

Initial carbon–carbon bond formation during synthesis gas conversion to higher alcohols on K–Cu–Mg₅CeO_x catalysts

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Isotopic tracer studies of alcohol synthesis pathways using ¹³CO/H₂/¹²CH₃OH mixtures have shown that ethanol is formed predominantly by direct reactions of ¹³CO on Cu_{0.5}Mg₅CeO_x promoted with K at short residence times, without significant involvement of the ¹²CH₃OH present in the feed. The observed decrease in ¹³C content in ethanol with increasing residence time is caused by reverse aldol reactions of higher alcohols, which contain lower ¹³C contents because of the significant involvement of ¹²CH₃OH in their formation, and by reactions of methyl formate with ¹²CH₃OH-derived species. The effects of residence time on the ¹³C distribution within reaction products and on the rates of formation of ethanol, methyl formate, and methyl acetate are consistent with the intermediate role of methyl formate and methyl acetate in ethanol formation.

Keywords: alcohol synthesis, isotopic tracers, modified Cu catalysts, synthesis gas conversion, aldol condensation

1. Introduction

The formation of higher alcohols from synthesis gas (CO/H₂) has been widely studied, predominantly on alkali-modified methanol synthesis catalysts, but significant details about the reaction pathways involved in the formation of initial carbon–carbon bonds remain unresolved. Elliot and Pennella [1] and Nunan et al. [2] used isotopic tracer methods in order to identify the intermediate species involved in the formation of ethanol from CO/H₂ on Cu/ZnO/Al₂O₃ and on Cs-promoted Cu/ZnO catalysts.

The addition of ¹³C-labeled methanol to CO/H₂ feeds on Cs-promoted Cu/ZnO led to ethanol with substantial ¹³C content [2]. The concentration of injected methanol was much lower than the equilibrium methanol concentration at their reaction conditions. ¹³C NMR analysis of reaction products confirmed the presence of a large fraction of doubly-labeled ethanol and showed that the ¹³C atom in singly-labeled ethanol molecules was distributed with equal probability among the two carbon positions. These data led to the conclusion that secondary reactions of primary methanol products were the predominant and possibly exclusive pathways for the formation of ethanol. Nunan et al. [2] proposed that the initial C–C formation occurs by the nucleophilic attack of formaldehyde by an adsorbed formyl species on Cs⁺. Both formyl and formaldehyde species are believed to be formed from methanol.

A similar study on Cu/ZnO/Al₂O₃ was reported by Elliot and Pennella [1] at reaction conditions leading to very low conversions of CO and H₂. The experiments were carried out at conditions far removed from methanol synthesis

equilibrium in order to minimize isotopic contamination of ¹²CO by decomposition of ¹³CH₃OH. Both unlabeled and labeled ethanol were detected, even at very low conversions, suggesting that both ¹²CO and ¹³CH₃OH participate in the synthesis of ethanol. Calverley and Smith [3] also reported that both methanol and CO are direct precursors to the C₁ species that lead to ethanol formation on these catalysts. Our studies extend these previous studies by exploring reaction pathways for the formation of initial C–C bonds during synthesis gas conversion to higher alcohols on K–Cu–Mg₅CeO_x catalysts. K–Cu_{0.5}Mg₅CeO_x materials are among the most active and selective catalysts for the synthesis of isobutanol and other higher alcohols from CO/H₂ mixtures at low temperatures [4–6].

2. Experimental

Isotopic tracer studies of alcohol synthesis pathways were carried out on 1.0 wt% K–Cu_{0.5}Mg₅CeO_x catalysts using a mixture of ¹³CO/H₂ and ¹²CH₃OH in order to probe the roles of CO and methanol in chain growth pathways. These catalysts were prepared by co-precipitation synthesis procedures described in the literature [5,6]. ¹³CO (¹³C: 99%, ¹⁸O < 1%, Cambridge Isotope) was used as the labeled reactant because an ¹⁸O impurity typically present in ¹³C-labeled methanol complicates the isotopic analyses of reaction products.

