Isobutanol and Methanol Synthesis on Copper Supported on Alkali-Modified MgO and ZnO Supports

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K-CuMgCeOₓ and Cs-Cu/ZnO/Al₂O₃ catalyze isobutanol and methanol synthesis from H₂-CO mixtures, but synthesis rates are inhibited by CO₂ and H₂O formed during reaction. The initial C-C bond in ethanol forms directly from CO on K-Cu₀.₅Mg₀.₅CeOₓ catalysts, but via CH₃OH coupling reactions on Cs-Cu/ZnO/Al₂O₃ catalysts. Reactions of pure ethanol on these catalysts show that chain growth occurs via bifunctional aldol-type condensation pathways requiring Cu metal crystallites and basic sites on alkali-modified MgO and ZnO. On both types of catalysts, cross-coupling reactions of aldehydes and ¹³C-labeled methanol suggest that chain growth occurs by condensation of C₂⁺ alcohols or aldehydes with a reactive intermediate derived from methanol.

1. INTRODUCTION

Isobutanol synthesis provides a potential route to methyl-tert-butyl-ether (MTBE) via isobutanol dehydration to isobutene and reactions of isobutene with methanol. Li-Pd/ZrOₓ/MnOₓ/ZnO catalysts produce significant isobutanol yields, but only at very high temperatures (750-800 K) and pressures (10-30 MPa) [1]. Alkali-promoted Cu/MgO/CeOₓ and Cu/ZnO/Al₂O₃ catalyze the higher alcohol synthesis at lower temperatures (~573 K) and pressures (~5 MPa), but isobutanol yields are significantly lower [2-4]. Our work includes CO₂ addition studies, isotopic tracer probes of the initial C-C bond formation pathways, and kinetic and isotopic analyses of alcohol dehydrogenation and condensation steps leading to chain lengthening of C₂⁺ alcohols. In this study, we focus on the comparison of the behavior of copper supported on alkali-modified MgO and ZnO supports on the synthesis of branched alcohols from H₂-CO mixtures.

2. EXPERIMENTAL

K-CuMgCeOₓ and Cs-Cu/ZnO/Al₂O₃ samples were prepared by pH-controlled coprecipitation and incipient wetness impregnation methods [3-5]. Copper surface areas were measured by N₂O decomposition on pre-reduced samples. The density and strength of basic sites were determined using a new method based on the isotopic exchange of ¹³CO₂/¹²CO₂ mixtures [4,6]. Characterization data are shown in Table 1 for all catalysts.

High-pressure alcohol synthesis from H₂-CO mixtures (4.5 MPa, 583 K, CO/H₂=1) was performed in a packed-bed reactor. Isotopic tracer studies of alcohol synthesis pathways were carried out on K-CuₓMg₀.₅CeOₓ and Cs-Cu/ZnO/Al₂O₃ catalysts using ¹³CO/H₂/¹²CH₃OH
reactant mixtures. Ethanol reactions were carried out in a gradientless recirculating batch reactor at 573 K and atmospheric pressure. Reduced catalyst samples were exposed to the reactant mixture C$_2$H$_5$OH/CH$_4$/He (4.0/2.7/94.6 kPa). Cross-coupling reactions of $^{13}$CH$_3$OH ($^{13}$C: 99 %, $^{18}$O: < 1 %) with acetaldehyde and propionaldehyde were carried out using similar procedures and $^{13}$CH$_3$OH/CH$_2$O ($^{14}$C$_2$H$_6$O)/CH$_4$/He (7.3/4.0(4.0)/2.7/87.3 kPa) reactant mixtures. Mass spectrometric analysis after chromatographic separation was used to determine $^{13}$C content, position, and distribution in reactants and products.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu [wt %]</th>
<th>K (Cs) a) [wt %]</th>
<th>BET area [m$^2$/g]</th>
<th>Cu b) Dispersion (at 573 K) [~tmol/m$^2$]</th>
<th>Exchangeable CO$_2$ (at 573 K) [μmol/m$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_{0.5}$Mg$_5$CeO$_x$</td>
<td>7.7</td>
<td>1.0</td>
<td>147</td>
<td>0.14</td>
<td>2.3</td>
</tr>
<tr>
<td>Cu$_{7.5}$Mg$_5$CeO$_x$</td>
<td>49</td>
<td>1.2</td>
<td>92</td>
<td>0.05</td>
<td>3.3</td>
</tr>
<tr>
<td>Cu/ZnO/Al$_2$O</td>
<td>44</td>
<td>(2.9)</td>
<td>62</td>
<td>0.05</td>
<td>1.1</td>
</tr>
</tbody>
</table>

a) Bulk composition measured by atomic absorption. Values in parenthesis are for catalysts promoted with Cs instead of K. 
b) Cu dispersion was determined by N$_2$O decomposition at 363 K.

