The synthesis of higher alcohols using modified Cu/ZnO/Al₂O₃ catalysts

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Abstract

This paper gives a review of research work in the synthesis of higher alcohols over catalysts based on Cu/ZnO/Al₂O₃, emphasizing three main topics: (i) the effect on selectivity of the addition of several compounds to this catalyst, (ii) the effect on selectivity of the reaction conditions used, and (iii) the reaction network leading to the different products found. Although the use of alkali compounds has been studied most extensively, other compounds, for example those containing manganese, also appear to be promising additives. The process conditions are rather critical and this may cause some practical difficulties in industrial plants. An extended aldol condensation mechanism is proposed which can explain the product distribution found.

INTRODUCTION

Several review articles have appeared during the last ten years concerning the synthesis of methanol from synthesis gas over copper-containing catalysts. In 1982, Klier [1] gave a detailed review of the work which had been done until then on this industrially important process, for which materials based on Cu and ZnO have proved to be good catalysts. The synthesis of methanol proceeds from either CO or CO₂ according to the following equations

An adsorbed formate species appears to play an important role in the reaction mechanism. Although Cu and ZnO alone constitute an active catalyst, a third component is often added

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(in most cases Al_2O_3 or Cr_2O_3) in order to stabilize the catalyst against sintering. According to Klier a good methanol synthesis catalyst has the composition $\text{Cu/ZnO/Al}_2\text{O}_3 = 60/30/10$. In another extensive review by Bart and Sneed [2], the optimum composition of the catalyst is given to be $\text{Cu/Zn/Al} = 60/35/5$.

A new potential market for methanol has recently been opened up, namely its use as a motor fuel. However, in such a use methanol has to compete with reformulated gasoline to which ethers (especially MTBE) have been added. Several new developments in this field were reported in a recent symposium on alternative fuels [3]. The advantages of the use of methanol were summarized by Gray and Alson [4]: (i) it has a low price (almost comparable with petrol); (ii) it is a liquid; (iii) the emissions of CO , NO_x and hydrocarbons are claimed to be 90% lower than those using petrol; and (iv) it has properties which make efficient combustion possible. One possible drawback is that a methanol-fuelled automobile will produce some formaldehyde, but this can easily be decomposed using a simple exhaust catalyst [5]. A review of the current research and industrial activities, including automobile fleet tests, has been given by Sinor Consultants [6]. Although the use of methanol as a fuel has great environmental advantages, the main problem to be overcome is that both the distribution network for motor fuels and automobile engines have been developed for use with petrol. In California, the current strategy is that methanol should be added to petrol in amounts which will increase with time in such a way that the fuel will be 100% methanol in about 15 years. Phase separation problems due to the presence of some water in the mixture of methanol and petrol may be overcome by the addition of higher alcohols to this mixture; from the composition of the Octamix alcohols mixture described by Hiller and Supp [7], the fraction of higher alcohols needed is estimated to be somewhere between 30 and 45 w%. The addition of branched chained alcohols is then preferred to that of linear alcohols, because the former further increase the octane number of the fuel.

The synthesis of a mixture of methanol with isobutanol (2-methyl-1-propanol) may also be of importance for the production of methyl-tert-butyl-ether (MTBE), a molecule which is normally synthesized from methanol and isobutene. Isobutene is a by-product of oilrefineries and is available in large but relatively limited quantities; isobutanol may therefore be an alternative source of isobutene.

The synthesis of a mixture of methanol and higher alcohols can proceed in one step over several different types of catalyst; a comprehensive review of this subject has been given by Mills [8]. However, when a $\text{Cu/ZnO/Al}_2\text{O}_3$ -based catalyst is used, the selectivities to both methanol and to isobutanol can be high as can the overall activity. In order to achieve this high selectivity to higher alcohols, the catalysts containing $\text{Cu/ZnO/Al}_2\text{O}_3$ have been doped with various additives in order to change the product composition from pure methanol to a mixture of alcohols.

This paper reviews the effect on the product composition of several of these additives. Since the selectivity of the catalysts appears to depend on the process conditions used, these will also be discussed briefly. The second half of this paper consists of a review of the current ideas on the reaction mechanisms which have been put forward to obtain the compositions of the alcohols mixtures found. Using our own results we will finally make a choice from these reaction mechanisms with a proposal for some extension of that mechanism.

IMPROVEMENT OF THE CATALYST SELECTIVITY BY THE ADDITION OF PROMOTERS

Xiaoding et al. [9] have recently reviewed several patents on catalysts for the synthesis of higher alcohols from synthesis gas. They have shown that modified Cu/ZnO/Al₂O₃ catalysts are in most cases doped with an alkali or alkaline earth compound, while other elements such as rare earth oxides have been added either as a promoter or as a stabilizer. In the following sections these two groups of additives will be discussed separately. Table 1 shows the activity and selectivity data for the main types of catalyst.

