Higher oxygenate formation from ethanol on Cu/ZnO catalysts: Synergism and reaction mechanism

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Abstract

A remarkable synergism was observed in the higher oxygenate formation from ethanol on Cu/ZnO catalysts compared to one component catalyst of Cu or ZnO. The reaction mechanism was examined by ^{13}C labelling studies and selective feeding methods. A ^{13}C NMR and a GC/MS were used to determine the structure of the labelled products. A mass spectrometer was used to trace the dynamic change of the product distribution. A comprehensive reaction mechanism for the carbon chain growth on Cu/ZnO catalysts was proposed. The synergism could be explained by different intrinsic characteristics of copper and ZnO in the dehydrogenation of ethanol. Nucleophiles are produced preferentially on ZnO and electrophiles are produced preferentially on copper, and they would associate to form dioxygenated C_4 intermediates, which are converted to various higher chain products. A stabilization of ethoxy carbanion on ZnO was suggested, which would participate in the chain growing reaction.

Keywords: Cu/ZnO catalyst; Higher oxygenate formation from ethanol

1. Introduction

It has been known that primary C_{2+} alcohols grow to higher oxygenates on Cu based catalysts [1]. It is quite interesting to observe the fact that Cu/ZnO catalysts exhibit remarkable synergism in the higher oxygenate formation. In the previous study [2], it was found that the dehydrogenation of ethanol takes place mostly at the 1-carbon on copper catalyst and mostly at the 2-carbon on ZnO catalyst. It is assumed that the higher oxygenates are produced from the reaction between the electrophiles and nucleophiles formed on copper and ZnO, respectively. Based on these intrinsic characteristics of the copper and the ZnO, the mechanism of the higher oxygenate formation from ethanol on the Cu/ZnO catalysts was investigated in the present work.

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2. Experimental

2.1. Chemicals

EP grade chemicals were used as received for catalyst preparations and reaction experiments. Ethanol-1-^{13}C (99%) supplied by Cambridge Isotope Inc., was used for labelled studies. Carrier helium (99.99%) was purified by passing through an oxygen trap and a moisture trap, both supplied by Alltech Associates Inc. 5% H_2/N_2 was used in the reduction of the catalysts. Nitrogen (99.99%) and CO (99.99%) were used in the surface area measurement.

2.2. Catalyst preparation

The catalysts of different composition (Cu/ZnO = 0/100, 30/70, 50/50, 80/20, 100/0) were prepared by a coprecipitation method at 60°C. The mixture solution of 1 M copper nitrate and zinc nitrate was added to 1 M sodium carbonate solution and the precipitation was completed at pH 7. The resultant precipitate was filtered, washed, dried at 120°C overnight, and calcined at 400°C for 4 h. The calcined catalyst was grounded to pass through 100 mesh screen, and ion-exchanged in 0.1% ammonium bicarbonate solution to eliminate residual sodium [3]. The ion-exchanged catalyst was dried, pelleted, crushed, and sieved to 16/40 mesh size. Alkali doped catalysts were prepared by an impregnation of K_2CO_3 on the ion-exchanged catalyst (Cu/ZnO = 30/70) followed by a recalcination. Physically mixed catalyst was prepared by mixing the calcined copper catalyst (Cu/ZnO = 100/0) with the calcined ZnO catalyst (Cu/ZnO = 0/100). The surface area of metallic copper in the catalyst was determined by the reversible CO chemisorption and the surface area of ZnO was determined from the difference between the copper area and the total BET area as described elsewhere [4].

2.3. Reaction and product analysis

About 0.2 g of the catalyst was loaded in a fixed bed continuous flow reactor made of a 316 stainless steel tube (4.9 mm i.d.), which was heated by a temperature controlled electric furnace. Before the reaction, the catalyst was reduced with 40 ml/min of 5% H_2/N_2 at 250°C for at least 2 h until water production ceased. Ethanol or acetaldehyde were vaporized in a saturator at room temperature and introduced to the reactor by carrier helium controlled by a mass flow controller (Brooks 5850E). The concentration of the feed was controlled by the temperature of the saturator. Butan-1.3-diol was injected as liquid onto the catalyst bed using a micro syringe.

The effluent gas from the reactor was analyzed by an on-line GC (Gow-Mac 580, FID/TCD, SPB-5 capillary column, 0.53 mm × 50 m), and the dynamic change of the product distribution was traced by a mass spectrometer (Balzers QMG 421C). In order to trace several products simultaneously, representative fragment peaks were selected avoiding overlaps between different products. However, butanal and butanone were treated as a sum because their spectra overlap each other.

