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Heterogeneous Catalytic Conversion of Dry Syngas to Ethanol and Higher Alcohols on Cu-Based Catalysts

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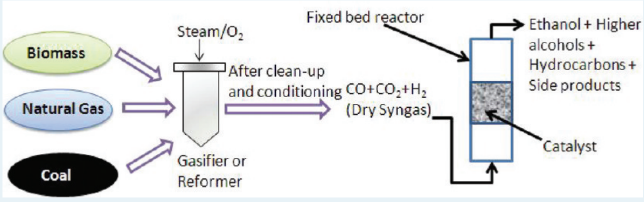

ABSTRACT: Ethanol and higher alcohols have been identified as potential fuel additives or hydrogen carriers for use in fuel cells. One method of ethanol production is catalytic conversion of syngas (a mixture of CO, H_2, CO_2, and H_2O), derived from biomass, coal, or natural gas. Thermodynamics of CO hydrogenation shows that ethanol is favored as the sole product at conditions of practical interest, but if methane is allowed as product in this analysis, essentially no ethanol is formed at equilibrium. The kinetics of ethanol formation must therefore be maximized. Although rhodium-based catalysts give C_2^+ oxygenates with high selectivity, their prohibitive cost has spurred research on less expensive copper-based alternatives. Copper-based catalysts require an optimum amount of promoter to suppress undesired reactions and maximize the yields of ethanol and higher alcohols. Common promoters include alkali, transition metals and their oxides, and rare earth oxides. Careful selection of operating variables is also necessary to achieve the desired activity and selectivity. This review describes the effects of promoters, supports, and operating conditions on the performance of copper-based catalysts for conversion of dry syngas to ethanol and higher alcohols. Proposed mechanisms from the literature for ethanol and higher-alcohol synthesis are outlined.

KEYWORDS: Cu-based catalyst, CO hydrogenation, syngas, ethanol, higher alcohols, fuel

1. INTRODUCTION

1.1. Alternative Fuel/Additives: Ethanol and Higher Alcohols. The prospect of limited oil supplies, increased demand, and the resulting persistent increase in prices has spurred the search for alternative fuels.[1,2] According to the Hubbert peak theory, oil production has already peaked in non-Organization of the Petroleum Exporting Countries (non-OPEC) and non-Former Soviet Union (non-FSU) countries and is now declining (Figure 1). According to U.S. Energy Information Administration, world liquids consumption is projected to increase from 86.1 million barrels per day in 2007 to 110.6 million barrels per day in 2035[3] in the reference case, an increase of more than 25%. These liquids include petroleum-derived fuels and nonpetroleum-derived liquid fuels, such as ethanol and biodiesel, coal-to-liquids and gas-to-liquids, petroleum coke, natural gas liquids, crude oil consumed as a fuel, and liquid hydrogen. To meet the increased demand, world liquid (both conventional and unconventional) production will be 26 million barrels per day more in 2035 than in 2007 in the reference case. In addition, oil prices are increasing, which is evident from Figure 2.[2] In the reference case, the average world oil price is forecast to increase from \$61/barrel in 2009 to \$110/barrel in 2015 and \$130/barrel in 2030.

This will have an adverse impact on the world's economy and social infrastructure unless the production of alternative fuels is increased significantly. Therefore, unconventional fuels, such as biofuels, oil sands, extra-heavy oil, coal-to-liquids, gas-to-liquids, and shale oil are being examined. According to International Energy Outlook 2010, for the period 2007−2035, unconventional liquids production will increase by ∼5%, on average, annually because of high oil prices. For example, in the US, production of biofuels is expected to increase from 0.46 million barrels to per day in 2007 to 1.6 million barrels per day in 2035 in the reference case.[3]

One such fuel/additive is ethanol or a mixture of ethanol and higher alcohols.[4−6] Ethanol is already in use as a fuel additive in the US and many other countries, such as Canada, Brazil, and Sweden. Developing countries such as India and China have also started promoting ethanol as a fuel additive on a pilot basis.

Ethanol and higher alcohols can be added to gasoline to increase octane rating[5] and reduce emissions of NO_x, CO_2, and unburned hydrocarbons;[7] however, there are some disadvantages, such as increased fuel cost and less overall energy efficiency.[5]

Another important potential application of ethanol is that it can be used to transport hydrogen chemically as a liquid by incorporating hydrogen atoms in the alcohol molecule, which can then be transported and reformed to a hydrogen-rich gas that can be used in a fuel cell.[4,8,9] This cycle takes advantage of the efficiency of fuel cell power and eliminates emissions that characterize conventional combustion processes.

Ethanol is of particular interest because it can be produced from renewable energy sources,[10] such as biomass. Ethanol is produced commercially in two ways: (1) hydration of ethene and

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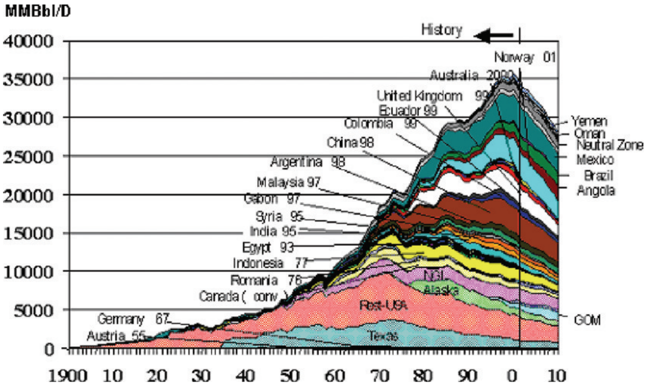


Figure 1. Oil production of non-OPEC and non-FSU countries.[1]

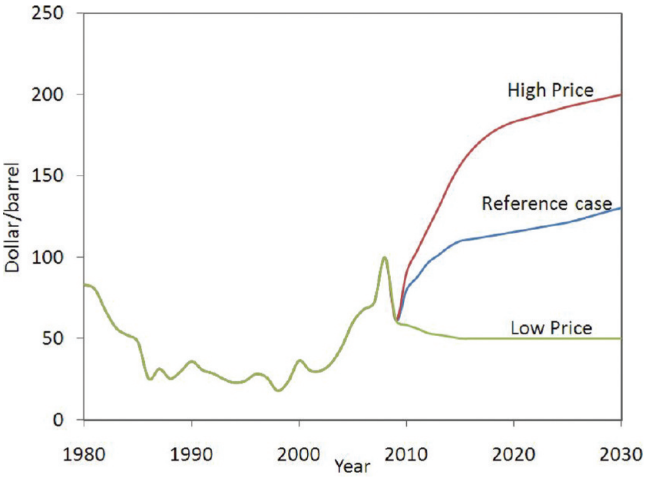


Figure 2. World oil prices, 1980−2030.[2] Source: Energy Information Administration (2009).