Table 1

Activities and selectivities for different types of copper catalysts used for the synthesis of methanol and higher alcohols

Catalyst	Act. /mmol g ⁻¹ h ⁻¹	Sel. MeOH /% C	Sel. H.A. /%C	T °C	P /MPa	H ₂ /CO	GHSV /h ⁻¹	Ref
Cu/ZnO/Al ₂ O ₃	9.15	57.4	11.9	280	4	1	2500	12
	10.12	29.6	14.3	300	4	1	2500	12
+0.5wt% K ₂ CO ₃	8.76	63.9	19.0	280	4	1	2500	12
	9.51	33.3	16.9	300	4	1	2500	12
Cu/ZnO	50.5	65.8*	34.4*	285	13.2	0.44	4300	11
+0.5wt% K ₂ CO ₃	58.5	48.6*	51.4*	285	13.2	0.47	3300	11
CZA+Mn+K	2.7 ¹	40.5	26.2	350	10	2.38	2600	16
CZA+Cr+K	3.7 ¹	39.3	29.8	350	10	2.38	2600	16
CZA+Th+K	3.7 ¹	40.3	29.1	350	10	2.38	2600	16
CZA+6%Mn	7.47	72.3	6.5	280	4	1	2500	23
	8.97	35.1	17.2	300	4	1	2500	23
Cu/ZnO+Ga	2.59	n.a.	n.a.	320	3.5	1	95000	24
Cu/ZnO+Ni	0.76	38.1*	61.8*	320	3.5	1	95000	24
CuZn+Mn+K	46.9 ¹	54.3	24.5	325	25	1	20000	20
CuZn+Ce+K	30.8 ¹	54.2	22.4	275	20	1	20000	20

*only alcohols in the product are considered

¹calculated using data from reference

The addition of alkali additives

The addition of alkali compounds to ZnO/Cr₂O₃ has been reviewed extensively by Natta et al. [10]. The addition of these compounds causes an increase in the selectivity to alcohols higher than methanol and this is attended by a decrease in the conversion of CO. The promoting action increases in the order Li-Na-K-Rb-Cs. The promoting effect of K₂CO₃ on

a Cu/ZnO catalyst has also been examined by Smith and Anderson [11], who found a maximum butanol selectivity at 0.5 wt% K_2CO_3 and a maximum conversion at 1.0 wt% K_2CO_3 ; at a pressure of 132 bar, a temperature of 285°C, an H_2/CO ratio of 0.47 and a space velocity of 3300 h^{-1} , the selectivity to isobutanol obtained (based on the % of CO converted) was 18.8%. We have confirmed these results at a pressure of 40 bar using Cu/ZnO/ Al_2O_3 catalysts doped with K_2CO_3 and have also found that there is an optimum for the productivity of the other higher alcohols at 0.5 to 1.0 wt% K_2CO_3 [12]. Klier et al [13, 14] studied the effect of the addition of various alkali compounds to a Cu/ZnO catalyst and found with this type of catalyst an improvement of the selectivity to higher alcohols in the following sequence: Cs>Rb>K>Na>Li.

The addition of non-alkaline compounds

Hofstadt et al. [15] have patented the addition of a variety of dopants, e.g. compounds of Cr, Ce, La, Mn or Th, to a Cu/ZnO/ Al_2O_3 catalyst; they claimed that the presence of an alkali compound in addition is always necessary. According to their patent, the composition of these catalysts should be 25-40 wt% CuO, 30-45 wt% ZnO, 10-18 wt% Al_2O_3 and 1.7-2.5 wt% K_2O ; the other components should then be present in amounts of 3-18%. The addition of the various dopants is claimed to bring about an increase of the fraction of higher alcohols in the product to values up to 30 wt%. The addition of chromium, thorium, cerium and lanthanum is claimed to give large amounts of isobutanol (2-methyl-1-propanol), whereas a catalyst promoted with both chromium and manganese is claimed to produce a large amount of ethanol. The same authors have reported in a scientific paper [16] that the addition of MnO favours the formation of ethanol, the addition of Cr_2O_3 that of propanol, and the addition of ThO_2 that of isobutanol; in each case, a potassium compound was added with the dopant.

Natta et al. [10] reported in their review article that the addition of compounds of Mn, Cr and Th together with alkali compounds to ZnO or Cr_2O_3 catalysts improved the selectivities to higher alcohols, especially to isobutanol; however, these catalysts needed high temperatures (up to 500°C) and high pressures (up to 250 bar). The addition of compounds of Cr, Mn and Th has also been reported for copper based catalysts. For example, Hardman and Beach [17] have patented Cu/Th/alkali catalysts to which Ca, Mo, Rh, Mn, Pt, Ce, Cr, Zn, Al, Ti, La, V, U, Ru, Re, or Pd compounds have been added; the catalyst composition will then be $Cu_{0.5-2.5}ThM_{0.01-1.0}A_{0.05-0.9}O_x$, in which M is one of the aforementioned elements. The product mixture obtained over the catalyst of Hardman and Beach is claimed to contain up to 60% of higher alcohols (of which up to 70% may be isobutanol). The idea of the addition of Th-oxide to copper-containing catalysts is apparently based on the catalysts used for isosynthesis; this reaction, which normally produces isobutane from synthesis gas over $ThO_2/ZnO/Al_2O_3+K$ catalysts at temperatures of 400-500°C and pressures of 100-1000 bar, produces mainly branched chained alcohols at temperatures below 375°C, according to Shah and Perrotta [18]. The same authors point out that ceria may be used instead of thoria in the isosynthesis reaction.

