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# EFFICIENT CARBON–CARBON BOND FORMATION IN ETHANOL HOMOLOGATION BY $CO/H_2$ WITH SPECIFIC $C_1$ OXYGEN RETENTION OVER Cs/Cu/ZnO CATALYSTS

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The reactions of ethanol with $CO/H_2$ or $CH_3OH$ to form 1-propanol proceed most efficiently over Cs/Cu/ZnO catalysts with selective oxygen retention from $CO/H_2$ or $CH_3OH$ and removal of oxygen associated with the OH group of ethanol, in contrast to that predicted by the classic aldol condensation mechanism. Isotopic labeling experiments reveal a novel path

$$^{12}CH_3{}^{13}CH_2OH + {}^{12}CO/H_2 \rightarrow {}^{13}CH_3{}^{12}CH_2{}^{12}CH_2OH.$$

## 1. Introduction

One of the most effective catalysts that produce methanol via monocarbon oxygenated intermediates is the Cu/ZnO catalyst [1]. When the methanol synthesis is carried out from $CO/H_2$ synthesis gas, surface promotion by a cesium salt greatly enhances the reaction rates at moderate temperatures ($< 520$ K), high $H_2/CO$ ratios ($\sim 2$), and pressures of 2–10 MPa while retaining high selectivity to methanol [2]. Under more severe conditions of temperatures exceeding 550 K and, low $H_2/CO$ ratios ($\lesssim 1$), alkali promotion of the Cu/ZnO catalysts results in the synthesis of higher oxygenated products [3], which was demonstrated to proceed via chain growth by step-wise additions of $CO/H_2$ with a high degree of branching at $C_4^+$ alcohols [4]. Kinetically significant aldehydic surface intermediates have been identified by a range of techniques including IR spectroscopy [5,6] and chemical trapping [7]. In the specific case of trapping by amines, this trapping reaction was shown to be a selective route to the synthesis of methylated amines [8,9]. In this communication, the addition of $CO/H_2$ to ethanol to form 1-propanol is shown not only to be greatly enhanced by the Cs promoter but also to embark on a selective course, specific to the Cs promoter only, that favors the retention of oxygen originating from the $C_1$ intermediate and the removal of the oxygen associated with the $CH_2OH$ group of ethanol. This synthetic pattern has the general consequence that products are selectively formed that are different from and complementary to those usually obtained in aldol syntheses followed by dehydration and hydrogenation of the higher molecular weight products (cf. Schemes II and III below).

## 2. Results and discussion

The Cu/ZnO catalyst was prepared by coprecipitation of a hydroxycarbonate aurichalcite precursor, calcination at 623 K and reduction in 2% $H_2/N_2$ at 523 K as described in detail earlier [10], and surface-doped with HCOOCs after calcination [2]. The 0.4 mol% Cs-doped catalyst used in the present work had a surface coverage of $\simeq 0.85 \times 10^{18}$ HCOOCs molecules per $m^2$ of the Cu/ZnO catalyst dispersed in a sub-monolayer [11]. Catalyst testing was carried out in a continuous flow reactor operating at a total pressure of 7.6 MPa using procedures described earlier [10]. The reactor was equipped with a liquid metering pump [12] that permitted injection of liquid alcohols, in this work ethanol and ethanol-methanol mixture. The liquid alcohols were vaporized in the reactor preheater section and entered the catalyst bed mixed with $CO/H_2$ in vapor phase. The catalyst activities and steady state product compositions were determined by on-line gas chromatography [10] at 523–583 K with $H_2/CO = 0.45$ and gas hourly space velocity (GHSV) = 3260 $\ell$(STP)(kg catalyst)$^{-1}$h$^{-1}$.