(2) fermentation of sugars. Hydration of ethene is a proven industrial process, but it depends on petroleum-derived ethene and, thus, does not reduce dependence on imported oil. Fermentation can interfere with food supplies because sugars come from biomass feedstocks, such as corn/maize, sugar cane, and sugar beets. For instance, in the US, corn-based ethanol has caused a sudden rise in the price of corn when the demand for corn exceeded its supply.[11] Hence, there is a drive to explore new methods that can supplement these resources to meet the increasing fuel demand in the future.

One method is the conversion of carbon-based feedstocks, such as biomass, coal, or natural gas, to syngas, which can then be converted catalytically to ethanol and higher alcohols. Thermochemical conversion of biomass to ethanol and higher alcohols seems to be a promising renewable alternative source of energy because of its environmental friendliness and cost due to easily accessible raw materials. One of the main merits of this process over fermentation is that it does not require any specific type of biomass feedstock. For example, nonfood biomass sources that require little in the way of soil quality and agricultural input can be used.[12] Another advantage is that syngas production does not require separation of biomass components, such as cellulosic material and lignin.[13]

1.2. Syngas to Ethanol and Higher Alcohols. Research on the production of alcohols from syngas has been going on for over 90 years.[6] A comprehensive overview of syngas production can be found elsewhere.[14,15] Figure 3 is a schematic of production of alcohols from syngas produced via gasification of biomass,[16] coal,[14] or natural gas.[17] Syngas is fed into a chemical reactor over a dry catalyst to produce alcohols and other side products.

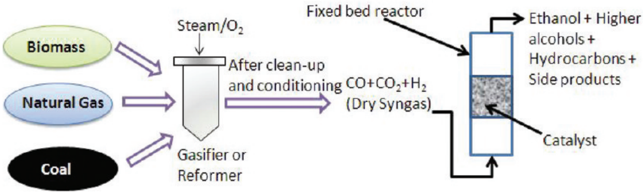


Figure 3. Generic schematic of thermochemical conversion of biomass, natural gas, and coal to alcohols.

The catalysts to produce ethanol and higher alcohols from CO hydrogenation can be divided into the following categories: (1) Cu-based catalysts, (2) Rh-based catalysts, (3) modified Fischer−Tropsch catalysts, and (4) Mo-based catalysts. Only the first category (i.e. Cu-based catalysts) is discussed here. A comprehensive review of other types of catalysts can be found elsewhere.[4,18−20]

Ethanol and higher-alcohol synthesis from syngas is being explored by many researchers using different types of catalysts.[4,18−21] Although the conversion of syngas to methanol over Cu/ZnO supported with Al_2O_3 or Cr_2O_3 catalysts is a very efficient industrial process with over 99% yield,[6,22] the yields of ethanol and higher alcohols from CO hydrogenation are generally low, even though ethanol is thermodynamically favored compared with methanol.[4,18] Therefore, the problem is one of kinetic control,[21] suggesting that an appropriate selection of catalysts and operating conditions should be used to increase the ethanol and higher-alcohol yield.

1.2.1. Thermodynamics. Ethanol can be produced via CO hydrogenation (eq 1).[4,18]

$$2CO + 4H_2 \rightarrow C_2H_5OH + H_2O \tag{1}$$

$$\Delta H_r^\circ = -253.6\ \text{kJ/mol}$$

$$\Delta G_r^\circ = -221.1\ \text{kJ/mol}$$

This reaction is thermodynamically favorable and highly exothermic. Figure 4 shows the equilibrium composition of various reactants and allowed products for reaction 1. Formation of ethanol and water decreases with increasing temperature, while that of CO and H_2 increases. Thermodynamics suggests that CO hydrogenation should be done below ∼300 °C. Although methanol is less thermodynamically favorable than ethanol, it is typically one of the main products of this reaction and must be limited kinetically.

Ethanol can also be produced via homologation of methanol (eq 2). The reaction involves reductive carbonylation of methanol over a redox catalyst to form a C−C bond and, thus, ethanol.[18]

$$CH_3OH + CO + 2H_2 \rightarrow C_2H_5OH + H_2O \tag{2}$$

$$\Delta H_r^\circ = -165.1\ \text{kJ/mol}$$

$$\Delta G_r^\circ = -97.0\ \text{kJ/mol}$$

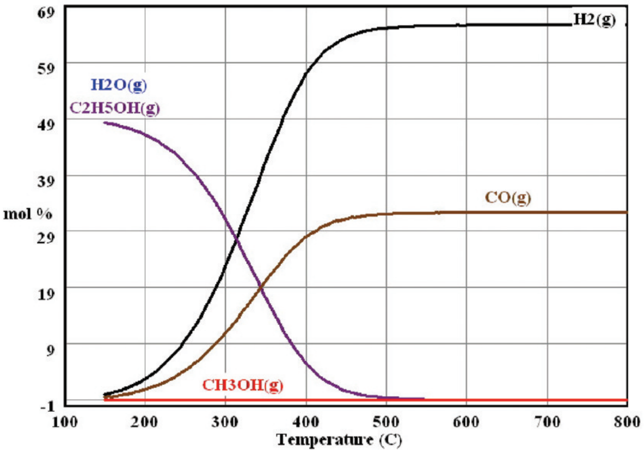


Figure 4. Equilibrium composition for the hydrogenation of CO to ethanol ($H_2/CO = 2.0$, 10 bar) (software used, HSC Chemistry 7.0).

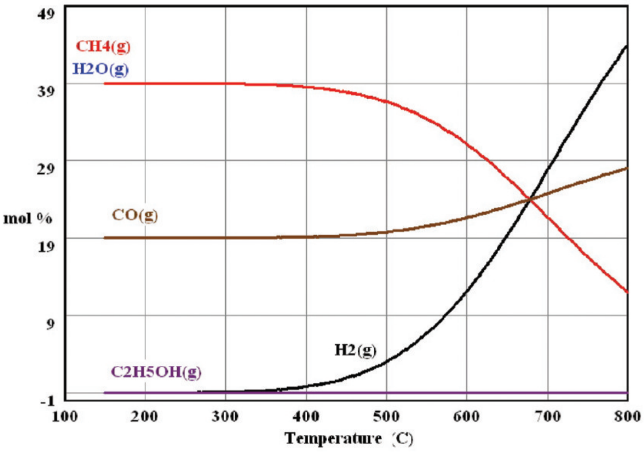


Figure 5. Equilibrium composition for the hydrogenation of CO to ethanol when methane is allowed as a product ($H_2/CO = 2.0$, 10 bar) (software used, HSC Chemistry 7.0).