Tronconi et al. [19] have shown that the pure oxides of Mn and Cr can produce methanol, some higher alcohols as well as hydrocarbons at a temperature of 405°C and a pressure of 85 bar; however, the selectivities to higher alcohols found are not such that these pure materials can be held responsible for the high selectivities found when they were added to methanol synthesis catalysts. Falter [20] added MnO and CeO_2 to a CuO/ZnO catalyst and found a decrease in the production of methanol with an associated increase in the selectivity to higher

alcohols and a much lower overall activity. Herman et al. [21] compared a Cu/ZnO/CeO₂ catalyst with a Cu/ZnO/Al₂O₃ material and found a lower activity to methanol using the former which they suggested was due to loss of Cu-ZnO interaction. Kotowski et al. [22] showed that the addition of Mn to a Cu/ZnO catalyst increased the rate of production of methanol at a temperature of 230°C and a pressure of 50 bar. In our own experiments [23] 0-10 mole% Mn (percent of metal ions) was added to a Cu/ZnO/Al₂O₃ catalyst with the result that there was a gradual increase in the selectivity to both methanol and isobutanol at a temperature of 280°C and a pressure of 40 bar; the selectivity to ethanol and methyl esters decreased, as did the selectivity to CO₂. We also showed that small quantities of cerium ions (up to 4 mole%) increased the selectivity to isobutanol, but that the cerium ions moved to the surface of the catalyst, thereby changing the selectivity towards hydrocarbons; the cerium ion is apparently too large to remain within the catalyst structure. Some rather uncommon additives were used by Kunz et al. [24, 25]: they added gallium and nickel ions to the Cu/ZnO catalysts and found that gallium stabilized the catalyst against sintering while nickel improved the selectivity to higher alcohols. The enhancement of the rate of production of the higher alcohols when nickel was used as a promoter is probably similar to the effect found when Co is used as a promoter, as discussed in another chapter of this volume. A related catalyst, patented by Stiles [26], and consisting of Cu/Zn/Co/Mn oxide + alkali, gives a mixture of normal C₁ to C₆ alcohols containing up to 25% of alcohols higher than methanol.

In order to illustrate that the dopants mentioned above favour the synthesis of higher alcohols not only when added to Cu/ZnO based catalysts, several other systems in which they are encountered will be given. Van den Berg [27] has shown that the addition of as little as 0.3% Mn to a Rh/SiO₂ catalyst gives a marked increase in the rate of production of ethanol (a factor of 10). Yu-Hua et al. [28] have reported that the addition of Ce and other lanthanides to a Rh/SiO₂ material also increases the selectivity to ethanol. Nix et al. [29] and Owen et al. [30] have reported another interesting development, namely the use of copper-lanthanide alloys for the synthesis of methanol: this type of catalyst behaves very differently from Cu/ZnO/Al₂O₃ catalysts, this being most obvious with respect to the very low temperature needed for the production of methanol (as low as 125°C for a cerium-copper alloy) and with respect to the high sensitivity to poisoning by CO₂. This last example shows that the presence of cerium can lead to modified selectivities which depend on the interaction of cerium ions with the other ions present in the catalyst.

ALTERATION OF OTHER CATALYST PROPERTIES BY THE ADDITION OF PROMOTERS

The addition of a number of different dopants to a catalyst based on Cu/ZnO may not only have an effect on the activity and selectivity of the resultant materials but also on properties such as the total surface area, the metal surface area and the degree of Cu-ZnO interaction. Smith and Anderson [11] and Fornasari et al. [31] have shown that the addition of K₂CO₃ to Cu/ZnO causes a decrease in its copper surface area; these authors explained this in terms of a partial coverage of the copper surface by the potassium compound. We have shown that when K₂CO₃ is added by impregnation, the basicity of the impregnating solution can cause a restructuring of the surface of the material, thereby affecting both the total and the copper surface area [12]; the decrease of the copper surface area, however, was also found to be

brought about partially by the potassium compound covering part of the copper. Such a restructuring effect has also been reported by Nunan et al. [32] in relation to Cs-doped Cu/ZnO/Al₂O₃ catalysts; the same authors found that when Al was replaced by Cr, this effect did not occur. We have shown from temperature programmed reduction profiles that the addition of K₂CO₃ also influences the Cu-ZnO interaction in a Cu/ZnO/Al₂O₃ catalyst [12]; when K₂CO₃ had been added, the copper oxide appeared to be more easily reduced than when no dopant had been added.