Isotopic tracer experiments were carried out at low temperatures (538 K) in order to maintain low conversions. Reaction rates were first measured at 2.0 MPa and a gas hourly space velocity of 6000 cm³(CO + H₂)/(g-cat h) using an equimolar mixture of ¹³CO and H₂ and a 100 mg catalyst sample. After steady-state rate measurements, the

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equimolar $\text{H}_2/^{13}\text{CO}$ mixture was routed through a saturator containing liquid $^{12}\text{CH}_3\text{OH}$ at room temperature and isotopic tracer experiments were carried out at several space velocity and CO conversion levels. All inlets and effluent lines were heated to 363 K in order to prevent condensation of reactants and products. The effluent stream was analyzed by extracting a sample using a syringe and injecting it into a gas chromatograph-mass spectrometer system (Hewlett-Packard, model 5890 II plus GC; Hewlett-Packard, model 5972 mass selective detector). Reaction products were also trapped after the reactor using a tube cooled by liquid nitrogen. This method allowed the accumulation of larger amounts of products for the multiple GC-MS analyses required to increase the accuracy of isotopic content measurements. The ^{13}C content in reactants and products was calculated from mass spectra using a matrix deconvolution method that accounts for natural abundance ^{13}C and for mass fragmentation kinetics [7]. Similar analyses of the smaller fragments of molecular ionization processes were used to determine the location of ^{13}C atoms in labeled reaction products.

3. Results and discussion

At the conditions of our study (538 K, 2.0 MPa, and $\text{H}_2/^{13}\text{CO} = 1$) the equilibrium partial pressure of methanol is 86.6 kPa [8]. The partial pressure of $^{12}\text{CH}_3\text{OH}$ in the feed was 13.3 kPa; and the ratio of $^{12}\text{CH}_3\text{OH}$ to ^{13}CO was 1:75. All experiments were carried out at CO conversions below 1%. The most abundant reaction products were $^{13}\text{CH}_3\text{OH}$ and $^{13}\text{CO}_2$. Ethanol, 1-propanol, isobutanol, methyl formate, and methyl acetate were also detected and their concentrations in the effluent stream and their formation rates as a function of bed residence time are shown in figures 1 and 2. The bed residence time is calculated using the gas volumetric flow rate at reaction temperature and pressure and the catalyst bed volume.

Ethanol and 1-propanol concentrations in the reactor effluent increased with increasing bed residence time (figure 1), suggesting that neither reaction product approaches thermodynamic equilibrium. The increase in the rates of ethanol and 1-propanol formation with increasing residence time suggests that these products are formed in secondary reactions (figure 2). Both methyl formate and methyl acetate, however, reached a maximum concentration with increasing residence time (figure 1), indicating that they are reaction intermediates or that primary reactions leading to their formation approach thermodynamic equilibrium. In either case, formation rates of methyl formate and methyl acetate would decrease as residence time increases, as observed experimentally (figure 2).

^{13}C contents as a function of bed residence time are shown in figure 3 for each alcohol product detected. The ^{13}C content in methanol increases with increasing bed residence time because ^{13}CO hydrogenation leads to the formation of labeled methanol. The ^{13}C content in ethanol

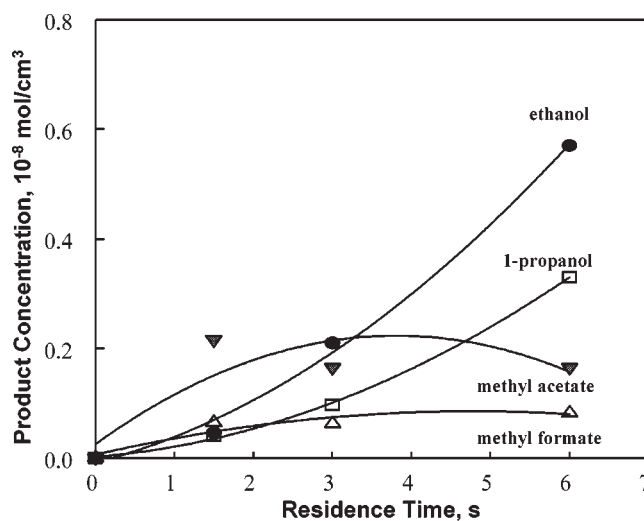


Figure 1. Effect of bed residence time on product concentration for 1.0 wt% $\text{K-Cu}_{0.5}\text{Mg}_5\text{CeO}_x$. (538 K, 2.0 MPa, $^{13}\text{CO}/\text{H}_2/\text{CH}_3\text{OH} = 100/100/1.3$.)