The products from the ethanol-1-^{13}C ($CH_3{}^{13}CH_2OH$) labelling experiments were analyzed by ^{13}C NMR (Varian UNITY + 300) and also by GC/MS (HP 5890/HP 5971, HP-1 capillary column, 0.2 mm × 50 m).

3. Results and discussion

3.1. Reactions on one component catalysts

When ethanol was introduced onto the copper catalyst (Cu/ZnO = 100/0), ethanol was converted mostly into acetaldehyde together with a very small amount of butanal/butanone and ethylacetate. When acetaldehyde was introduced, very small amounts of 2-butenal and

Table 1
Composition of the product from the reaction of ethanol or acetaldehyde on copper catalyst

| Component | Composition (GC area %) | | | |
| | reaction of ethanol | reaction of acetaldehyde | | |
	280°C	200°C	240°C	280°C [a]
Acetaldehyde	74.5	99.7	97.7	99.3
Ethanol	23.0	—	—	—
Butanal/butanone	0.5	—	—	—
2-butenal	—	0.3	0.9	trace
ethylacetate	0.6	—	—	—
Acetic acid	—	—	1.4	0.4
Etc. [b]	1.4	—	—	0.3

Cu/ZnO = 100/0, partial pressure of ethanol in feed stream = 8 kPa, partial pressure of actetaldehyde in feed stream = 8 kPa, GHSV = 4000/h.
[a] The copper catalyst was deactivated fast at 280°C with the acetaldehyde feed.
[b] Mostly CO and CO_2.

acetic acid were produced. The typical product distributions on copper catalyst are summarized in Table 1. When ethanol was introduced onto ZnO catalyst (Cu/ZnO = 0/100), small amounts of ethylene and acetaldehyde were produced together with ethylacetate. When acetaldehyde was introduced, a small amount of 2-butenal was produced together with trace amount of ethylene. When ethanol and acetaldehyde were introduced together, very small amounts of ethylacetate and 2-butenal were produced with a trace amount of ethylene. The typical product distributions on ZnO catalyst are summarized in Table 2. Those results showed

that the formation of the higher chain products was negligible on the one component catalysts.

3.2. Reaction on Cu / ZnO catalysts

3.2.1. Reaction of ethanol

When ethanol was introduced onto the Cu/ZnO catalysts, a substantial amount of ethanol was converted to various higher oxygenates mainly composed of propanone, butanal, butanone, 2-pentanone and ethylacetate. The typical product distribution is shown in Table 3. The physically mixed catalyst also showed considerable activity to higher oxygenates, although it was less active compared to the coprecipitated catalyst of the same composition. The activities of the catalysts of different composition are summarized in Table 4 together with the surface area of each catalyst. The production of the higher carbon chain products showed weak correlation to the surface area of copper, but the formation of ethylacetate did not show any correlation to the surface area of copper or ZnO. The active sites for the higher oxygenate formation are left to be investigated.

3.2.2. Effect of potassium

In the higher alcohol synthesis on Cu/ZnO catalysts, alkali metals have been known to promote the formation of the higher alcohols [5,6]. In order to examine the effect of the alkali metal in the carbon chain growth, the reaction of ethanol was performed on the potassium

Table 2
Composition of the product from the reaction of ethanol and/or acetaldehyde on ZnO catalyst

| Component | Composition (GC area %) | | |
	reaction of ethanol	reaction of acetaldehyde	reaction of ethanol/acetaldehyde
Ethylene	1.6	trace	trace
Acetaldehyde	4.0	98.5	46.4
Ethanol	92.9	—	52.8
Butanal/butanone	—	—	—
2-butenal	—	1.5	0.3
Ethylacetate	1.5	—	0.4

Cu/ZnO = 0/100, reaction temperature = 280°C, partial pressure of ethanol in feed = 8 kPa, partial pressure of actetaldehyde in feed = 8 kPa, GHSV = 4000/h.