3. RESULTS AND DISCUSSION

3.1. Isobutanol synthesis from CO/H$_2$ mixtures

Methanol, isobutanol, and CO$_2$ are the most abundant alcohol products of H$_2$-CO mixtures on K-Cu$_{7.5}$Mg$_5$CeO$_x$ and Cs-Cu/ZnO/Al$_2$O$_3$ catalysts. Ethanol, 1-propanol, 1-butanol, methyl formate, methyl acetate dimethyl ether, and hydrocarbons were also formed [4,7]. Oxygen rejection during higher alcohol synthesis occurred predominantly by CO$_2$ formation [8]. The inhibition effects of CO$_2$ were examined by adding CO$_2$ to H$_2$-CO on K-Cu$_{7.5}$Mg$_5$CeO$_x$ and Cs-Cu/ZnO/Al$_2$O$_3$. The results are shown in Table 2.

Table 2

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Methanol Productivities [g/kg-cat-h]</th>
<th>Isobutanol Productivities [g/kg-cat-h]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No CO$_2$ added</td>
<td>CO$_2$ added</td>
</tr>
<tr>
<td>K-Cu$_{0.5}$Mg$_5$CeO$_x$</td>
<td>81.1 (0.03)</td>
<td>45.1 (0.10)</td>
</tr>
<tr>
<td>K-Cu$_{7.5}$Mg$_5$CeO$_x$</td>
<td>129.4 (0.06)</td>
<td>133.3 (0.11)</td>
</tr>
<tr>
<td>Cs-Cu/ZnO/Al$_2$O</td>
<td>164.8 (0.06)</td>
<td>158.5 (0.14)</td>
</tr>
</tbody>
</table>

[583 K, 4.5 MPa, H$_2$/CO=1, 3000 cm$^3$/g/h]. Values in parenthesis are the average CO$_2$ pressure in MPa.

Methanol and isobutanol synthesis steps are inhibited by CO$_2$ (Table 2). On catalysts with high density of Cu surface atoms (K-Cu$_{7.5}$Mg$_5$CeO$_x$ and Cs-Cu/ZnO/Al$_2$O$_3$), methanol synthesis rates decreased only slightly when CO$_2$ was added. In contrast, on catalysts with lower density of Cu surface sites (K-Cu$_{0.5}$Mg$_5$CeO$_x$), methanol synthesis rates were strongly inhibited by CO$_2$. This reflects the closer approach to thermodynamic equilibrium on catalysts with higher Cu surface densities, which render them less sensitive to a loss of active sites by CO$_2$ inhibition. These catalysts maintain equilibrium methanol concentration even after a large fraction of the Cu surface is covered by oxygen adatoms during steady-state alcohol synthesis.
As a result, detectable CO₂ inhibition effects require higher CO₂ concentrations on catalysts with high Cu loading. CO₂ inhibits isobutanol synthesis steps on catalysts with low Cu atom surface densities more strongly than on those with higher Cu site densities. This reflects the reversible titration of Cu and basic sites, both of which are required for isobutanol synthesis. Aldol-type coupling reactions of alcohols require both Cu and basic sites [9]; thus, blockage of Cu surface atoms by adsorbed oxygen can decrease isobutanol synthesis rates, even when the rate of quasi-equilibrated methanol synthesis steps is unaffected by this reversible titration of active Cu surface atoms. On catalysts with low Cu content, chain growth reactions are limited by the availability of Cu sites, required for hydrogen removal of H-atoms formed in C-H activation steps on basic sites; consequently, reversible oxidation of surface Cu atoms by CO₂ decreases chain growth rates.