Isotopically labeled ethanol, $CH_3{}^{13}CH_2OH$ (24% $^{13}C$ at $CH_2$) and ethanol-methanol, $CH_3CH_2OH/{}^{13}CH_3OH$ (100% $^{13}C$) mixtures were injected at the rate of 0.245 cm$^3$ (liquid)(g catalyst)$^{-1}$h$^{-1}$, 1 cm$^3$ of liquid product was collected at intervals in a liquid nitrogen cooled trap, transferred to sealed vials, and subjected to $^{13}C$ NMR analysis. Quantitative $^{13}C$ analysis for isotopic enrichment at each of the carbons of $CH_3OH$, $CH_3CH_2OH$, $CH_3CH_2CH_2OH$, and $(CH_3)_2CH_2CHOH$ was achieved with an accuracy of a relative $\pm 5\%$ by the use of an extended pulse delay and removal of Nuclear Overhauser Effect by standard procedures in a 90 MHz Jeol XT 100 FT NMR.

In table 1a is shown the effect of cesium doping on the higher oxygenate synthesis activities under optimum higher alcohol synthesis conditions and cesium loading. The greatest effect of cesium is clearly displayed in the synthesis of 1-propanol ($C_2 \rightarrow C_3$) where the rate is promoted by a factor of approximately 4. Table 1b further shows that the injection of ethanol into the $H_2/CO$ synthesis gas under similar conditions results in a dramatic increase in the $C_2^+$ oxygenate synthesis rates, clearly showing that $C_2$ incorporation in the synthesis of $C_2^+$ oxygenates occurs. In fig. 1 are shown typical $^{13}C$ NMR spectra of the product collected after $^{12}CH_3{}^{12}CH_2OH$ and $^{12}CH_3{}^{13}CH_2OH$ ethanol injection under identical conditions into unlabeled $^{12}CO/H_2$ over the 0.4 mol% Cs/Cu/ZnO catalyst at 573 K. An identical set of injection experiments was carried out at 553 K over the above catalyst and at 533 and 573 K over the undoped Cu/ZnO

Table 1

Effect of (a) cesium doping on the methanol and higher oxygenate synthesis rates over the binary Cu/ZnO catalyst under the optimum higher oxygenate synthesis conditions shown and (b) of ethanol injection (0.245 $cm^3$ (liquid) (g catalyst)$^{-1}$ hr$^{-1}$) on the $C_2^+$ higher oxygenate synthesis rates over a 0.4 mol% Cs/Cu/ZnO catalyst.

| | *(a) Reaction conditions*:<br>$T = 583$ K, $H_2/CO = 0.45$,<br>$P = 7.6$ MPa,<br>GHSV = 3260 ℓ(STP)/kg cat/hr. | | *(b) Ethanol injection*<br>Reaction conditions: $T = 573$ K,<br>$H_2/CO = 0.45$, $P = 7.6$ MPa,<br>GHSV = 3260 ℓ(STP)/kg cat/hr. | |
|---|---|---|---|---|
| | *Product yield g/kg cat/hr* | | *Product yield g/kg cat/hr* | |
| Reaction product | Undoped Cu/ZnO | 0.34 mol% Cu/ZnO | No ethanol injection | With ethanol injection |
| Methanol | 204 | 157 | 171 | 160 |
| Ethanol | 22.6 | 17.0 | 19 | 29 |
| Methyl acetate | 10.5 | 9.9 | 8 | 11 |
| 1-propanol | 10.1 | 38.1 | 19 | 44 |
| 2-methyl-1-propanol | 20.7 | 48.6 | 17 | 43 |
| Other $C_4^+$ products | 46.1 | 106 | 6 | 25 |