We have also studied the effect on a Cu/ZnO/Al₂O₃ catalyst of the addition of Cr, Mn and Ce compounds by either impregnation or during coprecipitation of the precursor material [23, 33]. The addition of Cr during coprecipitation decreased the copper surface area; an observation which we attributed to the formation of a larger fraction of hydrotalcite in the precursor phase. The addition of Ce by coprecipitation did not change the copper surface area at all, whereas Mn added by coprecipitation increased the copper surface area slightly (by about 10%). Temperature programmed reduction of the Mn-doped catalysts showed an increase in the Cu-ZnO interaction with increasing Mn content. When the Mn or Ce compounds were added by impregnation, the copper surface area decreased with increasing number of ions added; furthermore, both the Ce and the Mn compounds appeared to decrease the Cu-ZnO interaction. Both effects, i.e. a decrease in copper surface area and the decrease in Cu-ZnO interaction, were explained by assuming that the ions added preferentially cover the edges of the copper crystals, these being sites where the Cu and ZnO interact.

THE INFLUENCE OF PROCESS VARIABLES ON THE CATALYST SELECTIVITY

Not only the type of dopant but also the process conditions can affect the selectivity during the synthesis of alcohols over modified Cu/ZnO/Al₂O₃ catalysts. Natta et al. [10] have pointed out that the space velocity, the temperature, the pressure and the H₂/CO ratio of the feed gas influences the product distribution. Since the syntheses of methanol and higher alcohols appear to occur consecutively (see the section on reaction mechanisms below), it is not surprising that the formation of higher alcohols is favoured by longer contact times (lower space velocities), an observation which has been confirmed in our own experiments [34]; our results show that large amounts of CO₂ are also formed at these long contact times, this CO₂ having the function of balancing the excess of oxygen associated with the formation of the longer chains. Fink [35] has recently described an extensive study of the effect of process variables on the synthesis of alcohols over a Cu/ZnO catalyst. His conclusions are as follows:

- (i) the rate of production of methanol is strongly influenced by the equilibrium concentration of methanol;
- (ii) the rate of reaction to linear higher alcohols is independent of the methanol concentration in the reaction mixture, whereas the rate of formation of branched higher alcohols increases with the methanol concentration;
- (iii) the equilibrium concentration of methanol increases with increasing H₂/CO ratio in the reaction mixture; a maximum selectivity to higher alcohols has been found to lie in the range of $0.5 < \text{H}_2/\text{CO} < 0.9$;
- (iv) the rates of reaction to give both methanol and higher alcohols increase with increasing pressure (pressure ranging from 50 to 100 bar);
- (v) the equilibrium concentration of methanol in the reaction mixture decreases with

increasing temperature and the selectivity to higher alcohols is therefore enhanced at higher temperatures (280-300°C);

- (vi) the concentration of CO_2 (1-8%) in the reaction mixture does not have a large effect on the rate of production of methanol, but the selectivity to higher alcohols decreases with increasing CO_2 content.

Some of these effects have also been described by other authors. Klier et al. [36] and Smith and Anderson [11] have reported high selectivities to higher alcohols at H_2/CO ratios of 0.5. We have also measured the effect of the reaction temperature using a K_2CO_3 doped $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst [34]; the rates of production of the different alcohols as a function of temperature are given in Figure 1. From this figure it can be seen that all the alcohols have maxima with temperature, and that around 280°C an optimum selectivity to alcohols is

Fig. 1. The rate of production (productivity) of several alcohols as a function of the temperature, using a $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst to which 0.5 w% K_2CO_3 had been added.

achieved; above 280°C the production of CO_2 and alkanes becomes more important.

As reported by Klier [1] and Chinchin et al. [37], the presence of a small amount of CO_2 in the synthesis gas used appears to be beneficial to the rate of synthesis of methanol. Fink [35] has shown (see above) that CO_2 decreased the rate of formation of alcohols higher than methanol over a Cu/ZnO catalyst, and Tronconi et al. [38] reported the same behaviour using a Zn-Cr-K-oxide catalyst. Elliot [39], however, found a higher rate of production of both methanol and higher alcohols when CO_2 was present using a Cu/ZnO catalyst. Calverley and Smith [40] have derived a kinetic model for the synthesis of alcohols over a $\text{Cu}/\text{ZnO}/\text{Cr}_2\text{O}_3$ catalyst promoted with K_2CO_3 using a $\text{CO}/\text{CO}_2/\text{H}_2/\text{Ar}$ gas mixture; when CO_2 was present in concentrations up to 5%, they found an enhancement of the synthesis of both methanol and higher alcohols, and this effect was more pronounced with the unpromoted than with the promoted catalyst.