Table 3
Composition of the product from the reaction of ethanol or acetaldehyde on Cu/ZnO catalysts

Components	Composition (GC area %)	
	reaction of ethanol	reaction of acetaldehyde
Propanone	13.8	5.9
Butanal	7.8	—
Butanone	2.3	—
2-butenal	—	1.7
1-butanol	0.7	—
2-pentanone	7.1	—
Ethylacetate	8.2	—
Acetic acid	0.5	1.5
Ethanol	13.2	0.5
Acetaldehyde	45.9	90.1
Others	0.5	0.3

Cu/ZnO = 30/70, reaction temperature = 280°C, partial pressure of ethanol in feed stream = 8 kPa, partial pressure of acetaldehyde in feed stream = 8 kPa, GHSV = 4000/h.
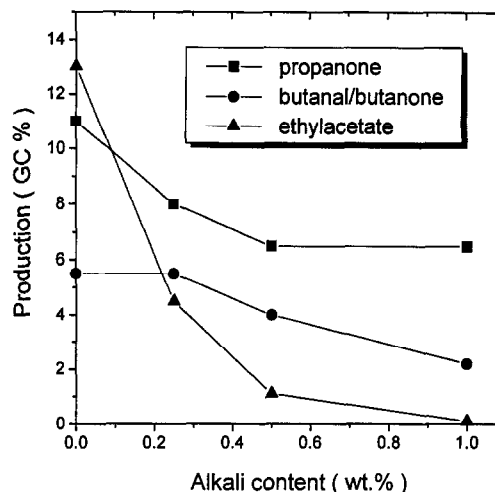

Fig. 1. Effect of potassium on the production of higher oxygenates from ethanol on Cu/ZnO catalysts. (Cu/ZnO = 30/70, reaction temperature = 280°C, partial pressure of ethanol = 8 kPa, GHSV = 4000/h.)

doped catalysts. Unexpectedly, the formation of higher oxygenates rather decreased with the increase of potassium content, and ethylacetate showed distinctive decrease as shown in Fig. 1. Potassium did not give any positive effect to the chain growth under the given condition.

3.2.3. Reaction of acetaldehyde

Many authors [1,7,8] proposed that aldol condensation of acetaldehyde might be the major reaction route in the carbon chain growth. When acetaldehyde was introduced onto the catalyst instead of ethanol, the overall conversion was

decreased and the product distribution was significantly different from the reaction of ethanol. The major products from the ethanol reaction were not detected from the acetaldehyde reaction, except propanone. Instead, small amounts of 2-butenal and acetic acid were produced, and those are the typical products from the aldol condensation and the Cannizzaro reaction, respectively. The product distribution is summarized also in Table 3.

Product distribution change depending on the retention time was continuously analyzed by the mass spectrometer and the result is shown in Fig. 2. When the retention time was changed,

Table 4
Surface area and activity of Cu/ZnO catalysts of different composition

Catalyst composition Cu/ZnO (mole ratio)	Surface area (m²/g catalyst)			Conversion to ethylacetate (%)	Conversion to higher carbon chain oxygenates (%)
	Cu	ZnO	total		
0/100	—	21.6	21.6	0.8	—
30/70	13.1	29.4	42.5	20.1	34.9
50/50	17.4	15.5	32.9	19.5	45.1
80/20	12.6	3.5	16.1	1.9	44.1
100/0	0.9	—	0.9	1.8	1.7
30/70 mixed	3.2	14.5	17.7	12.1	13.1

Reaction temperature = 280°C, partial pressure of ethanol in feed = 8 kPa, GHSV = 4000/h.
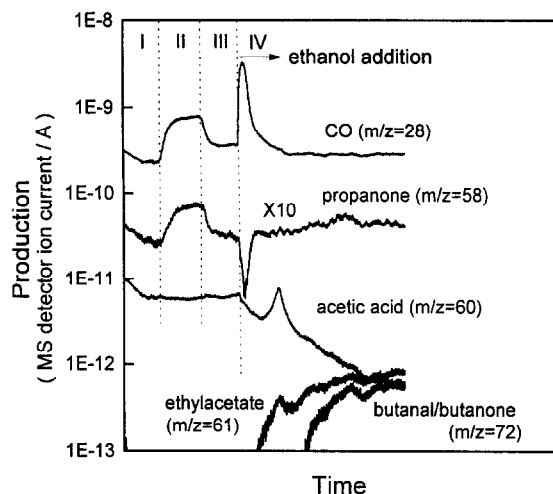
Fig. 2. Product distribution change in the reaction of acetaldehyde on Cu/ZnO catalyst depending on the retention time change and ethanol addition. (Cu/ZnO = 30/70, reaction temperature = 280°C, partial pressure of acetaldehyde = 9 kPa in I–III, 4 kPa in IV, partial pressure of ethanol = 4 kPa in IV, GHSV = 6500/h in I, 2000/h in II, 8000/h in III, 4000/h in IV.)