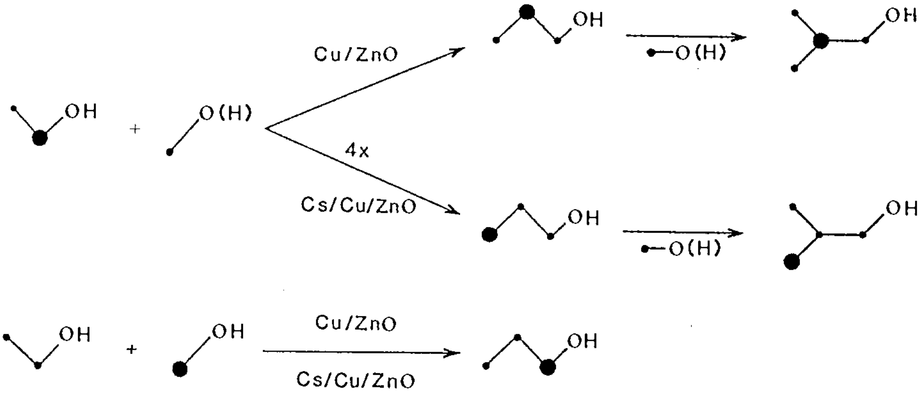
Table 2

Comparison of the relative intensities of the $^{13}C$ peaks of the carbons for the reaction products methanol, ethanol, 1-propanol and 2-methyl-1-propanol for the unenriched and $^{13}C$, C-1 enriched ethanol injection experiments. Reaction conditions: $H_2/CO = 0.45$, $P = 7.6$ MPa, GHSV = 3260 ℓ(STP)kg cat/hr, catalyst = 0.4 mol% Cs/Cu/ZnO.

| | Relative peak intensities | | | |
|---|---|---|---|---|
| Product | Undoped Cu/ZnO | | 0.4 mol% Cs/Cu/ZnO | |
| alcohol | 553 K | 573 K | 553 K | 573 K |
| $CH_3OH$ | 0.8 | 0.7 | 0.9 | 0.7 |
| $CH_3$ | 1.0 | 1.0 | 1.0 | 1.0 |
| $\vert$<br>$CH_2OH$ | 11.2 | 3.8 | 8.6 | 2.4 |
| $CH_3$ | 1.6 | 1.1 | 6.5 | 3.1 |
| $\vert$<br>$CH_2$ | 8.4 | 2.5 | 3.7 | 1.4 |
| $\vert$<br>$CH_2OH$ | 1.3 | 0.8 | 1.6 | 0.9 |
| $(CH_3)_2$ | 1.6 | 1.9 | 3.4 | 2.5 |
| $\vert$<br>$CH_2$ | 8.9 | 6.2 | 3.9 | 1.8 |
| $\vert$<br>$CH_2OH$ | – | 1.0 | – | 0.6 |

catalyst. In table 2 are presented the results of the above experiments in the form of relative $^{13}C$ NMR peak intensities for the non-enriched and $^{13}C$ enriched injection experiments. From the data in table 2, it is evident that for the undoped Cu/ZnO catalyst the $^{13}C$ label from the C-1 carbon of ethanol was incorporated preferentially into the C-2 carbon of 1-propanol and in a subsequent step into the C-2 carbon of 2-methyl-1-propanol. In marked contrast to this the Cs/Cu/ZnO catalyst steers the synthesis along a different pathway, especially at the higher temperature of 573 K. Over the Cs/Cu/ZnO catalysts $CH_3{}^{13}CH_2OH$ gave rise to 1-propanol enriched primarily in the C-3 position ($^{13}CH_3CH_2CH_2OH$). In a parallel set of experiments an injected mixture of unlabeled $CH_3CH_2OH$ with labeled $^{13}CH_3OH$ resulted in $CH_3CH_2{}^{13}CH_2OH$ over both the undoped and cesium doped catalysts.

These results clearly show that over the Cs/Cu/ZnO catalyst, (i) $CO/H_2$ or $CH_3OH$ adds one carbon unit at the C-2 position of ethanol, (ii) the oxygen associated with the C-1 carbon of ethanol is removed in the synthesis, and (iii) the oxygen associated with the $C_1$ source of carbon, i.e. $CO/H_2$ or $CH_3OH$, is retained in the $C_2 \rightarrow C_3$ synthetic step. The dominant features of the synthesis patterns as revealed by the flow of the $^{13}C$ label are shown in Scheme I, which also indicates how the label carries through in the subsequent $C_3 \rightarrow C_4$ synthetic step in which 1-propanol reacts with $CO/H_2$ to form 2-methyl-1-propanol.