3.2. Isotopic tracer studies of alcohol synthesis pathways

The synthesis of higher alcohols from CO/H₂ mixtures on alkali-modified methanol synthesis catalysts has been widely studied, but the pathways required for the formation of initial carbon-carbon bonds remain controversial. Several mechanisms for the formation of the initial ethanol C-C bond on (Cs)-Cu/Zn/(Al)O catalysts have been proposed [10,11].

Isotopic tracer studies of chain growth pathways on 1.0 wt % K-Cu₀.₅Mg₀.₅CeOₓ catalysts using ¹³CO/H₂/¹²CH₃OH have shown that the ¹³C content in ethanol (extrapolated to zero residence time) is 94% (Figure 1a); reflecting the predominant formation of ethanol from ¹³CO, without significant contribution from ¹²CH₃OH [12]. Also, at longer residence times, ethanol forms via reverse aldol reactions of higher alcohols, which contain lower ¹³C contents because ¹²CH₃OH participates in their formation. This reaction leads to the observed decrease in the ¹³C content of ethanol as residence time increases [12]. The ¹³C content in 1-propanol calculated by assuming it forms only via methanol aldol-coupling with ethanol (dashed line in Figure 1a) is lower than experimental values. This shows that some of the 1-propanol molecules are produced by carbonylation of C₂H₅OH with ¹³CO. This is consistent with slow linear chain growth pathways that also lead to the formation of 1-butanol during CO hydrogenation on K-Cu₀.₅Mg₀.₅CeOₓ [7].

![Figure 1. Effect of bed residence time on product ¹³C-distribution for: a)K-Cu₀.₅Mg₀.₅CeOₓ; b)Cs-Cu/ZnO/Al₂O₃. [538 K, 2.0 MPa, ¹³CO/H₂/¹²CH₃OH=100/100/1.3]. Similar isotopic tracer studies shown that ethanol is predominantly unlabeled (14% ¹³C content) at short bed residence times on Cs-Cu/ZnO/Al₂O₃ catalysts (Figure 1b), suggesting...](image-url)
that it forms by direct coupling of methanol-derived C\textsubscript{1} species, as reported previously by others [11]. The small amounts of labeled ethanol observed even after extrapolation to zero residence time could reflect minority pathways involving \textsuperscript{13}CO and reaction intermediates similar to those detected on K-Cu\textsubscript{0.5}Mg\textsubscript{3}Ce\textsubscript{0.5}O\textsubscript{x} catalysts. This is significantly different from the predominant pathway involving the direct reactions of CO on K-Cu\textsubscript{0.5}Mg\textsubscript{3}Ce\textsubscript{0.5}O\textsubscript{x}.

This feature might be attributed to different properties of alkali promoters. Cs\textsuperscript{+}-O\textsuperscript{2-} cation-anion pair is able to break the C-H bond of formaldehyde to form surface Cs\textsuperscript{+}(CHO\textsuperscript{−}) species [11], which then react with formaldehyde species to form the initial C-C bond. K\textsuperscript{+}-O\textsuperscript{2-} species, however, may not cleave C-H bonds in formaldehyde and may be unable to stabilize CHO\textsuperscript{−} intermediates because K\textsuperscript{+} is less acidic than Cs\textsuperscript{+} and the oxygen anion is less basic than in Cs\textsubscript{2}O. The other possibility is that the larger Cu surface area of Cs-CuZnAl\textsubscript{0.5}O\textsubscript{x} compared to K-Cu\textsubscript{0.5}Mg\textsubscript{3}Ce\textsubscript{0.5}O\textsubscript{x} enhances methanol dehydrogenation rate and therefore increases the local concentration of very reactive formaldehyde intermediates, which may favor direct coupling of methanol-derived C\textsubscript{1} species.

3.3. Condensation reactions of alcohols

The role of Cu and basic sites on dehydrogenation and condensation reactions was probed by measuring ethanol reaction rates on K-Cu\textsubscript{x}Mg\textsubscript{3}Ce\textsubscript{0.5}O\textsubscript{x} and Cs-Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalysts. Initial rates of dehydrogenation and condensation reactions are given in Table 3.