We have shown that also a few percent of CO_2 were produced at reaction conditions which were favourable for the formation of higher alcohols [34]. The water gas shift reaction

was calculated to be at equilibrium in these experiments; this means that CO_2 was present in much larger quantities than was H_2O . From the literature data given above the following tentative conclusion may be drawn: the presence of a small amount of CO_2 enlarges the amount of methanol formed which enhances the rates of formation of the higher alcohols. However, the CO_2 molecules themselves seem to decrease some of the chain growth steps, so that the final effect depends on the actual concentrations of at least CO_2 and methanol and on the degree of oxidation of the (promoted) catalyst surface.

Natta et al. [10] and Anderson [41, 42] have shown that the synthesis of higher alcohols is thermodynamically favoured over the synthesis of methanol; they therefore concluded that the selectivity (mostly to methanol) depends on the particular characteristics of the catalyst employed and upon kinetic factors. Fink [35] has also concluded that thermodynamics cannot explain the product distribution found and that this is thus determined by kinetic factors.

REACTION MECHANISMS

The product distribution found using Cu/ZnO-based catalysts differs from that found with materials containing elements (e.g. Co) characteristic of Fischer-Tropsch catalysts; the latter produce only linear alcohols [9, 43], whereas Cu/ZnO-based catalysts give a high selectivity to branched-chain alcohols. The synthesis of methanol and higher alcohols over Cu/ZnO/ Al_2O_3 catalysts must therefore be explained by a reaction mechanism which differs from the CO-insertion mechanism which has been suggested for the CuCo-containing materials [9].

Mechanisms proposed before 1950

Two review articles appeared in the literature in the 1950's describing the state of knowledge at that time. In the first of these, Anderson et al. [44] described mainly the work done by Frohlich and Cryder [45] who had measured the conversion of CO as a function of the space velocity. From those measurements, Frohlich and Cryder drew the conclusion that methanol is a primary product and that higher alcohols are formed by subsequent reactions. They suggested that the higher alcohols are formed by the addition (via the abstraction of H-atoms) of one alcohol to another at either the α - or the β -position; β -addition was supposed to be faster than α -addition, and it was suggested that addition to CH-groups does not occur. The positions of the carbon atoms were defined as follows:

The other review which appeared in the 1950's was written by Natta and his coworkers [10] and this concentrated on the early work of Natta himself [46], using ZnO/ Cr_2O_3 catalysts; in the early work Natta had suggested that the presence of K (e.g. in KOH) plays an important role by allowing the formation of the alkaline salts of carboxylic acids from the alcohols by CO insertion, for example

Hydrogenation of the salts then leads to higher alkoxides:

from which the chain can grow further.

According to Natta, a more rapid alternative, would be the formation and hydrogenation of aldehydes, for example:

This set of reaction equations, however, would not lead to the large amounts of isobutanol (i.e. a branched-chain alcohol) and to the low amounts of ethanol (i.e. deviating from the Schulz-Flory distribution) found in the product mixture. According to Natta et al. [10], a mechanism such as that proposed by Morgan et al. [47] is able to explain the formation of branched alcohols; this mechanism involves aldol condensation of two aldehyde species, this generally being written as follows:

Although such a reaction route leads to the formation of branched alcohols, the formation of ethanol in this way is considered to be unlikely because only a very small amount of formaldehyde is formed; furthermore, this mechanism cannot explain the formation of secondary alcohols.

More recently proposed mechanisms

Other mechanisms have more recently appeared in the literature, a noteworthy example being that given by Mazanec [48]; the most important steps of this scheme are given in Figure 2. The mechanism was derived for the catalysts composed of metal oxides such as ZnO and ThO₂ and involves the growth of a chain by insertion of CO. The initial step consists of the insertion of CO into an H-M bond, resulting in an adsorbed formyl species; this species can then be hydrogenated to a methoxy species, methanol and methane. However, another CO may insert into the C-M bond of the adsorbed formyl species, and this, after several shifts of hydrogen atoms or methyl groups and subsequent hydrogenation, leads to a negatively-charged enolate ion stabilized by a positively-charged surface metal ion. This enolate may either take up an H⁺ ion and be further hydrogenated to the corresponding alcohol or another CO molecule may insert into this species with subsequent growth to a longer chain. As shown in step 3 of Figure 2, branched chains may be formed from the intermediate species by the formation of two different structures, species B and C, respectively. The intermediate C appears to be the more favoured structure formed as it is less sterically hindered than is B and

Fig. 2. Chain growth scheme with branching according to Mazanec [48].

it has a more favoured electron distribution; species C in this figure leads to the formation of isobutanol after CO insertion, H-shift and hydrogenation, whereas species B would lead to the formation of n-butanol.