CO showed synchronous behavior to propanone, whereas other products showed independent behavior. The result indicates that the propanone and the CO are produced simultaneously from the acetaldehyde reaction. When ethanol was added to the reaction system, after a short transient period, butanal/butanone and ethylacetate started to show up on the MS detector. The results suggest explicitly that ethanol has a crucial role in the chain growing reaction.

3.2.4. Reaction of butan-1,3-diol

A few 1,3-dioxygenated species, e.g. butan-3-one-1-al [7], butan-3-ol-1-al [8], butan-3-one-1-ol or their alkoxides [9], were proposed as the intermediates in the carbon chain growing reaction from primary alcohols.

Butan-1,3-diol was injected to the reaction system to examine the behavior of 1,3-dioxygenated species on the Cu/ZnO catalyst. The effluent gas was analyzed by the mass spectrometer, and the results are shown in Fig. 3(A). The intensity of the fragment peak at $m/z = 72$ showed a remarkable increase after each injection indicating the formation of bu-

tanal and/or butanone. A slight decrease in the formation of ethylacetate ($m/z = 61$) and propanone ($m/z = 58$) could be attributed to a dilution effect due to the addition of the foreign component, and/or decreased conversion of ethanol due to the occupation of the active sites by butandiol. The slight increase of ethanol could be explained by the decreased conversion and/or the formation of ethanol from the decomposition of the butandiol.

When ethanol was purged out by helium gas and only butandiol was introduced with carrier helium, then acetaldehyde and ethanol were produced together with propanone and butanal/butanone as shown in Fig. 3(B). The results support that the dioxygenated C_4 species could be the reaction intermediate of the carbon chain growing reaction.

3.3. ^{13}C labelling study

The product distribution from ethanol and that from acetaldehyde showed great difference
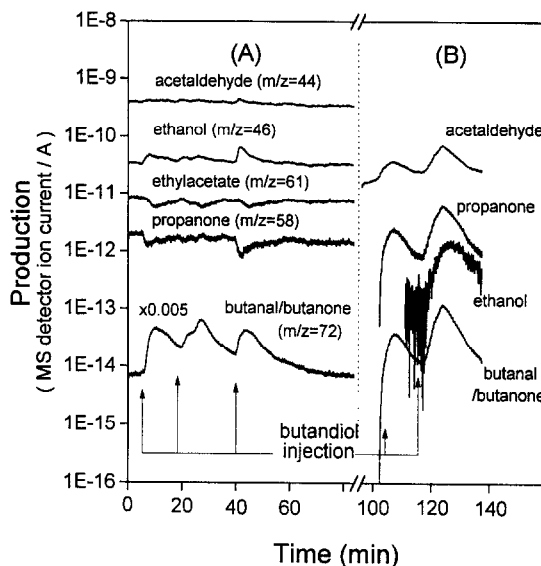

Fig. 3. (A) Product distribution change due to the injection of butan-1,3-diol into the reaction system of ethanol on Cu/ZnO catalyst. (B) Product distribution from butan-1,3-diol on Cu/ZnO catalyst. (Cu/ZnO = 30/70, reaction temperature = 280°C, GHSV = 4000/h, partial pressure of ethanol = 8 kPa in (A), no ethanol supply in (B).)

on the contrary to the widely accepted reaction mechanism via the aldol condensation reaction of acetaldehyde. It could be suggested that some C_2 species originated from ethanol, but different from acetaldehyde, would participate in the chain growing reaction. However, the reaction between acetaldehydes needs hydrogen to dehydrate the higher dioxygenated products, and ethanol might act as a hydrogen source through the facile decomposition to hydrogen and acetaldehyde. In order to examine the major role of ethanol, ^{13}C labelling experiments were performed with the mixture of labelled ethanol and unlabelled acetaldehyde.

3.3.1. Structure of the labelled products

Ethanol-1-^{13}C was introduced to the reactor and the reaction products were analyzed by ^{13}C NMR to determine the labelled structure, and the result is shown in Fig. 4. Reference ^{13}C NMR spectra of the concerned compound were obtained from the authentic sample mixture containing natural abundant ^{13}C, and the results agreed well with other references [10]. The labelled products and the authentic sample mixture were analyzed also by the GC/MS to obtain the reference mass spectrum for the determination of ^{13}C enrichment.