Table 3
Effects of Cu- and basic sites on Ethanol Conversion and Product Formation

<table>
<thead>
<tr>
<th>Initial Ethanol Dehydrogenation a)</th>
<th>Initial Condensation Rate b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-Cu\textsubscript{0.5}Mg\textsubscript{3}Ce\textsubscript{0.5}O\textsubscript{x}</td>
<td>0.22</td>
</tr>
<tr>
<td>K-Cu\textsubscript{7.5}Mg\textsubscript{3}Ce\textsubscript{0.5}O\textsubscript{x}</td>
<td>0.24</td>
</tr>
<tr>
<td>Cs-Cu/ZnO/Al\textsubscript{2}O\textsubscript{3}</td>
<td>0.14</td>
</tr>
</tbody>
</table>

a) Turnover rates per Cu surface atom, in s\textsuperscript{−1}; b) Product formation rates, in \times 10\textsuperscript{−8} mol / m\textsuperscript{2}-support \cdot s

Aldol condensation rates increase with increasing Cu content in the catalysts, even though ethanol dehydrogenation turnover rates (per Cu surface atom) are very similar on Cs-Cu/ZnO/Al\textsubscript{2}O\textsubscript{3}, K-Cu\textsubscript{0.5}Mg\textsubscript{3}Ce\textsubscript{0.5}O\textsubscript{x}, and K-Cu\textsubscript{7.5}Mg\textsubscript{3}Ce\textsubscript{0.5}O\textsubscript{x} catalysts. This suggests that Cu sites catalyze ethanol dehydrogenation steps leading to acetaldehyde, and also they are involved in rate-determining steps required for ethanol condensation reactions. Cu sites provide ethanol dehydrogenation sites and also dispose of H-atoms abstracted by oxygen anions during direct C-H and O-H activation reactions of ethanol [4,9]. Reactions of C\textsubscript{2}H\textsubscript{5}OH/D\textsubscript{2} mixtures [9,13] show that Cu sites increase the rate of hydrogen adsorption-desorption, a step that is effectively irreversible (rate-determining) in ethanol reactions on Cu-free K-Mg\textsubscript{3}Ce\textsubscript{0.5}O\textsubscript{x} catalysts.

Ethanol reactions lead mainly to acetone and n-butyraldehyde, which form only 2-propanol and 1-butanol after subsequent hydrogenation during CO/H\textsubscript{2} reactions. 2-Propanol and 1-butanol cannot, however, form isobutanol precursors, such as isobutyraldehyde and propionaldehyde. \textsuperscript{13}C-tracer studies of methanol-acetaldehyde and methanol-propionaldehyde cross-coupling reactions were carried out in order to examine reaction pathways that can actually lead to the C\textsubscript{3} and C\textsubscript{4} oxygenate precursors required for isobutanol formation. Table 4 shows \textsuperscript{13}C-distribution in products of \textsuperscript{13}CH\textsubscript{3}OH-C\textsubscript{2}H\textsubscript{4}O reactions on K-Cu\textsubscript{7.5}Mg\textsubscript{3}Ce\textsubscript{0.5}O\textsubscript{x} and Cs-Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalysts. Although reaction pathways for ethanol formation from
$^{13}$CO/H$_2$/$^{12}$CH$_3$OH differ on these two catalysts, reaction pathways for C$_2$ formation from $^{13}$CH$_3$OH/$^{12}$C$_2$H$_4$O are similar on both catalysts.

Table 4

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>K-Cu$_{7.5}$Mg$_5$CeO$_x$</th>
<th>Cs-Cu/ZnO/Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of $^{13}$C</td>
<td>0 1 2 3 4</td>
<td>0 1 2 3 4</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.0 100 -- -- -- 100(100)</td>
<td>0.0 100 -- -- -- 100</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>99.1 0.9 0.0 -- -- -- 0.5(0.2)</td>
<td>99.3 0.7 0.0 -- -- -- 0.4</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>35.6 64.4 -- -- -- 64(86)</td>
<td>31.7 68.3 -- -- -- 68</td>
</tr>
<tr>
<td>Ethanol</td>
<td>98.4 0.6 1.0 -- -- -- 1.3(0.8)</td>
<td>98.7 0.4 0.9 -- -- -- 1.1</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>16.8 73.4 9.8 0.0 -- -- 31(33)</td>
<td>6.7 82.6 10.7 0.0 -- 35</td>
</tr>
<tr>
<td>i-Butyraldehyde</td>
<td>0.0 18.9 60.9 20.2 0.0 50(53)</td>
<td>0.0 3.2 66.3 30.5 0.0 57</td>
</tr>
<tr>
<td>n-Butyraldehyde</td>
<td>83.5 16.5 0.0 0.0 0.0 4.1(1.5)</td>
<td>82.0 18.0 0.0 0.0 0.0 4.5</td>
</tr>
</tbody>
</table>