Although branched alcohols may be formed in the scheme proposed by Mazanec, it does not explain the observed deviation from the Schulz-Flory distribution, there being less ethanol than expected. In order to explain this finding, Mazanec added an aldol condensation reaction to his mechanism, suggesting that this is slow compared with CO insertion reactions and yet kinetically significant due to large surface concentrations of methoxide groups providing acetaldehyde. According to Mazanec, only the coupling of two C_2 aldehyde species providing acetaldehyde occurs in this aldol condensation step; C_1 , C_3 and C_4 aldehyde species all have too low a concentration to be of any importance. Measurements of Nunan et al. [57] in which injection of 2-propanol were made to the feed gas did not lead to 2-methyl-1-propanol (isobutanol); this

result appears to contradict the reaction mechanism put forward by Mazanec [48]. Since Nunan et al. have used a Cu/ZnO+Cs catalyst and Mazanec a ZnO or ThO₂ catalyst, different reaction routes probably occur over the different catalysts.

Elliot [39] has described experiments carried out in order to obtain information on the active sites and intermediates leading to either methanol or higher alcohols. He found correlations with the composition of the catalyst which were similar for the synthesis of both methanol and higher alcohols; furthermore, he found that the presence of CO₂ in his experiments appeared to enhance both syntheses. From these results and also from data obtained by selectively poisoning some of the active sites by the addition of Co, he concluded that either a common active site or a common intermediate must exist for the formation of both methanol and higher alcohols. In a second paper [49] in which Elliot and Pennella reported results on the addition of ¹³C-labelled methanol, they concluded that there must be a common intermediate which leads to the formation of both methanol and ethanol. They found the ¹³C in both possible positions in the ethanol, and they observed also both doubly-labelled and unlabelled ethanol. Elliott and Pennella therefore suggested that there was a reaction sequence such as:

In a third publication [50], the same authors proposed that the intermediates in the chain growth mechanism giving rise to the formation of higher alcohols are aldehydes (i.e. I in the reaction sequence of equations (10)-(12) is formaldehyde), which may undergo aldol condensation to form longer chains. They found that when an alcohol containing *n* carbon atoms was added to the feed gas in the absence of hydrogen, the corresponding 2*n*-ketone was formed; the only exception was ethanol, for which the formation of a ketone was not observed. The ketones found contained the oxygen of the CO but not the carbon. The intermediate suggested in the aldol condensation mechanism proposed was a β-keto-aldehyde; this can react to give an alkoxide which ultimately forms the ketone. Although the authors did not indicate so, it is probable that, with hydrogen present in the feed gas, such a mechanism would lead to the corresponding alcohols instead of to the ketones. A more detailed description of aldol condensation mechanisms will be given in a subsequent section.

An interesting reaction scheme proposed by Falter [20] is shown in Figure 3. This also includes an aldol-type growth, but the striking step is the formation of ethanol from methanol via dimethyl ether (DME). This was included because the author found substantial amounts of DME in the product over the Zr-Zn-Mn-Li-Pd-K catalyst used. Falter suggested that the rate determining step in this mechanism is the synthesis of acetaldehyde and ethanol from the DME by a Wittig-type reaction. This reaction, which normally needs a phosphorus ylide as one of the reagents, is an established route for the synthesis of alkenes and proceeds via a cyclic oxygen-containing intermediate; such an intermediate permits the oxygen to move from the centre of the DME molecule to the terminal position, required for the formation of ethanol. Furthermore, Falter concluded from experiments in which either methanol or one of the higher alcohols had been added to the feed of the reactor that the coupling of formaldehyde and

Chain growth via dimethylether

Fig. 3. Chain growth with dimethylether in rate determining step, according to Falter [20].

propionaldehyde is a fast reaction leading to isobutanol; as the addition of ethanol did not enhance the formation rate of isobutanol, this is evidence against the aldol-coupling route proposed by Mazanec.

The aldol condensation mechanism

Smith and Anderson [11, 51] examined the synthesis of alcohol mixtures using Cu/ZnO catalysts which had been doped with Cs- or K-compounds and they proposed the reaction network shown in Figure 4. This scheme was based on an earlier mechanism suggested by Graves [52] which depended on the following ideas.

- (i) two lower alcohols condense to give a higher alcohol, thereby losing H at either the α - or β -position, the loss of H at the β -carbon being faster;
- (ii) the rate of loss of hydrogen from methanol is slower than that from a β -carbon position and
- (iii) secondary alcohols react by losing OH instead of H.

Smith and Anderson checked the validity of this mechanism by adding various alcohols to the feed gas and concluded that the following assumptions had to be added either to explain the formation of the products found or for reason of simplifying their calculations:

Fig. 4. Reaction scheme for the growth of higher alcohols, according to Smith and Anderson [51].

- (iv) addition does not take place at a CH group;
 - (v) the species added consist of one or two C-atoms;
 - (vi) an intermediate containing two C-atoms does not add to the α -position of a growing chain;
 - (vii) the chain growth reactions are irreversible and have rate constants which are independent of the chain length of the growing intermediate, and
 - (viii) the reactions are first order in the concentration of the growing intermediate.
- The large amounts of methanol formed compared to those of the other alcohols was explained by a slow step for the initial growth from methanol to ethanol.