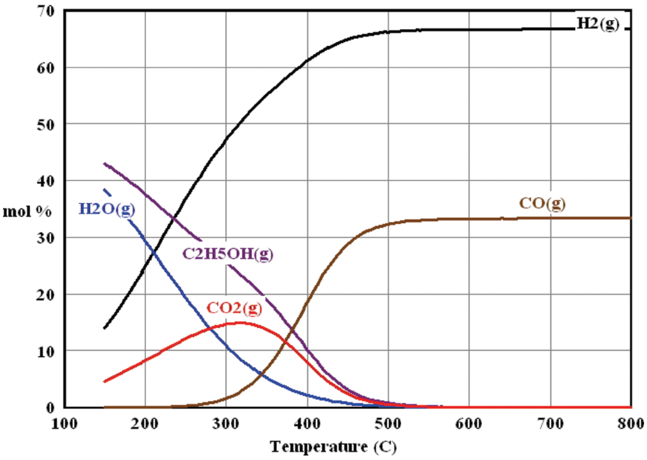


Figure 6. Equilibrium composition for the hydrogenation of CO to ethanol with CO_2 allowed as a product, but not methane ($H_2/CO = 2.0$, 10 bar) (software used, HSC Chemistry 7.0).

Both of the above reactions are accompanied by side reactions that produce many products, such as methanol, isopropyl alcohol, *n*-propyl alcohol, *n*-butyl alcohol, isobutyl alcohol, acetone, acetaldehyde, isobutane, *n*-butane, hexane, methane, CO_2, ethane, propadiene, propylene, and propane. The most undesirable side reaction is methanation (eq 3).

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (3)$$

$$\Delta H_r^{o} = -205.9 \text{ kJ/mol}$$

$$\Delta G_r^{o} = -141.9 \text{ kJ/mol}$$

Methanation is a highly exothermic reaction. It should be avoided because heat dissipation is a problem at industrial scale during higher-alcohols synthesis.[6] Methane is the most thermodynamically favored product of CO hydrogenation. Figure 5 shows that when methane is allowed as a product, the equilibrium yield of ethanol is essentially zero at all conditions of interest.

Another important side reaction is the water gas shift (WGS) reaction (eq 4) because it can affect the H_2/CO ratio, since it produces H_2 along with CO_2.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (4)$$

$$\Delta H_r^{o} = -41.1 \text{ kJ/mol}$$

$$\Delta G_r^{o} = -28.6 \text{ kJ/mol}$$

WGS is desired for feeds containing lower H_2/CO ratios but undesirable for feed with a high H_2/CO ratio.[18] Figure 6 shows that CO_2 is favored in the temperature range where ethanol is also a favored product; however, its amount is less than ethanol, and this can further be decreased if the reaction is carried out below 300 °C.

1.2.2. Cu-Based Catalysts. To date, rhodium-based catalysts have been the most promising, but their prohibitive cost and limited supply restrict their ability to be used as industrial catalysts.[18] Thus, much less expensive copper-based catalysts[23,24] are an attractive option. These catalysts are typically alkali-promoted $Cu/ZnO/Al_2O_3$ or $Cu/ZnO/Cr_2O_3$,[19,23,25−28] nonalkali-promoted $Cu/ZnO/Al_2O_3$,[23] $Cu/Mn/ZrO_2$,[29−31] and alkali-promoted/unpromoted combinations of all or some of these components (Cu, Co, Zn, Al).[32−35] Promoters are added to Cu-based catalysts to enhance ethanol and higher-alcohol selectivity.[4,18,28] An optimum promoter concentration is necessary to obtain higher selectivity[26−28,36] and activity of a catalyst.[37−39] In general, Cu-based catalysts have been widely used and produced promising results in the temperature range of 280−310 °C[23,24,26,29,30,34,35,38,40−43] at pressures of about 40−100 bar.[25,27,29,31,32,35,38,41,42,44−48] A pressure range of 55−70 bar seems to be the optimum for higher-alcohol synthesis.[43,49] The H_2/CO ratio is another important parameter and reported to be between 0.45 and 2.33 by various researchers.[24,26,27,29−31,38,41,42,44,48,50] In general, low H_2/CO ratios (≤ 2) favor the selectivity toward higher alcohols,[6,34,43,49] but a H_2/CO ratio as low as 0.5 gives greatly reduced activity.[34,43,49]

2. SYNGAS CONVERSION ON Cu-BASED CATALYSTS

During methanol synthesis on Cu-based catalysts, small amounts of higher alcohols were observed on catalysts containing a trace amount of alkali. This led researchers to explore the addition of alkali to these catalysts to produce higher alcohols.[26] As early as 1923−24, these types of catalysts attracted attention due to their ability to produce higher alcohols along with methanol.[19] Most of the catalysts in this category are $Cu/ZnO/Al_2O_3$ or $Cu/ZnO/Cr_2O_3$ modified/promoted with one or more alkali.[4,18] Others are nonalkali-promoted $Cu/ZnO/Al_2O_3$,[23] $Cu/Mn/ZrO_2$,[29−31] and different alkali promoted/unpromoted combinations of all or some of these components (Cu, Co, Zn, Al).[32−35] Cu-based catalysts should be modified in such a way that they increase the formation of higher alcohols and at the same time reduce the formation of unwanted products, such as methane and other hydrocarbons.[6] The main products on these catalysts are methanol, ethanol, methane, CO_2, 1-propanol, acetaldehyde, and isobutyl alcohol.

Selectivity to ethanol and higher alcohols depends on many parameters, such as type and amount of promoter(s), feed composition, pressure, temperature, and space velocity (contact time). The effect of all these variables and some plausible reaction mechanisms found in the literature are discussed in the following sections.