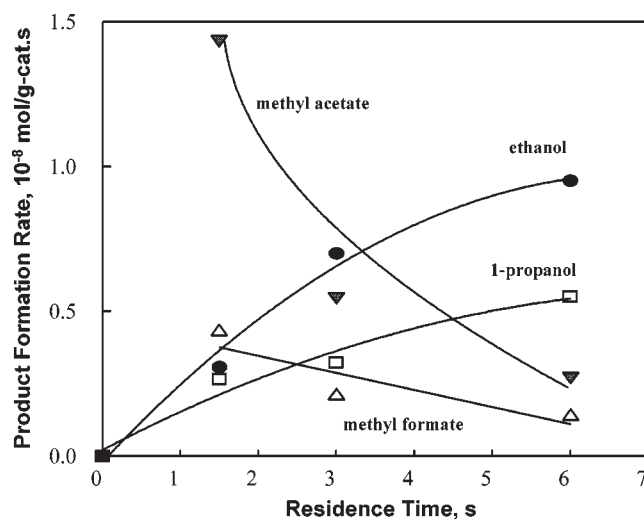


Figure 2. Effect of bed residence time on product formation rate for 1.0 wt% $\text{K-Cu}_{0.5}\text{Mg}_5\text{CeO}_x$. (538 K, 2.0 MPa, $^{13}\text{CO}/\text{H}_2/\text{CH}_3\text{OH} = 100/100/1.3$.)

decreases with increasing bed residence; extrapolation of the ethanol isotopic content to zero residence time shows that the initial ethanol product is predominantly labeled (94% ^{13}C). Thus, ethanol is formed predominantly by direct reactions of ^{13}CO without significant involvement of the $^{12}\text{CH}_3\text{OH}$ present in the feed, at least at our experimental conditions for a $^{13}\text{CO}/^{12}\text{CH}_3\text{OH}$ ratio of 75 in the reactant mixture.

At longer residence times, ethanol is also formed by reverse aldol reactions of higher alcohols after keto-enol isomerization of surface intermediates formed in condensation steps, as described in the scheme below. As a result, the ^{13}C content in ethanol decreases because of the significant involvement of $^{12}\text{CH}_3\text{OH}$ in the formation of C_2 +aldol species. This reverse aldol reaction leads to the observed decrease in ^{13}C content in ethanol with increasing

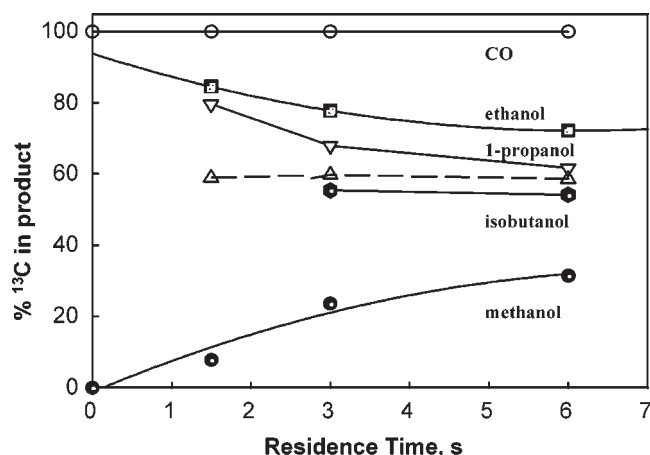


Figure 3. Effect of bed residence time on product carbon-13 distribution for 1.0 wt% K-Cu_{0.5}Mg₅CeO_x. (538 K, 2.0 MPa, ¹³CO/H₂/CH₃OH = 100/100/1.3.)

residence time. Indeed, ¹³C contents in 1-propanol and 2-methyl-1-propanol (isobutanol) are significantly lower than in ethanol. This is consistent with synthesis pathways involving condensation reactions of ethanol and methanol, leading to the formation of 1-propanol and 2-methyl-1-propanol [6]. The detailed pathways mechanism for reverse aldol-condensation reactions that lead to the decrease in the ¹³C content in ethanol as bed residence time increases are shown in scheme 1.