Basing their work on the mechanism proposed by Smith and Anderson, Klier and various coworkers have carried out experiments aimed at revealing the mechanism on a molecular scale, i.e. at the surface of the catalyst. For example, Vedage et al. [14] have suggested that a C_1 species containing an intact C-O bond is attached to the growing chain; this C_1 species

Fig. 5. Chain growth routes according to Vedage et al. [14]. l: linear growth, β : β -addition, α_o : methyl ester formation by α_o -addition.

may thus also be CO. They also proposed that growth proceeds via the three routes given in Figure 5 and discussed further below; these lead to linear alcohols, branched alcohols and methyl esters. The formation of methyl esters together with that of the higher alcohols was not described before. Nunan et al. [53] argued that the method of formation of methyl formate differs from that of the other methyl esters and proposed that it is formed from methanol and CO by the reaction:

Klier et al. [13] have reviewed data obtained for Cu/ZnO, Cs/Cu/ZnO, Cs/MoS₂ and Cs(K)/Co/MoS₂ catalysts and concluded that there are different mechanisms for the MoS₂-based catalysts and the Cu/ZnO-based catalysts; CO insertion occurring on the MoS₂-based materials, results in linear growth, while CO insertion is excluded on the Cu/ZnO-based materials. Nunan et al. [54] showed, using ¹³C-NMR, that methyl formate is indeed directly formed from methanol and CO, and they also demonstrated that ethanol is formed from C₁ intermediates originating from the methanol, probably formyl and formate species. Nunan et al. [55] also suggested an additional novel aldol condensation step, "aldol condensation with oxygen retention reversal". This step will also be discussed below.

Smith et al. [56] have given a comprehensive review of their work and have drawn it together in all-over schemes. Their starting-point lies in the three routes given in Figure 5. Linear growth in this scheme is depicted as taking place by the addition of an oxygenated C₁ species to a growing chain (*I*), probably proceeding via an S_N2 reaction between formaldehyde and an alcohol (not an aldehyde as in aldol condensation!) in which the OH group of the alcohol is the leaving group; after dehydration and subsequent hydrogenation this leads to linear alcohols. 2-Methyl-branched primary alcohols are formed by an aldol condensation in which an oxygenated C₁ species adds to the β-position of an aldehydic C_n (β) and subsequent dehydration and hydrogenation. Finally, the addition of methoxide to a growing chain leads to the formation of methyl esters (α_o). These authors suggest that β-addition is faster than linear growth; they consider that the addition of a C₁ species to the α-position of a growing alcohol is unimportant, as this will lead to secondary alcohols, these being found only in very small amounts. As mentioned above, β-addition is considered to be faster than linear growth; since the growth of ethanol to 1-propanol could proceed by either linear growth or β-addition, the formation of 1-propanol may be somewhat faster than a normal β-addition. As a result of experiments involving the addition of several alcohols to the feed gas, Klier et al. came to the conclusion that the following assumptions have to be added to the model of Smith and Anderson [51]:

- (i) further growth of 2-methyl branched alcohols by linear growth will either be slow or cannot occur, an assumption also made by Mazanec [48];
- (ii) the reaction rates are dependent on the chain length of the growing chain.
- (iii) β-addition of a species containing three C-atoms may also occur.

The second assumption was based on the following observations:

- a. a difference was found between the rate of formation of methyl formate and that of other methyl esters and the methyl formate was therefore assumed to be formed directly from methanol and CO;
- b. the rate of β-addition in the growth from C₂ to C₃ species was found to be higher than that of the growth of C₃ and higher species.

Fig. 6. Reaction mechanism for the formation of higher branched alcohols, according to Nunan et al. [55].

When these considerations were added to the model used, Klier et al. were able to give a very reasonable prediction of the composition of the product mixture.

Nunan et al. [57] have provided further details of the surface involved in this kinetic model. Using ^{13}C -NMR they have derived the scheme given in Figure 6. Linear growth is assumed to lead to the formation of ethanol, the scheme involving a formaldehyde species. The formyl species and the enolate species involved in the branching scheme are both stabilized by positive surface ions, in this case Cs^+ ions. The cesium ions are alkaline and therefore enhance the base-catalyzed β -additions. The attack by C_1 species is most important in the β -addition reactions, but the addition of species containing two or three C-atoms may also occur. The enolate formed may react with an aldehyde to form a β -keto-alkoxide, which may then form various products by a sequence of reactions involving hydrolysis, dehydration,

a. Regular aldol condensation reaction

b. Aldol coupling with oxygen retention reversal

Fig. 7. Aldol condensation with retention of different oxygen atoms, according to Nunan et al. [55]. M= metal atom or H in the adsorbed formaldehyde. Indicated are the O or OH species retained in the final product.