2.1. Role of Promoters. *2.1.1. Alkali Promoters.* Alkali promoters have been found to enhance the selectivity toward higher alcohols following the general trend Li < Na < K < Rb < Cs.[28] These basic promoters neutralize the acidity of catalysts and thus suppress the undesired reactions, such as dehydration,[25] isomerization, coke formation,[18] and methanation.[33,51,52] For example, on $Cu/Co/Cr_2O_3/ZnO$ or $Cu/Co/Al_2O_3/ZnO$ catalysts, it has been reported that alkali (K, Na, or both) promotion was necessary to suppress methanation below 290 °C.[25]

In general, promoters such as Cs or K on Cu/ZnO, $Cu/ZnO/Al_2O_3$, and $Cu/ZnO/Cr_2O_3$ show maxima in selectivity toward ethanol and higher alcohols with increasing alkali loading.[26−28,34,36,45] Higher alkali content also suppresses the activity of the catalyst.[37−39] Stiles et al.[6] reported that alkali (K/Cs/Rb) loading even as low as 1% reduced the activity of their $Cu/ZnO/Al_2O_3$ catalyst drastically. On K- or Cs-promoted Cu/MgO catalysts, with methanol in the feed at atmospheric pressure, C_2 oxygenate selectivity passed through a maximum with increasing intrinsic basicity.[53] This is due to the bifunctional nature of alkali-promoted Cu-based catalysts. The Cu/ZnO of the catalyst provides sites for hydrogenation, and Cs and its counterion provide basic sites that catalyze C−C and C−O bond-forming reactions. A higher Cs content inhibits the alcohol synthesis by blocking the hydrogenation sites.[38]

However, ethanol yield seems to follow a different trend with Cs loading on some catalysts. For example, it was reported that ethanol yield on Cu/ZnO first increased up to 1.5 mol % Cs and then became constant thereafter, as shown in Figure 7.[27] Methyl formate shown in the figure forms by methanol carbonylation. Authors also mentioned that methyl formate is not a precursor of ethanol. More details about ethanol formation are covered later in the Reaction Pathways section. In another study,[41] the same workers reported for a similar catalyst (Cu/ZnO) that Cs loading had an adverse effect on ethanol yield, as can be seen in Table 1. The difference in these two studies could be due to the different reaction conditions used. The yields of C_3^+ alcohols increased significantly up to 0.34 mol % alkali loading and then decreased. Higher levels of Cs loading reduced the catalytic activity significantly. Nevertheless, methanol and CO_2 remained the dominant products at any Cs loading.[41]

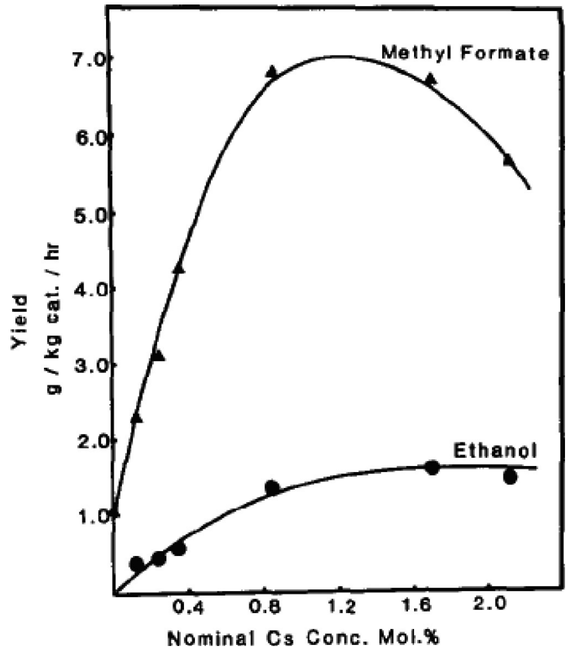


Figure 7. Yield of methyl formate and ethanol as a function of cesium loading over the calcined−doped Cu/ZnO catalyst. Experimental conditions: T = 250 °C, P = 76 bar, H_2/CO = 2.33[27] (reprinted from ref 27, copyright 1988, with permission from Elsevier).

In one study, cesium loading seemed to have no effect on ethanol yield on Cs/Cu/Zn/Cr catalysts.[38] However, cesium doping enhanced the yields of C_3^+ alcohols such as 1-propanol, isobutyl alcohol, and 2-methyl-1-butanol. Later, Hilmen et al.[54] reported that the addition of Cs on a $Cu/ZnO/Al_2O_3$ catalyst enhanced selectivity to ethanol, 1-propanol, and isobutyl alcohol. However, only two levels of doping were used.

K_2CO_3 was used by Smith and Anderson[26] to promote $Cu/ZnO/Al_2O_3$ catalysts. They reported that the addition of K_2CO_3 enhanced selectivity toward higher alcohols, particularly isobutyl alcohol. Maximum selectivity for higher alcohols was obtained at 0.5 wt % K_2CO_3 loading. Similarly, Boz et al.[34] used a commercial $CuO/ZnO/Al_2O_3$ catalyst and promoted it with potassium. Methanol selectivity increased and hydrocarbons decreased with K_2O loading. The selectivity to C_2^+ alcohols and aldehyde was maximum at 0.5 wt %. Maximum yield for propanol, *n*-butyl alcohol, and isobutyl alcohol occurred at low K_2O loading, but for methanol and ethanol, maxima occurred at a higher loading (1.0 wt %). This effect of K_2O loading is in agreement with Smith et al.[26]

On a $Cu/ZnO/Cr_2O_3$ catalyst, Calverley and Smith[45] reported that promotion with K showed a maximum toward methanol and higher-alcohol yield with K loading, with a 0.5% K_2CO_3 loading showing more activity than 4% loading toward C_2^+ alcohols as well as methanol. Similarly, on a Co/Cu/ZnO catalyst, Boz[33] reported a maximum in ethanol and higher-alcohols selectivity at 5% K loading. Similar effects were observed with Cs addition by others and were attributed to the blockage of the active sites of the catalyst at higher alkali loadings.[37−39,41] Promotion by potassium may have some disadvantages, as well; for example, on a $Cu/Co/ZnO/Al_2O_3$ catalyst, it accelerated sintering and was gradually removed due to extraction by steam.[55,56]

Alkali promoters also caused unusual behavior in some unsupported copper catalysts.[57] Methanol was the major product when Na, K, Rb, or Cs was added to copper by complexation of an alkali/copper nitrate solution with citric acid, followed by

Table 1. Product Yields over the Cu/ZnO = 30/70 Catalyst and the Cesium-Doped Cu/ZnO Catalyst Obtained with H_2/CO = 0.45 Synthesis Gas at 585 K and 7.6 MPa with GHSV = 3260 L (STP)/kg cat/h[41]