As shown in Fig. 4, the structure of the labelled propanone was C-^{13}CO-C, that of butanal was C-^{13}C-C-^{13}CO and butanone was C-^{13}CO-C-^{13}C. The structure of ethylacetate was C-^{13}COO-^{13}C-C. Those results indicates that the carbon chain growing reaction proceeds through the combining of the 1-carbon with the 2-carbon of the ethanol molecules. It is the typical pattern of aldol condensation which is a representative reaction between an electrophile
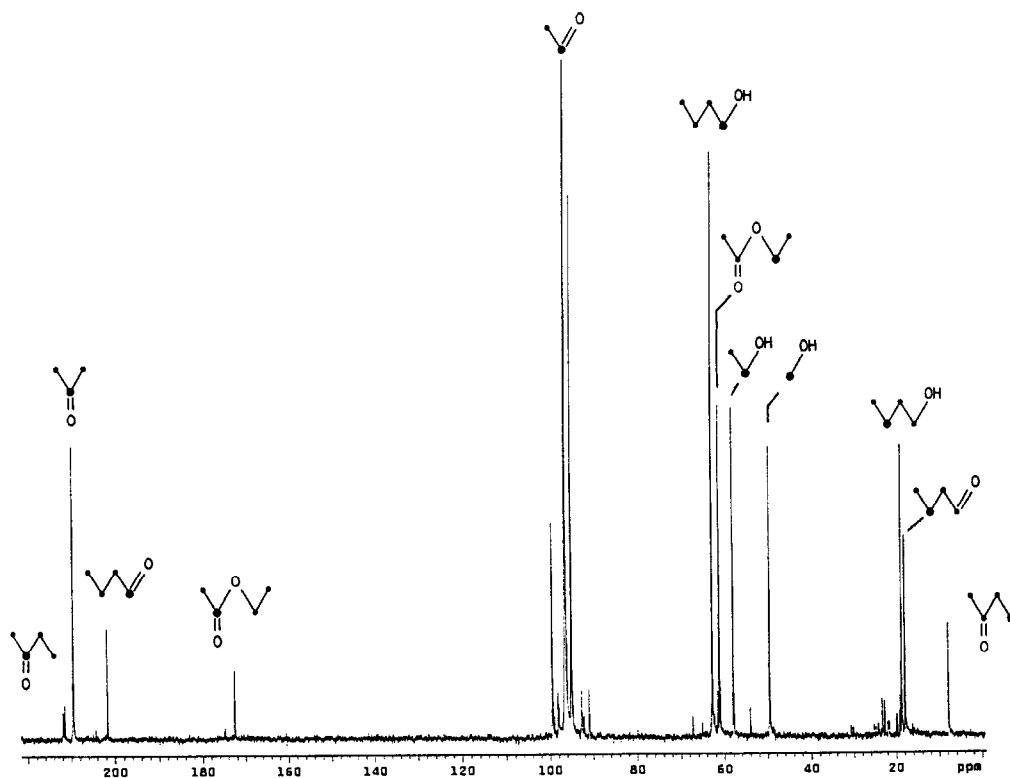

Fig. 4. ^{13}C NMR spectrum of the product from the reaction of ethanol-1-^{13}C on Cu/ZnO catalyst. (Cu/ZnO = 30/70, reaction temperature = 280°C, GHSV = 4000/h. Methanol was added as an internal reference. Peaks at 94.96 ppm and 99.44 ppm were not identified, however, it could be confirmed that those peaks, as well as all the other unidentified peaks, did not come from the higher oxygenates of our concern.)

and a nucleophile. Therefore, it could be strongly suggested that the higher chain product was formed by combining of the electrophilic 1-carbon in an electrophile with the electron rich 2-carbon or oxygen in a nucleophile, even though the reaction might not be a simple aldol condensation.

3.3.2. Reaction of the labelled ethanol and unlabelled acetaldehyde

The labelled ethanol and unlabelled acetaldehyde were introduced together into the reactor. The reaction product was analyzed by the GC/MS to determine the ^{13}C enrichments in each component, and the results are summarized in Table 5.