(de)hydrogenation and isomerization. Steric, electronic and thermodynamic effects determine which of these products is the most favoured. An important reaction in this mechanism is the "aldol coupling with oxygen retention reversal", schematically shown in Figure 7; the term "oxygen retention reversal" is to indicate that the oxygen of the formaldehyde remains in the final product, whereas the oxygen of the growing intermediate in the normal aldol condensation reaction remains in the final product. The normal and the reversed aldol coupling reaction compete with each other and the balance between them depends on the type of catalyst used and on the reaction step involved. For example, the reaction of C₂ to C₃ proceeds by linear growth over a Cu/ZnO catalyst, whereas the β-addition via aldol coupling with oxygen retention reversal is enhanced strongly over a Cs+Cu/ZnO catalyst; in the reaction of a C₃ species to give a C₄ species, however, the normal aldol condensation reaction appears to be somewhat faster than the reverse condensation step on both types of catalyst. Except for the case of the formation of methyl formate, the methyl ester formation appears to occur by the addition of either a methoxy or a formaldehyde intermediate to a surface bonded aldehyde.

A mechanism involving aldol condensation has been adopted by several other authors; of these, Riva et al. [58] and Tronconi et al. [59] deserve special mention, as they used catalysts which did not contain copper: ZnCrO or MnCrO, with or without added Cs or K. Riva et al. [58] suggested that the adsorption of methyl formate might give rise to the formation of the C₁ species involved in chain growth; methyl formate might also rearrange to give acetic acid, a molecule which upon reduction by hydrogen leads to ethanol. Our own infrared measurements [60] seem to support such an idea: there was an increase in the rate of formation of methyl formate at low pressures (1-3 bar) when a Cu/ZnO/Al₂O₃ catalyst was doped with K₂CO₃; methyl formate may thus play a role in the chain growth mechanism at higher pressures.

We studied the influences on the reaction mechanism of the addition of either K₂CO₃ or

cerium ions to a $\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst by adding either methanol or ethanol to the gas feed [61] and found that the reaction scheme proposed by Smith et al. [56] seems to be the most likely route for the formation of both methyl esters and higher alcohols. In such a mechanism a positive surface ion (K^+ , Ce^{++} , see also Fig. 6) stabilises the intermediates leading to the formation of higher alcohols. Sheffer and King [62] found that potassium was most likely present at the surface of the catalyst as K_2CO_3 ; this is in agreement with thermodynamic calculations of Van Ommen et al. [63] who showed that K_2CO_3 was the most stable component in a reducing gas mixture containing some CO_2 .

The mechanism proposed by Smith et al. [56], however, should be extended with a separate route for the formation of lower alkanes. By analyzing the deactivation behaviour of cerium-promoted catalysts, it was found that cerium ions moved to the surface of the catalyst, resulting in the loss of reactive surface sites for the formation of isobutanol, and at the same time covering sites which are important for the synthesis of methanol, and forming a CeO_2 phase which is probably active in the formation of alkanes. Our results indicated that ethanol was formed from methanol at sites different from those at which dimethyl ether was synthesized, this being an argument against the mechanism proposed by Falter (in which methanol reacts to ethanol via DME). Our observation that the addition of cerium ions decreased the formation of ethanol and 1-propanol (i.e. linear alcohols), whereas it did not change the amount of isobutanol (branched alcohol) produced and thus enlarged the deviation of the Schulz-Flory distribution of the alcohols in the product, indicates that the aldol condensation mechanism is more likely than the CO insertion mechanism proposed by Mazanec. However, we found that CO must be present for the formation of higher alcohols from methanol; we concluded that CO is probably involved in the formation of an intermediate species such as formaldehyde or methyl formate.

CONCLUSIONS

It has been shown that a $\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst which is highly selective for methanol synthesis from synthesis gas can be modified in such a way that a mixture of methanol and higher alcohols (mainly isobutanol) is produced. Many additives are able to achieve this change in selectivity; of these, the use of alkali compounds has been studied most extensively. Manganese appears to be another promising additive.

The fractions of higher alcohols in the product mixture can reach the required levels (30 wt% higher alcohols), especially when the proper process conditions are used; e.g. somewhat higher temperatures are needed for the synthesis of higher alcohols than for the synthesis of methanol. The process conditions are rather critical and this may cause some practical difficulties in industrial plants. No studies of the stability of the catalysts described above are to be found in the literature. Such studies therefore need to be performed, special attention then being paid to changes in selectivity during long-term operation; the activities of the fresh catalysts are so high that they can tolerate some decrease.

The reaction mechanisms suggested in the literature for the formation of higher alcohols all include a slow step for the formation of C_2 species from C_1 species; this step can be activated by the use of higher temperatures and by doping the catalysts with various compounds capable of forming positive surface centres. It is possible that different mechanisms are necessary to describe the chain growth over various different catalysts.

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