	Product yield (g/kg cat/h)								
catalyst	CO_2	alkanes[a]	methanol	ethanol	1-propanol	2-methyl-1-propanol	1-butanol	2-methyl-1-butanol	others[b]
undoped Cu/ZnO	367	16.8	204	22.6	10.1	20.7	3.4	8.6	34.1
0.25 mol % Cs/Cu/ZnO	412	16.2	181	22.7	29.6	28.9	8.6	11.5	53.8
0.34 mol % Cs/Cu/ZnO	403	13.4	157	17.0	38.1	48.6	8.2	15.5	82.3
0.43 mol % Cs/Cu/ZnO	430	14.0	162	18.2	24.1	33.6	4.6	11.7	37.3
1.5 mol % Cs/Cu/ZnO	403	4.3	213	8.1	18.0	4.8	–	–	10.9

[a] Alkanes = methane, ethane, and propane. [b] Others = methyl esters, aldehydes, ketones, C_4^+ linear primary and secondary alcohols, C_4^+ branched primary and secondary alcohols, and methyl formate.

decomposition of the resulting precursor. Conversely, unsupported Li-promoted copper produced a mixture of hydrocarbons and linear alcohols with differing chain growth probability factors (0.53 and 0.30, respectively).[57] In general, the chain growth probability factor, α, originates from applying the Schulz–Flory equation (eq 5) to an observed product distribution (where w_n is the weight fraction of a product with n carbon atoms).

$$w_n = n(1-\alpha)^2\alpha^{n-1} \quad (5)$$

2.1.2. Nonalkali Promoters. One of the nonalkali promoters is manganese.[6,48] Stiles et al.[6] recommended that the amount of Mn be tightly controlled because it may decrease the total productivity due to catalyst deactivation. Slaa et al.[48] reported that the addition of Mn increased higher-alcohol production only at 300 °C, whereas at lower temperatures, Mn enhanced methanol selectivity and decreased higher-alcohol selectivity, as shown in Table 2. Addition of K to this catalyst decreased selectivity to higher alcohols, CO_2, and methane, but increased methanol selectivity. Chen et al.[58] found that at 230 °C, Mn added by coprecipitation to a Cu/Zn/Al catalyst increased methanol yield by 5–10%; no other products were observed. The report also described coimpregnated Cu/Mn/Al catalysts, on which methanol yield showed a maximum with Mn loading while dimethyl ether yield increased with increasing Mn content. In a study of dimethyl ether synthesis at 245 °C, Fei et al.[59] showed that Mn can also work synergistically with zinc to promote dehydration of methanol on Cu/zeolite-Y. Ethanol and higher alcohols were not considered.

Other nonalkali promoters include the lanthanides. Ce (added by coprecipitation) was found to enhance selectivity toward isobutyl alcohol on $Cu/ZnO/Al_2O_3$ catalysts.[42,48] A small amount of Ce (2 wt %) was reported to enhance selectivity toward isobutyl alcohol, slightly decrease ethanol selectivity, and have no effect on methane and CO_2 formation. Higher amounts (4 wt % Ce) had an adverse effect on higher-alcohol formation and increased undesired reactions, such as methanation and CO_2 formation.[42]

Bourzutschky et al.[60] studied a set of catalysts, including Cu/SiO_2 unpromoted and promoted with La_2O_3, and Cu/La_2O_3 unpromoted and promoted with MnO_2. They found that adding La_2O_3 to Cu/SiO_2 increased both catalytic activity and the selectivity to alcohols. However, methanol was the dominant alcohol on $Cu/La_2O_3/SiO_2$; the only higher alcohol was isobutyl alcohol, which was observed in trace amounts. The addition of MnO_2 to Cu/La_2O_3 reduced the activity and overall selectivity to higher alcohols, but slightly increased the ethanol selectivity.

Table 2. The Selectivities of Promoted Catalysts Compared to Those of a Nonpromoted Catalyst at Different Temperatures[a]

	T (°C)	none	4% Mn	4% Mn + 0.5% K	4% Ce
activity (mmol/g/h)	260	7.2	6.7	5.3	7.1
	280	8.9	7.9	6.5	8.3
	300	9.9	9.2	6.9	–
S_{tot} (C atoms converted)	260	85.9	92.5	93.7	84.3
	280	74.4	77.4	84.1	68.2
	300	44.9	51.0	58.5	–
S_{ha} (C atoms converted)	260	5.5	4.9	1.1	6.6
	280	15.2	9.5	4.2	19.9
	300	14.2	17.0	13.7	–

[a] P = 40 bar; H_2/CO = 1; 1 g of catalyst; flow rate = 1.92 L/h. S_{tot} gives the total selectivity to all alcohols (including methanol); S_{ha} gives the selectivity to higher alcohols.[48]

Lin et al.[61] studied the addition of other promoters, such as Fe, Co, Ni, and Cr, to $Cu/ZnO/Al_2O_3$ catalysts. On the basis of the yields of C_2–C_4 alcohols, they concluded that Fe_2O_3 was the most suitable additive. The most favorable CuO/Fe_2O_3 ratio for yield of C_2–C_4 alcohols was ~1.5. Higher Fe_2O_3 content led to formation of ethers and hydrocarbons.

Fe and Ni have also been used to promote $CuMnZrO_2$ catalysts.[29–31] Xu et al.[29,30] reported that the Fe addition increased the selectivity to C_2^+ alcohols, CO_2, and hydrocarbon and decreased the selectivity to methanol with an overall reduction in catalytic activity. Similar results were reported when Ni was used as a promoter, but in this case, catalytic activity improved.[31] Addition of Co was similar to Ni with regard to catalytic activity; however, higher-alcohol selectivity increased. This was ascribed to the stronger chain growth ability of Co compared with Ni. Unlike the findings of Lin et al. reported above, the addition of Fe produced much less higher alcohols and more hydrocarbons than the Ni- and Co-modified catalysts.

When 40% $CuLa_2Zr_2O_7$ was modified by even a small amount of impregnated Co, the methanol yield decreased drastically.[62] As the Co content increased, so did the yields of higher alcohols and, to a greater degree, hydrocarbons; a loading of 5% Co was offered as a reasonable compromise between activity and selectivity. The means by which Cu interacts with promoters such as

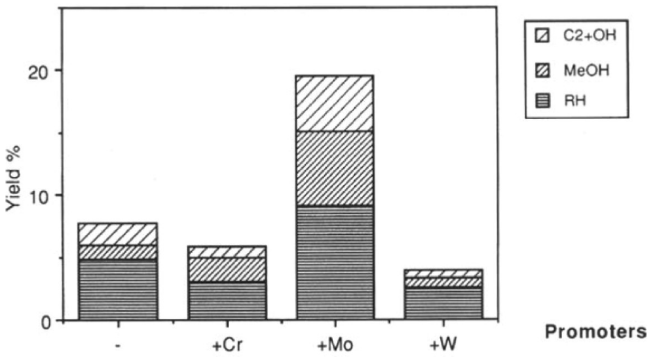


Figure 8. Promotional effect of Cr, W, and Mo on a Co/$CuLa_2Zr_2O_7$ catalyst. Catalyst 3% (Cr, Mo, W) + 5% Co/50% $CuLa_2Zr_2O_7$. Reaction conditions: CO + $2H_2$ gas flow 4 L h^{-1} $g_{cat}{}^{-1}$, $P = 6$ MPa, $T = 270$ °C[62] (reprinted from ref 62, copyright 1995, with permission from Elsevier).