When the labelled ethanol and the unlabelled acetaldehyde are introduced together onto the catalyst, mixing of the ^{13}C carbon is inevitable due to the reversible dehydrogenation reaction between ethanol and acetaldehyde. Labelled acetaldehyde is produced from the labelled ethanol and unlabelled ethanol is produced from the unlabelled acetaldehyde. Therefore, the enrichment of ^{13}C at the 1-carbon of the ethanol decreases from its initial value 0.99, at the inlet of the catalyst bed, to a finite value at the outlet. Likewise, the enrichment at the 1-carbon of the acetaldehyde increases from its natural abundance 0.01 at the inlet to a finite value at the outlet. In the present experiment, the enrichment in the acetaldehyde and the ethanol at the outlet became 0.47 and 0.71, respectively.

In ethylacetate, the enrichment in CH_3CO- segment was 0.49 and that in the $-OCH_2CH_3$ segment was 0.67, which was very close to the enrichment in the acetaldehyde and the ethanol, respectively. The results suggest that the CH_3CO- segment comes from acetaldehyde, but the $-OCH_2CH_3$ segment comes more probably from ethanol rather than from acetaldehyde. The relevant argument was made in the methylformate formation from formaldehyde and/or methanol [20].

In propanone, the enrichment at carbonyl carbon was 0.47, which was very close to that in

the acetaldehyde. The result suggests that the carbonyl group comes from acetaldehyde and it agrees well with the above experimental result where propanone was produced from acetaldehyde even in the absence of ethanol.

In butanal and butanone, all the four C_2 segments showed different enrichment values of 0.61, 0.41, 0.33 and 0.52. It was suggested that the chain growing reaction proceeds through the association of an electrophile with a nucleophile, however, the simple aldol condensation reaction between acetaldehydes cannot explain the widely scattered enrichment values. The ^{13}C enrichment value in the C_2 segment from an

Table 5

Enrichment of ^{13}C and isotopic composition of the products produced from the reaction of ethanol-1-^{13}C with natural abundant acetaldehyde on Cu/ZnO catalyst

Products	Enrichment [a]		Composition [b]	
Ethanol	$CH_3{}^{13}CH_2OH$	0.71	$C^{13}COH$	0.71
			$CCOH$	0.39
Acetaldehyde	$CH_3{}^{13}CHO$	0.48	$C^{13}C=O$	0.48
			$CC=O$	0.52
Propanone	$CH_3{}^{13}CO-CH_3$	0.47	$C^{13}CO-C$	0.47
			$CCO-C$	0.53
Butanal	$CH_2{}^{13}CH_2-$	(0.61)	$C^{13}C-CC=O$	0.29
	$CH_2{}^{13}CHO$	0.41	$C^{13}C-C^{13}C=O$	0.32
			$CC-C^{13}C=O$	0.09
			$CC-CC=O$	0.30
Butanone	$CH_3{}^{13}CO-$	0.33	$C^{13}CO-CC$	0.14
	$-CH_2{}^{13}CH_3$	(0.52)	$C^{13}CO-C^{13}C$	0.19
			$CCO-C^{13}C$	0.33
			$CCO-CC$	0.34
Ethylacetate	$CH_3{}^{13}CO-$	0.49	$C^{13}CO-OCC$	0.17
	$-O^{13}CH_2CH_3$	(0.67)	$C^{13}CO-O^{13}CC$	0.32
			$CCO-O^{13}CC$	0.35
			$CCO-OCC$	0.16

Cu/ZnO = 30/70, reaction temperature = 320°C, GHSV = 4000/h.

[a] The enrichment was estimated from the corresponding fragment peaks. The values in parentheses were derived from the isotopic composition that was estimated on the assumption that the resultant mass spectrum was constructed by a linear combination of the spectrum from differently labelled isotopes.

[b] The isotopic composition was estimated from the distribution patterns of $M-1/M/M+1$ peaks. The distribution pattern of one ^{13}C labelled product was assumed to be the mean of the unlabelled one and the two ^{13}C's labelled one.

electrophile was 0.61 in butanal while it was 0.33 in butanone. It suggests that there should be more than one electrophile which participates in the chain growing reaction. Acetaldehyde is a well known electrophile with the electrophilic carbonyl carbon. Although for ethanol it is difficult to behave as an electrophile, when it is adsorbed on copper, the 1-carbon would become more electron deficient because the hydrogen at the 1-carbon is easily pulled away by the substrate copper to form acetaldehyde. Hence, it could be suggested that an ethanol molecule adsorbed on copper can behave as an electrophile even before it changes to acetaldehyde.