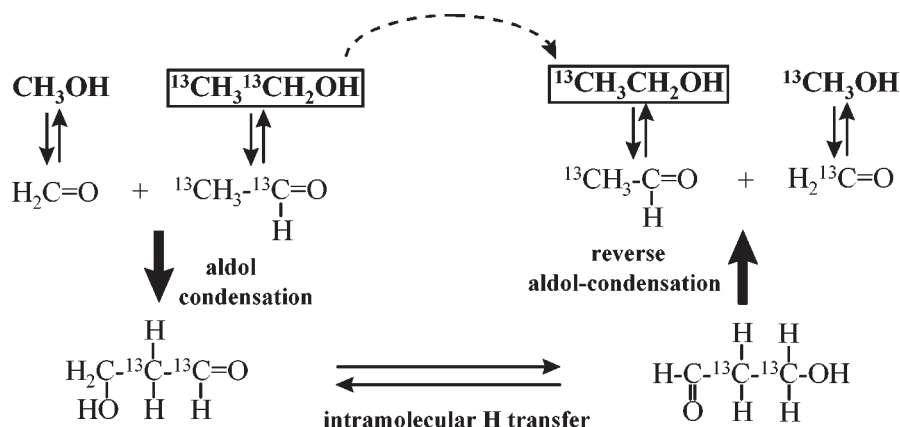
The ¹³C content in 1-propanol calculated by assuming that it formed exclusively via ethanol addition to ethanol in aldol-condensation steps (dashed line in figure 3) is, however, lower than the values measured. This indicates that one pathway for ethanol to 1-propanol chain growth involves carbonylation of C₂H₅OH by ¹³CO. Some of the 1-propanol may form by linear chain growth pathways that also lead to the formation of some 1-butanol during CO hydrogenation on K-Cu_{0.5}Mg₅CeO_x [9]. These pathways may involve the intermediate formation of methyl propionate in pathways similar to those discussed below for the formation of ethanol products. A large fraction of the 1-propanol forms, however, via aldol-condensation reac-

Table 1
Isotopic composition of methyl formate formed from ¹³CO/¹²CH₃OH/H₂ reactants on 1.0 wt% K-Cu_{0.5}Mg₅CeO_x at bed residence times of 1.5, 3.0 and 6.0 s (538 K, 2.0 MPa, ¹³CO/H₂/CH₃OH = 100/100/1.3).

	¹³ C (%)		
	1.5 s	3.0 s	6.0 s
H- ¹³ CO-O- ¹³ CH ₃	7.8	21.7	29.5
H- ¹³ CO-O- ¹² CH ₃	88.9	68.3	60.7
H- ¹² CO-O- ¹³ CH ₃	3.3	4.8	4.4
H- ¹² CO-O- ¹² CH ₃	0	5.2	5.4
Total ¹³ C content	52.3	55.9	59.9

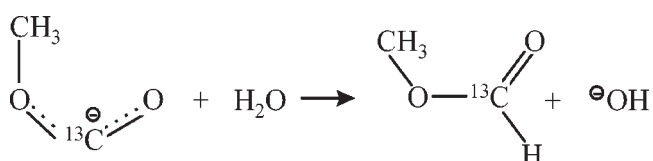
tions of ethanol with methanol; these pathways are unavailable for ethanol formation from two methanol molecules, because methanol molecules lack the two α-hydrogens required for aldol-type condensation pathways.

In addition to labeled higher alcohols, methyl formate and methyl acetate with significant ¹³C enrichment were also formed. The ¹³C content and the isotopic distribution in methyl formate are reported in table 1 at several values of residence time. The methyl formate products at short residence time (1.5 s) are mainly singly-labeled (90%), with about 95% ¹³C at the carbonyl carbon atom for the singly-labeled methyl formate. Methyl formate has been shown to form by reactions of methanol with CO on basic catalysts [2]. Our results are consistent with nucleophilic attack on ¹³CO by the oxygen atom in ¹²CH₃OH, leading to the predominant presence of ¹²C in the methyl group of methyl formate. The ¹³C content in the methyl group of methyl formate increases with increasing bed residence time, because the required methanol reactant acquires increasing amounts of ¹³C via ¹³CO hydrogenation. The ¹³C content in the carbonyl group remains high because CO retains its high isotopic purity throughout the entire range of residence time. As discussed below, reactions involving methyl formate or related surface precursors, such as CH₃O*CO⁻, may lead to the initial C-C bond formation during the synthesis of ethanol from H₂-CO mixtures. C-C bond formation, however, requires the isomerization of methyl formate, a step with a significant activation barrier [2].