Co to produce higher alcohols has been a source of controversy. Bailliard-Letournel et al.[63] claimed, on the basis of spectroscopic evidence, that a CoCu surface alloy was responsible for the selectivity to higher alcohols. Baker et al.[64] believed the role of Cu was to moderate the hydrogenation activity of Co to suppress hydrocarbon formation, without necessarily participating in the reaction itself.

When Mo alone was added to a similar system (50% $CuLa_2Zr_2O_7$), it deactivated the catalyst for methanol synthesis without increasing the formation of higher alcohols.[62] In contrast, addition of Mo to a 5% Co/50% $CuLa_2Zr_2O_7$ formulation increased the yield of higher alcohols, with both activity and selectivity attaining a maximum at 3% Mo. The increased yields from Mo addition were attributed to the hydrogen absorption capability of Mo oxides. In contrast to Mo, the other Group VIB elements (Cr and W) did not increase the yield of higher alcohols (Figure 8).

Mixtures of both alkali and nonalkali promoters can also be promising.[23] For example, Hofstadt et al.[46] used nonalkali promoters such as MnO, Cr_2O_3, and ThO_2 with methanol synthesis catalysts ($CuO/ZnO/Al_2O_3/K$) to increase the selectivity toward higher alcohols. MnO was particularly found to improve the selectivity toward ethanol. Cr_2O_3- and ThO_2-promoted catalysts favored the formation of propanol and butanol, respectively. The promoters were assumed to influence the Cu^+/Cu^0 ratio and thereby change the balance of surface species as described in Section 2.10.

Inui et al.[65,66] found that physically mixing Fe/Cu/Al/K and Cu/Zn/Al/K catalysts increased the space time yield of ethanol from CO_2 hydrogenation over that of the Fe-based catalyst alone. When alumina-supported Pd was combined with a mixture of Cu/Zn/Al/K and Ga-promoted Fe/Cu/Al/K, the ethanol space time yield increased by 48%. This catalyst mixture gave an ethanol yield more than twice the value expected on the basis of a Schulz–Flory plot. Pd and Ga were added to optimize the oxidation state of the catalyst by hydrogen spillover and inverse spillover, respectively.

It can be inferred from the above findings that the role of a promoter is dependent on reaction conditions, catalyst composition, and support; nevertheless, promoters do play an important role in enhancing ethanol and higher alcohol selectivity. An optimum amount of promoter is always necessary to achieve this goal.

2.2. Effect of Preparation Variables and Methods in Conventional Synthesis. The ability of a promoter to modify a catalyst also depends on how it has been added to the catalyst[30,42] and subsequently conditioned. For example, Slaa et al.[42] reported that the addition of Mn to Cu/ZnO by coprecipitation (Mn was present throughout the catalyst) increased methanol and methane selectivities and slightly increased isobutyl alcohol but decreased ethanol formation. However, Mn addition by impregnation (with Mn primarily at the surface) had no effect on ethanol and methane formation and increased the selectivity toward CO_2 and isobutyl alcohol. They also reported that when Ce was present at the surface, the catalyst was more selective toward alkanes and CO_2. When it was present in bulk, the catalyst was more selective toward isobutyl alcohol.

The performance of Cu/Co/Zn/Al and Cu/Co/Cr catalysts was found to depend on preparation variables, such as calcination temperature, atmosphere,[32,52,67,68] and precipitation pH.[69] For example, with increasing calcination temperature, Cu/Co/Cr catalysts prepared from citrate complexes showed decreasing activity for oxygenate synthesis but almost constant hydrocarbon yield. The carbon number distributions of alcohols and hydrocarbons were not much affected.[52] Mahdavi and Peyrovi[68] found that calcination of coprecipitated Cu/Co/Zn/Al at moderate temperatures (350–450 °C) with air flow was necessary to generate active, selective catalysts for synthesis of $C_2{}^+$ alcohols. Calcination at 600 °C with air flow or at 450 °C without air flow produced catalysts with reduced copper surface areas, activities, and $C_2{}^+$ alcohol selectivities.

Among impregnated $CuCo/SiO_2$ catalysts, those prepared by coimpregnation showed higher selectivity and space time yield to $C_2{}^+$ alcohols than those prepared by stepwise impregnation.[70] Anchoring of a bimetallic cyanide complex to alumina led to higher $C_2{}^+$ alcohol selectivity, compared with a catalyst prepared by impregnation of copper and cobalt nitrates.[71]

When a $CuO/ZnO/SiO_2$ catalyst was physically mixed with $Rh/Mn/Li/SiO_2$, the acetaldehyde produced by the latter was hydrogenated to ethanol by the former, and hydrocarbon yield from $Rh/Mn/Li/SiO_2$ was suppressed.[72] Rhodium was responsible for initial oxygenate formation and copper for further hydrogenation, but an intimate degree of mixing led to poisoning. A coimpregnated $Rh/Mn/Li/Cu/Zn/SiO_2$ catalyst was completely inactive for CO hydrogenation.

2.3. Novel Preparation Methods. Generally, heterogeneous catalysts are prepared by conventional methods, such as coprecipitation and impregnation. To further enhance the performance of these catalysts, the ability to tailor the atomic level morphology is essential. Therefore, it has become necessary to explore novel catalyst preparation methods that can provide some control over the morphology and structure of these catalysts that cannot be achieved with conventional methods. To further improve the activity and selectivity toward ethanol and higher alcohols, nonconventional catalysts, such as Co/Cu based perovskites,[49,51,73–75] Co/Cu[76,77] supported on carbon nanotubes, Co/Cu nanoparticles,[78] and sol–gel-derived Cu/ZrO_2,[79] have been investigated.