The ^{13}C enrichment value in the C_2 segment from a nucleophile was 0.41 in butanal while it was 0.52 in butanone. It also suggests that there should be more than one nucleophile. A carbanion from acetaldehyde is a widely accepted nucleophile because it can be stabilized through the well known enol–keto resonance. Although a carbanion from ethanol is believed to be unstable, it could be stabilized on ZnO by an incorporation of the substrate ZnO into the resonance hybrid as described in Scheme 1.

Even though any rigorous assignment of the reaction intermediate for each C_2 segment could not be made at the present stage, it is not unreasonable to say that the lower enrichment indicates more aldehydic character and the higher enrichment indicates more ethanolic character. Then, it can be proposed that the butanal is formed through the association of the ethanolic electrophile and the aldehydic nucleophile, whereas the butanone is formed from the aldehydic electrophile and the ethanolic nucleophile.
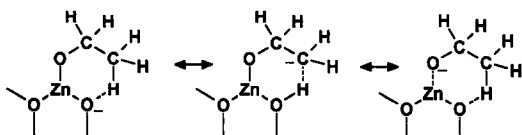
Scheme 1. Stabilization of an ethoxy carbanion on ZnO surface.
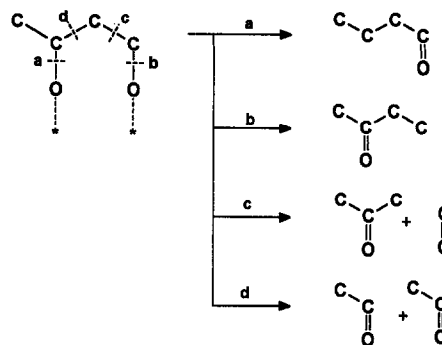
Preference of bond dissociation   C-O > C-C > C=O

Scheme 2. Comprehensive reaction mechanism for the carbon chain growth from ethanol on Cu/ZnO catalysts.

3.3.3. Adsorbed C_2 species on the catalyst surface

Many authors proposed that ethanol is adsorbed on metals or metallic oxides by a metal–oxygen bonding [11–14]. Methanol and other aliphatic alcohols are also proposed to be adsorbed as alkoxides on metals or metallic oxides [15–19]. It is believed that acetaldehyde is adsorbed also by a metal–oxygen bonding through an interaction between the lone electron pairs of carbonyl oxygen and the vacant orbitals of surface metals. Hence, the oxygenated intermediate species of our concern are considered to be adsorbed also by metal–oxygen bondings on the catalyst surface.

3.4. Reaction mechanisms

Based on the experimental results and the considerations made so far, a comprehensive reaction mechanism could be provided which can explain the formation of various oxygenates by a consistent theory. It is shown schematically in Scheme 2. An association proceeds through a combining of an electrophilic 1-carbon in a C_2 species with an electron rich 2-carbon in another C_2 species to produce a C_4 intermediate with two metal–oxygen adsorption bondings. Higher chain products are produced from the C_4

intermediate through a dissociation of the bonding chain connecting the two adsorption sites. The experimental results suggest that the preference of the bond cleavage is in the order of C–O > C–C > C=O. Propanone can be produced by the C–C bond cleavage in the C_4 species formed from two aldehydic species. Butanal can be produced by the C–O bond cleavage in the C_4 species formed from the alcoholic electrophile and the aldehydic nucleophile. Butanone can be produced by the C–O bond cleavage in the C_4 species formed from the aldehydic electrophile and the alcoholic nucleophile. The active site for the chain growing reaction is considered to be the periphery of copper particles on ZnO substrate or ZnO particles on copper substrate depending on the morphology of the catalyst, even though a more rigorous study should be made to prove it.

4. Conclusion

The formation of various higher oxygenates on Cu/ZnO catalysts could be explained comprehensively by consistent reaction mechanisms. Electrophiles with an electrophilic 1-carbon are produced preferentially on copper, while nucleophiles with an electron rich 2-carbon are produced preferentially on ZnO. Those different characteristics of the copper and the ZnO develop the significant synergism on the Cu/ZnO catalysts. Associations proceed between the nucleophiles and the electrophiles to produce various dioxygenated C_4 intermediates, and a bond cleavage occurs on the bonding

chain connecting two adsorption sites of each C_4 intermediate. The preference of the bond cleavage is in the order of C–O > C–C > C=O, and the formation of the different products can be explained satisfactorily by the different cleaving position due to the different combinations between various C_2 reaction intermediates.

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