Scheme 1.

At short residence times and low CO conversion levels, gas phase methanol and any surface intermediates derived from methanol are predominantly unlabeled. CO insertion into surface methoxide species could lead to an intermediate species ($\text{CH}_3\text{O}^*\text{CO}^-$) stabilized by alkali cations present in alkali-modified basic oxides [10]. Theoretical studies carried out by Klier et al. [11] show that nucleophilic attack of CO by surface methoxide species is an exothermic reaction without a significant activation barrier. These intermediates ($\text{CH}_3\text{O}^*\text{CO}^-$) lead to either methanol via hydrogenation reactions, as suggested for surface formate species [12–14] or to methyl formate with labeled ^{13}C predominantly in the carbonyl group via the following hydrolysis reactions [10]:



In addition to hydrogenation and hydrolysis reactions, surface $\text{CH}_3\text{O}^*\text{CO}^-$ species can also undergo isomerization reactions leading to acetate species that contain the initial carbon–carbon bond. Hydrolysis of these surface acetate species followed by esterification reaction with methanol can lead to methyl acetate. As mentioned earlier, methyl acetate production goes through a maximum with increasing bed residence time, suggesting that it is a reaction intermediate and the hydrogenolysis of which could form ethanol. Unlike the hydrolysis reactions of $\text{CH}_3\text{O}^*\text{CO}^-$, which are exothermic and require no activation energy, theoretical calculations show that isomerization of surface $\text{CH}_3\text{O}^*\text{CO}^-$ (via methyl shift) to $\text{CH}_3^*\text{COO}^-$ (acetate) on alkali cations, however, requires a very high activation energy [2]. Therefore, the formation of surface acetate species and the hydrogenolysis of such species to form ethanol are unlikely to occur. In addition, such pathways would predict the initial formation of ethanol molecules with a single ^{13}C atom at the 1-position. Our data show that the initial ethanol molecules formed are predominantly doubly-labeled (figure 3). At short residence times, doubly-labeled methyl acetate is also the predominant species and ^{13}C atoms are located in the $\text{CH}_3\text{--CO}$ group (table 2). Therefore, isomerization of surface methyl formate species cannot account for the formation of carbon–carbon bonds in either methyl acetate (table 2) or ethanol (table 3) on $\text{K--Cu--Mg}_5\text{CeO}_x$ catalysts.

The isotopic composition of methyl acetate is consistent with the pathways shown in figure 4, where M^+ represents coordinatively unsaturated cations, such as K^+ and Mg^{2+} . The nucleophilic attack of surface methyl formate (or formate) species containing ^{13}C in the carbonyl group by surface $\text{CH}_3\text{O}^*\text{CO}^-$ (or formate) species leads to the formation of the initial C–C bond (steps I and II, figure 4). Methyl formate ions could also react with surface formaldehyde species derived from methanol to form a singly-labeled carbon–carbon moiety (step III). Formaldehyde addition pathways lead to the observed formation

Table 2
Isotopic composition of methyl acetate formed from $^{13}\text{CO}/^{12}\text{CH}_3\text{OH}/\text{H}_2$ reactants on 1.0 wt% $\text{K--Cu}_{0.5}\text{Mg}_5\text{CeO}_x$ at bed residence times of 1.5, 3.0 and 6.0 s (538 K, 2.0 MPa, $^{13}\text{CO}/\text{H}_2/\text{CH}_3\text{OH} = 100/100/1.3$).