One method that has been explored is based on the application of a novel glow discharge plasma treatment to coprecipitated Cu/Co/Zn/Zr and coimpregnated $CuCo/\gamma\text{-}Al_2O_3$ catalysts.[80–82] The plasma post-treatment resulted in more uniform, disperse particles capable of adsorbing more CO than the conventional preparation methods alone. They also gave higher conversion, alcohol yield, and $C_2{}^+$ alcohol selectivity. For comparison, the

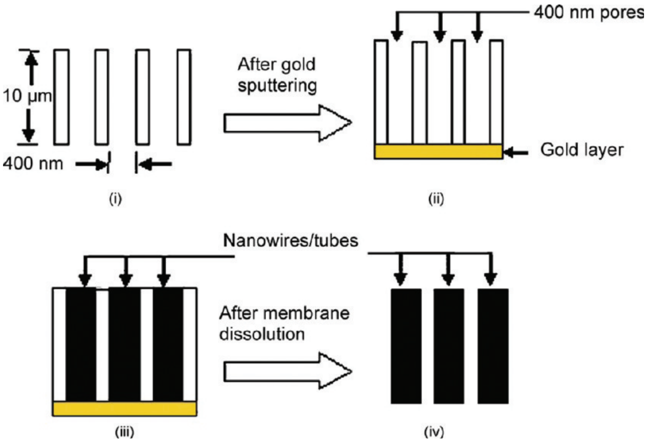


Figure 9. Schematic for nanowires fabrication (i) cross-sectional view of cylindrical pores in a polycarbonate membrane, (ii) gold-sputtered membrane, (iii) filled pores after electrodeposition, and (iv) nanowires after dissolution of membrane in CH_2Cl_2[84] (reprinted from ref 84, copyright 2009, with permission from Elsevier).

Cu/Co/Zn/Zr catalyst was also prepared by reverse coprecipitation, in which a solution of the catalyst precursors was added to an excess of the precipitating solution under ultrasound irradiation.[80] An additional comparison was made, using a conventionally coprecipitated sample prepared by simultaneous addition of the precipitating agent and metal ion solution to the same beaker. Compared with conventional coprecipitation, reverse coprecipitation increased the specific surface area by 52%; improved the dispersion, uniformity, and surface enrichment of the active components; increased the alcohol yield; and increased the CO conversion and higher-alcohol content of the total alcohols.

Assabbane et al.[83] used an unconventional electrochemical method to prepare Cu/Zn and Cu/Zn/Co catalysts for liquid-phase synthesis of methanol and higher alcohols. The Cu/Zn catalyst was prepared by reducing a solution of copper acetylacetonate under controlled potential at a platinum cathode in the presence of a sacrificial zinc anode. This catalyst produced methanol selectively. The cobalt-containing catalyst (Cu/Zn/Co = 0.4/0.08/1) was produced by reducing a solution of cobalt acetylacetonate under controlled potential at a platinum gauze with a soluble brass anode. The highest selectivities for oxygenate and ethanol were 53.4% and 13.6% C, respectively, at 255 °C and 50 bar. If the conditions of reduction were such that the Cu/Zn/Co ratio became 4/2.4/1, the catalytic results were similar to those obtained from the Cu/Zn catalyst.

Gupta and Spivey[84] have electrochemically synthesized nanowire/tube catalysts of Cu/ZnO (Figure 10, showing nanowires only) and Mn/Cu/ZnO using a template synthesis method. The technique is depicted in Figure 9. A membrane is coated and placed in an electrolyte solution containing ions of interest, and then an appropriate current is applied to deposit these ions in the pores of the membrane. The membrane is dissolved using methylene chloride. Mn/Cu/ZnO catalysts with a wire morphology seem to be promising, with a 15.7% C selectivity for higher alcohols at low reaction pressure (10 bar). Cu/ZnO catalysts with a tubular morphology showed very low selectivity toward alcohols due to very low Cu content (2 wt %). Therefore, optimization of electrochemical conditions is required to increase the amount of copper and compositional uniformity and to take advantage of the higher surface area of the tube morphology. Addition of manganese to Cu/ZnO nanowires improved the selectivity toward C_2-C_4 alcohols from 5.4% to 15.7% C while reducing methane and methanol formation.

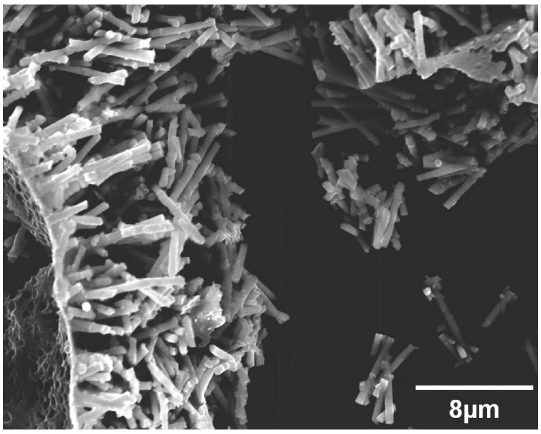


Figure 10. SEM micrograph of nanowire catalysts[84] (reprinted from ref 84, copyright 2009, with permission from Elsevier).

Microemulsions can provide localized reaction environments for the synthesis of fine particles. In an effort to prepare catalysts with small metal particles interacting strongly with the support, Su et al.[85] used a method involving water-in-oil microemulsions. Droplets of $Fe(NO_3)_3$ or $Cu(NO_3)_2$ aqueous solution were stabilized in a continuous toluene phase by the surfactant dodecylbenzenesulfonic acid sodium. After addition of NaOH, the pH was adjusted to 2.0−2.8 with HNO_3 to separate the organic sol. Following collection of this layer, the solvent was removed and "ultrafine" particles of $Fe(OH)_3$ or $Cu(OH)_2$ were obtained. The mean size of $Fe(OH)_3$ particles was 17.1 nm, whereas that of $Cu(OH)_2$ particles was 6.65 μm. Impregnation of activated Al_2O_3 into the organic sol of $Fe(OH)_3$ and $Cu(OH)_2$, followed by calcination, yielded the ultrafine catalysts. When CH_3COOK was also dissolved into the organic sol prior to impregnation (at a K loading of 1.6 wt %), the total alcohol yield and C_2^+ content of the alcohols reached 0.25 g mL^{-1} h^{-1} and 58.8 wt %, respectively. Without K loading, and at the same Al_2O_3 loading (88.61 wt %), these values were 0.154 g mL^{-1} h^{-1} and 59.8 wt %, respectively.