Scheme I

Labeled carbons are marked as heavy dots and unlabeled carbons as light dots in Scheme I. The results in tables 1 and 2 and fig. 1 confirm that cesium enhances the rate of $C_1$ addition to ethanol by a factor of four and gives rise to a new pathway that retains the oxygen of the $C_1$ intermediate with nearly one hundred percent selectivity under the specified conditions. At lower temperatures the selectivity and $^{13}C$ incorporation patterns show systematic changes, but the highest selectivities for $^{13}C$ retention at the $CH_3$ groups of 1-propanol and 2-methyl-1-propanol have been obtained under the conditions reported here for the Cs/Cu/ZnO catalyst.

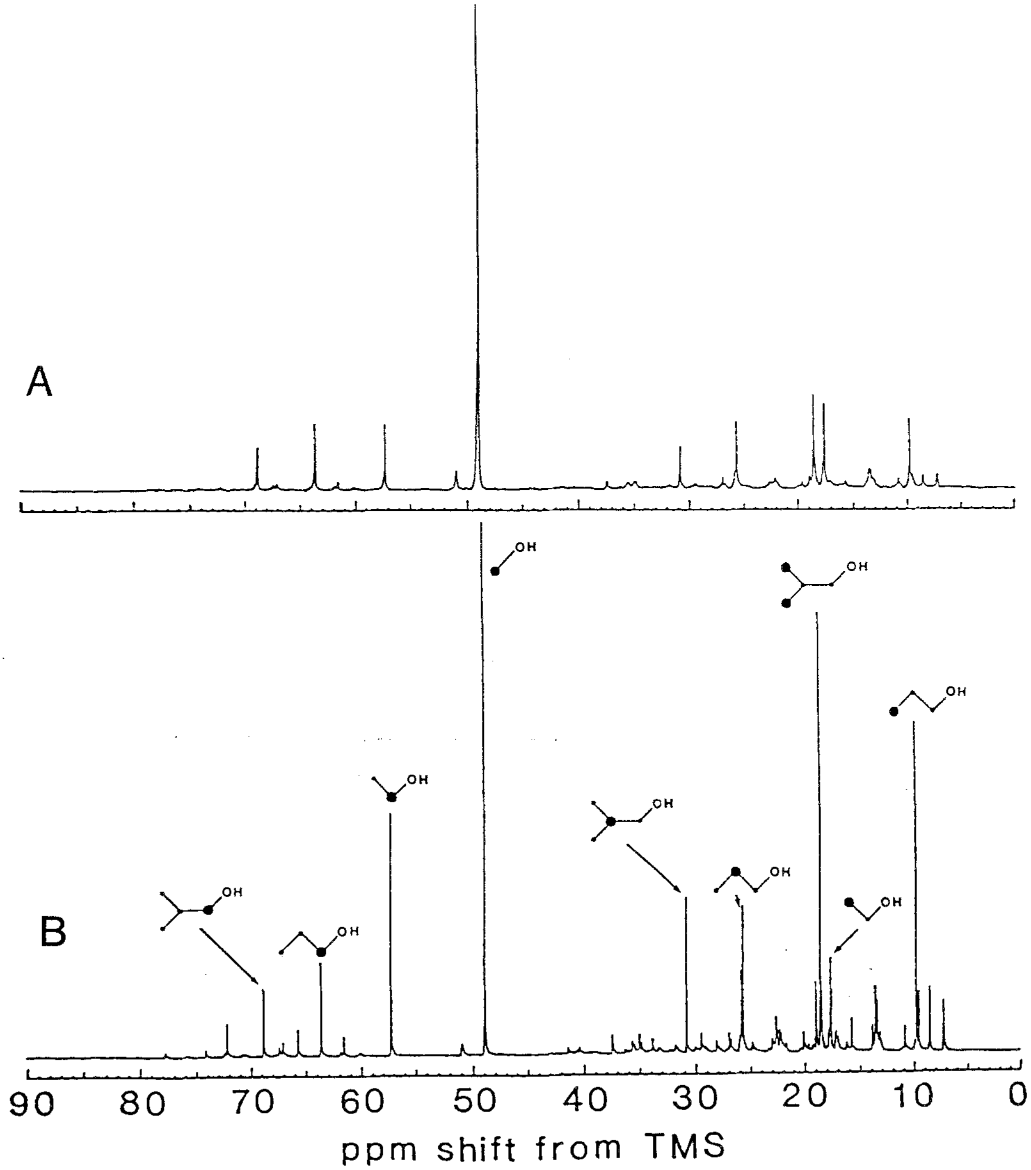
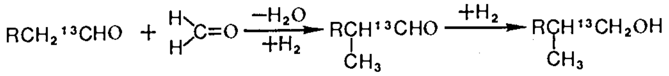