	^{13}C (%)		
	1.5 s	3.0 s	6.0 s
$^{13}\text{CH}_3\text{--}^{13}\text{CO--O--}^{13}\text{CH}_3$	5.5	15.8	26.8
$^{13}\text{CH}_3\text{--}^{12}\text{CO--O--}^{13}\text{CH}_3$	0.5	6.4	11.6
$^{12}\text{CH}_3\text{--}^{13}\text{CO--O--}^{13}\text{CH}_3$			
$^{13}\text{CH}_3\text{--}^{13}\text{CO--O--}^{12}\text{CH}_3$	63.1	51.5	42.8
$^{13}\text{CH}_3\text{--}^{12}\text{CO--O--}^{12}\text{CH}_3$	23.1	17.8	11.1
$^{12}\text{CH}_3\text{--}^{13}\text{CO--O--}^{12}\text{CH}_3$			
$^{12}\text{CH}_3\text{--}^{12}\text{CO--O--}^{13}\text{CH}_3$	1.4	2.8	7.7
$^{12}\text{CH}_3\text{--}^{12}\text{CO--O--}^{12}\text{CH}_3$	6.6	5.6	0
Total ^{13}C content	56.2	60.6	69.3

of $^{12}\text{CH}_3^{13}\text{CH}_2\text{OH}$, the concentration of which increases with increasing residence time. These pathways appear to involve reactions of methanol that increase in conversion with increasing residence time and account, in part, for the observed increase in $^{12}\text{CH}_3^{13}\text{CH}_2\text{OH}$ concentration with increasing residence time. Aldol self-condensation reactions of formaldehyde derived from methanol, as suggested by Klier et al. [2], would lead only to an unlabeled carbon–carbon moiety. Since most carbon–carbon moieties in ethanol and methyl acetate are doubly-labeled, reaction pathways I and II are most likely to occur. Hydrogenation of these surface oxygenated species leads to the formation of methyl acetate species that can desorb from the surface or undergo hydrogenolysis to form ethanol and methanol at the high hydrogen pressures typical of higher alcohol synthesis.

The hydrogenolysis of surface formate leads to the formation of methanol on methanol synthesis catalysts [12–14]. A similar type of reaction would lead to ethanol and methanol via hydrogenolysis of methyl acetate. This is consistent with the observed similarity between the ^{13}C content and distribution in the CH_3CO group within methyl acetate (table 2) and in the ethanol product of $^{13}\text{CO}/^{12}\text{CH}_3\text{OH}/\text{H}_2$ reactions (table 3). At short bed residence times, both carbon atoms in the C–C group of methyl acetate and ethanol are predominantly labeled (tables 2 and 3). The effects of residence time on the rate and selectivity for the formation of ethanol, methyl formate, and methyl acetate are consistent with the intermediate role of methyl formate in the formation of methyl acetate and with a subsequent role of the methyl acetate in the formation of ethanol during CO hydrogenation. Ethanol formation rates increase with increasing residence time, while formation rates for methyl acetate and methyl formate are only weakly affected. If ethanol were a precursor to methyl acetate, methyl acetate formation rates would increase as ethanol formation rate increases. Our experimental results show that methyl acetate is a likely precursor to ethanol. It is also possible that ethanol and methyl acetate are formed from a similar precursor, the concentration of which increases with increasing residence time. The rate of formation of methyl acetate goes through a maximum with increasing residence time,

Table 3
Isotopic composition of ethanol formed from $^{13}\text{CO}/^{12}\text{CH}_3\text{OH}/\text{H}_2$ reactants on 1.0 wt% K–Cu_{0.5}Mg₅CeO_x at bed residence times of 1.5, 3.0 and 6.0 s (538 K, 2.0 MPa, $^{13}\text{CO}/\text{H}_2/\text{CH}_3\text{OH} = 100/100/1.3$).

	^{13}C (%)					
	1.5 s		3.0 s		6.0 s	
	Expt.	Predicted ^a	Expt.	Predicted ^a	Expt.	Predicted ^a
$^{13}\text{CH}_3\text{--}^{13}\text{CH}_2\text{OH}$	77.0	68.6	63.1	67.3	57.0	69.6
$^{13}\text{CH}_3\text{--}^{12}\text{CH}_2\text{OH}$	4.6	23.6 ^b	9.8	24.2 ^b	11.8	22.7 ^b
$^{12}\text{CH}_3\text{--}^{13}\text{CH}_2\text{OH}$	10.4		16.5		19.2	
$^{12}\text{CH}_3\text{--}^{12}\text{CH}_2\text{OH}$	8.0	8.0	10.6	8.4	12.0	7.7
Total ^{13}C content	84.5		76.3		72.5	

^a Predicted values if ethanol formed from methyl acetate.