a) Values in parenthesis are %$^{13}$C in the products of $^{13}$CH$_3$OH-C$_2$H$_4$O reactions on K-Cu$_{0.5}$Mg$_5$CeO$_x$; [573 K, 101.3 kPa total pressure, 8.0 kPa methanol, 4.0 kPa acetaldehyde, balance He, 21 % methanol conversion].

On both catalysts, propionaldehyde molecules using $^{13}$CH$_3$OH-C$_2$H$_4$O mixtures contain predominantly one $^{13}$C atom, suggesting that they form via condensation of acetaldehyde with methanol-derived C$_1$ species. Isobutyraldehyde contains predominantly two $^{13}$C atoms, suggesting that it forms by condensation of propionaldehyde (with one $^{13}$C) with a C$_1$ species derived from methanol. Isotopic analyses of the reaction products of propionaldehyde-$^{13}$CH$_3$OH mixtures confirm these condensation pathways [9]. These studies also show that aldol formation and dehydration-decarbonylation pathways are reversible and that reverse aldol condensation steps after aldol-keto interconversion provide a pathway for acetone formation and for isotopic scrambling. The rate of reverse aldol condensation steps increased with increasing Cu content on these catalysts. This indicates that the rate of hydrogen transfer increases with Cu content. The increase in the $^{13}$C content of propionaldehyde as a contact time increase is consistent with the scheme shown in Figure 2, which includes reverse aldol reactions after aldol-keto isomerization.

4. CONCLUSIONS

Methanol and isobutanol are the most abundant alcohol products of CO hydrogenation on K-Cu$_{7.5}$Mg$_5$CeO$_x$ and Cs-Cu/ZnO/Al$_2$O$_3$ catalysts at relatively low temperature (583 K) and pressure (4.5 MPa). CO$_2$, formed in CO hydrogenation and water-gas shift reactions, strongly inhibits methanol and isobutanol synthesis. The formation of the initial C-C bond in ethanol occurs directly from $^{13}$CO, without significant involvement of methanol on K-Cu$_{0.5}$Mg$_5$CeO$_x$ catalysts. In contrast, Cs-Cu/ZnO/Al$_2$O$_3$ catalysts lead to ethanol synthesis via condensation reactions of the initial methanol product of CO hydrogenation. Ethanol dehydrogenation and coupling reactions at atmospheric pressures show that Cu sites are involved, through a bifunctional mechanism, in aldol condensation steps. Reactions of acetaldehyde with $^{13}$CH$_3$OH lead to singly-labeled propionaldehyde, consistent with chain growth via addition of a methanol-derived C$_1$ species to acetaldehyde on both catalysts. Similarly, isobutyraldehyde molecules formed from propionaldehyde-$^{13}$CH$_3$OH mixtures contain mostly one $^{13}$C, showing
that chain growth proceeds mainly via by aldol-type addition of a methanol-derived C\textsubscript{1} species to ethanol and higher alcohols or to the corresponding aldehydes.

\[\begin{align*}
13\text{CO} + H_2 & \rightleftharpoons 13\text{CH}_3\text{-OH} \\
& \quad \uparrow \quad \downarrow \\
H_213\text{C}=\text{O} + H_2 & \rightleftharpoons \text{propionaldehyde} \\
& \quad \uparrow \quad \downarrow \\
\text{methanol} & \quad \text{reverse aldol condensation} \\
& \quad \uparrow \quad \downarrow \\
\text{intermediate for normal aldol condensation} & \quad \text{intermediate for aldol condensation with oxygen retention reversal}
\end{align*}\]

Figure 2. Reaction scheme of the labeled propionaldehyde production.

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**REFERENCES**