_3$, subsequent chain growth from C_2 to C_3+ alcohols occurs predominantly via aldol condensation reactions involving methanol-derived C_1 intermediates and higher alcohols.

ACKNOWLEDGMENTS

This work was sponsored by the Division of Fossil Energy, U.S. Department of Energy, under contract DE-AC22-94PC94066. The authors thank Dr. Marcelo J.L. Gines for the synthesis and characterization of the catalysts used in this study.

REFERENCES

1. Nunan, J. G., Bogdan, C. E., Klier, K., Smith, K. J., Young, C. W., and Herman, R. G., *J. Catal.* **113**, 410 (1988).
2. Elliot, D. J., and Pennella, F. J., *J. Catal.* **114**, 90 (1988).
3. Calverley, E. M., and Smith, K. J., *Stud. Surface Sci. Catal.* **73**, 111 (1992).
4. Xu, M., and Iglesia, E., *Catal. Lett.* **51**, 47 (1998).
5. Xu, M., Gines, M. J. L., Hilmen, A.-M., Stephens, B. L., and Iglesia, E., *J. Catal.* **171**, 130 (1997).
6. Vedage, G. A., Himmelfarb, P. B., Simmons, G. W., and Klier, K., *ACS Symp. Ser.* **279**, 295 (1985).
7. Campos-Martin, J. M., Fierro, J. L. G., Guerrero-Ruiz, A., Herman, R. G., and Klier, K., *J. Catal.* **163**, 418 (1996).
8. Burcham, M. M., Herman, R. G., and Klier, K., *Ind. Eng. Chem. Res.* **37**, 4657 (1998).
9. Minahan, D. M., Epling, W. S., and Hoflund, G. B., *Appl. Catal.* **166**, 375 (1998).
10. Calverley, E. M., and Smith, K. J., *J. Catal.* **130**, 616 (1991).
11. Hilmen, A.-M., Xu, M., Gines, M. J. L., and Iglesia, E., *Appl. Catal.* **169**, 355 (1998).
12. Apesteguia, C. R., Soled, S. L., and Miseo, S., U.S. Patent 5,387,570, 1995. [Assigned to Exxon Research and Engineering Co.]
13. Apesteguia, C. R., DeRites, B., Miseo, S., and Soled, S. L., *Catal. Lett.* **44**, 1 (1997).
14. Price, G. L., and Iglesia, E., *Ind. Eng. Chem.* **28**, 839 (1989).
15. Thomas, W. J., and Portalski, S., *Ind. Eng. Chem.* **50**, 967 (1958).
16. Gines, M. J. L., and Iglesia, E., *J. Catal.* **176**, 155 (1998).
17. Gines, M. J. L., Oh, H.-S., Xu, M., Hilmen, A.-M., and Iglesia, E., *Stud. Surface Sci. Catal.* **119**, 509 (1998).