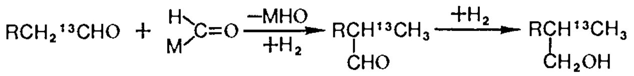
Fig. 1. $^{13}C$ NMR spectra of the liquid products collected over the Cs/Cu/ZnO catalyst at 573 K and 7.6 MPa with $H_2/CO = 0.45$ synthesis gas at GHSV = 3260 ℓ(STP)/kg cat/h during injection at the rate of 0.245 $cm^3$ liquid/g cat/h of (A) non-enriched ethanol and (B) $^{13}C$-enriched ethanol (24% $^{13}C$ in the C-1 position).

The differences between the performance and paths over the Cu/ZnO and Cs/Cu/ZnO catalyst indicate that the presence of the strong base counterion associated with Cs provides for a very efficient C–C bond formation, and this is accompanied by a high specificity for the retention of the oxygen associated with the $C_1$ carbon source. This result differs from that predicted by the classic aldol condensation reaction followed by partial dehydration and hydrogenation of the product, represented in general terms by Scheme II,



Scheme II

where R may be a hydrogen atom or methyl group. The $C_1$ intermediate, $H_2CO$, is derived from $CO/H_2$ or directly from the injected methanol, whereas $RCH_2CHO$ is the aldehyde produced by dehydrogenation of the injected or synthesized $C_2$ or $C_3$ alcohol. In contrast, the synthesis over the Cs/Cu/ZnO catalyst follows the pattern shown in Scheme III,



Scheme III

(M = catalyst or H in surface bonded formaldehyde) that is unique to the presence of cesium on the catalyst surface. The retention of oxygen associated with the $C_1$ intermediate is believed to be caused by the strong bonding of the alkyl oxygen of the dioxygenated $RCH(H_2CO^{\ominus})CHO$ intermediate anion to the $Cs^{\oplus}$ cations, which prevents hydrogenation of the $H_2CO^{\ominus}$ group while allowing full hydrogenation of the free -CHO group to $-CH_3$. The isotopic label incorporation over the Cu/ZnO catalyst in C-2 of 1-propanol, which runs contrary to the path over the Cs/Cu/ZnO catalyst, is reminiscent of the first step in the so called “formose” chemistry [13], and will be discussed in a full account of this work [14,15].

In conclusion, the carbon-carbon building reaction in oxygenate synthesis that occurs over Cs/Cu/ZnO catalysts has been demonstrated to be very efficient and to have the selectivity preferring oxygen retention on the nucleophilically attacked moiety, in this case the $C_1$ species, and this pattern results in a novel specific route to oxygenated compounds.

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