^b Percentage of singly-labeled ethanol with ^{13}C in either carbon group (methylacetate isotopomers leading to individual ethanol isotopomers cannot be distinguished by mass spectrometry).

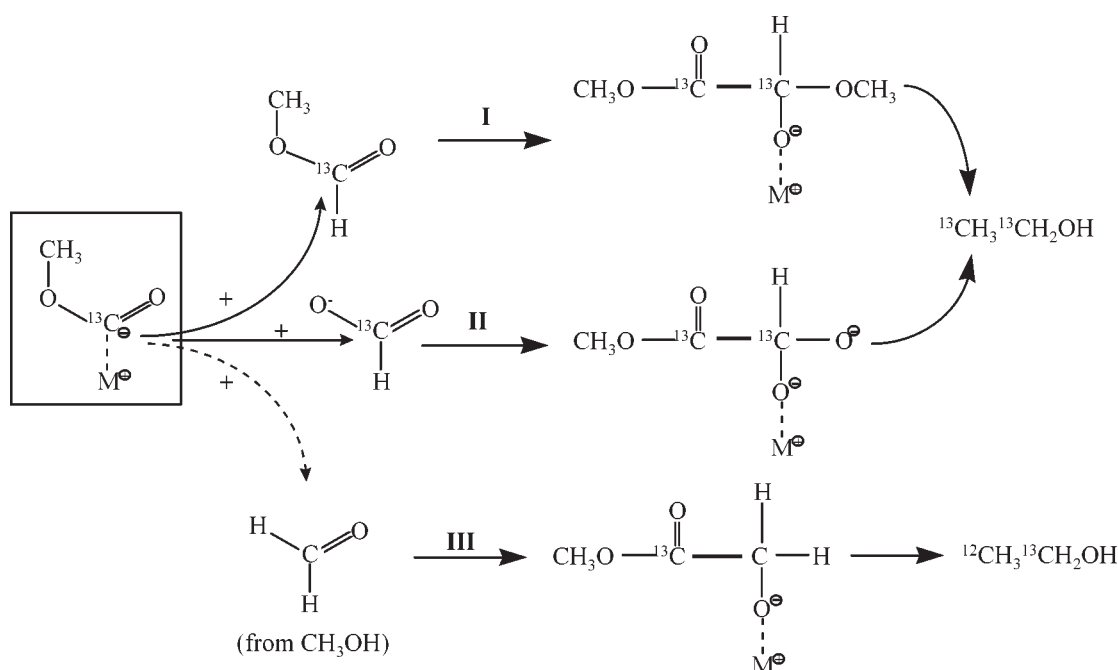


Figure 4. Pathways for carbon–carbon bond formation in methyl acetate.

suggesting that, in contrast with ethanol, methyl acetate is a reactive intermediate.

The hydrogenolysis of methyl formate or methyl acetate involves the use of Cu sites to dissociate H₂ and form the required H atoms. The hydrogenolysis steps using these hydrogen atoms may occur directly on such Cu sites or on basic sites using hydrogen atoms placed on oxide surface regions via hydrogen spillover.

These isotopic tracer studies have shown that ethanol is formed predominantly by direct reactions of CO on K–Cu_{0.5}Mg₅CeO_x at short residence time. The initial rate of ethanol formation is zero, suggesting that ethanol is a secondary reaction product. Therefore, a gas phase intermediate molecule, derived from CO, must be present for the formation of ethanol. This mechanism for C–C bond formation from CO/H₂ on K–Cu_{0.5}Mg₅CeO_x differs from those reported previously in the literature [1–3] and from our recent results on Cs-promoted CuZnAlO_x [15].

4. Conclusions

Pathways involving coupling reactions of surface formate and methyl formate species formed directly from ^{13}CO account for the formation of the initial carbon–carbon bond in ethanol from CO/H₂ on K–Cu_{0.5}Mg₅CeO_x. Reverse aldol condensation reactions of ethanol and methanol and reactions of methyl formate with $^{12}\text{CH}_3\text{OH}$ -derived intermediates become more important with increasing bed residence time. These reactions decrease the ^{13}C content in ethanol because $^{12}\text{CH}_3\text{OH}$ molecules are involved.

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