Conventional catalyst preparation techniques do not typically control metal particle size and shape with the type of atomic-level precision that is desirable. Novel wet chemical methods using nanoparticles can help achieve this type of control. To take advantage of the high surface area of nanomaterials, Subramanian et al.[78] synthesized Co/Cu nanoparticles by a wet-chemical method. Two types of nanoparticles were prepared: (1) Co core/Cu shell and (2) Co/Cu mixed nanoparticles. Mixed metal catalysts had higher selectivity toward ethanol and higher oxygenates. Core/shell (Co core and Cu shell) catalysts were more active but less selective to ethanol. The highest selectivity toward ethanol was 11.4% C. These catalysts seem to be promising owing to their high surface area and low pressure requirement (20 bar). Further changes in morphology that can enhance the mutual interaction of reduced Co and Cu[49] may prove these catalysts more suitable for ethanol and higher-alcohols synthesis.

Using a sol−gel method, Ma et al.[86] prepared two types of catalysts. A solution of zirconium *n*-propoxide and diglycol dissolved in ethanol was mixed with another ethanol solution containing $Cu(NO_3)_2$, $Mn(NO_3)_2$, and $Ni(NO_3)_2$. The gel was formed by stirring the mixture. One part was dried at 120 °C for

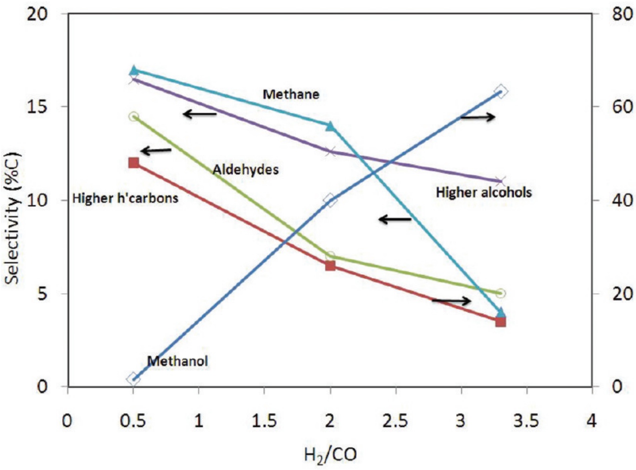


Figure 11. Effect of H_2/CO ratio on product selectivities on a K/Cu/ZnO/Al_2O_3 catalyst.[34]

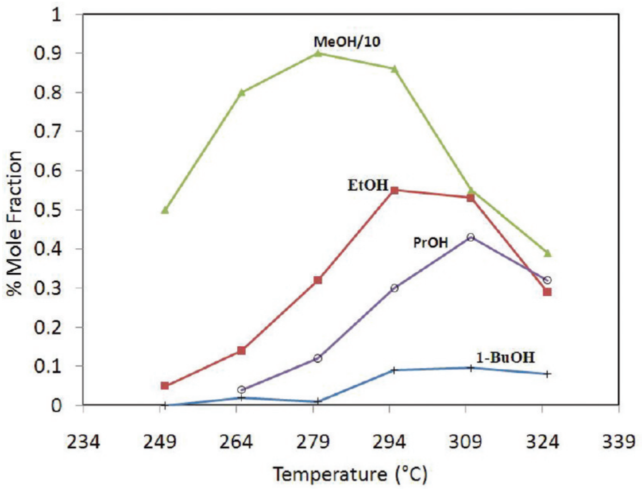


Figure 12. Effect of the reaction temperature on the product distribution observed over the Cs/Cu/Zn/Cr_2O_3 catalyst. Operating conditions: $H_2/CO = 0.8$, GHSV = 9000 Ncc/h/g_{cat}, $P = 75$ bar.[40]

12 h and calcined at 350 °C for 3 h, and it was named as noncrystallized CuNiMnZrO_2. The second part was sealed in an autoclave with ethanol as the medium, maintained at 210 °C for 24 h, then dried and calcined as described above, and named as crystallized CuNiMnZrO_2. The noncrystalline sol−gel-derived CuNiMnZrO_2 catalyst gave much higher CO conversion and isobutyl alcohol selectivity at both 340 and 380 °C, compared with the crystallized one. The crystallized catalyst showed lower dispersion, less uniform composition, and Ni enrichment at the surface, leading to methanation and high hydrocarbon selectivity. The results show how crystallization can affect the performance of catalysts.

2.4. Effect of H_2/CO Ratio. The H_2/CO feed ratio has a significant effect on higher-alcohol selectivity.[26] H_2/CO ratios ranging from 0.45 to 3[24,26,27,29−31,34,38,41,42,44,48,50] have been reported in the literature. Unless the experiments are carried out at differential conversions, the H_2/CO ratio within the reactor can change with reactor position because of the water−gas-shift reaction (WGS).[20] Usually, overall activity decreases with decreasing H_2/CO ratio.[43,49,52] In general, low H_2/CO ratios favor coke formation and C−C chain growth and, therefore, selectivity toward higher alcohols. Higher ratios favor methanol synthesis[20,26,40,87] and may either increase[49] or decrease[43] selectivity to methane.

In an effort to understand the effect of feed composition on higher-alcohol synthesis, Boz et al.[34] varied the H_2/CO ratio (0.5, 2, 3.3) using a K-promoted Cu/ZnO/Al_2O_3 catalyst. Selectivity to higher alcohols, hydrocarbons, and aldehydes was highest at the lowest H_2/CO ratio, whereas greater H_2/CO ratios favored methanol synthesis (Figure 11). Similar trends were found by other researchers.[20,28,88]

A kinetic study of a Cu/ZnO catalyst containing Zr, Fe, Mo, Th, and Cs was conducted at low conversion, such that reverse reactions were negligible, in a gradientless stirred tank reactor.[89,90] The data fit a simple power law expression (eq 6).

$$r = k_0 \exp(-E/RT) p_{H_2}^{n} \tag{6}$$

The reaction rate was independent of CO partial pressure. The reaction order, n, in H_2 was 2 for methanol synthesis and 1.5 for higher-alcohol synthesis. If other variables, such as temperature and total pressure, are fixed, these reaction orders are consistent with the observation that low H_2/CO ratios favor higher alcohols and higher ratios favor methanol synthesis.

2.5. Effect of Pressure. Higher-alcohol synthesis is thermodynamically favored at higher pressures.[20] Nevertheless, the effect of pressure on reaction kinetics is also catalyst specific to some extent.[6] Pressures as low as 10 bar[84,91] and as high as 400 bar[34] have been reported in the literature. In general, the average range is about 40−100 bar.[25,27,29,31,32,35,38,41,42,44−48]

Unfortunately, there are very few studies on the effect of pressure on higher-alcohol synthesis. Maxima in alcohol and hydrocarbon productivity have been observed, both at around 55 bar, with increasing syngas partial pressure ($H_2/CO/He$ = 8/4/3).[49] Only at higher pressures (greater than about 60 bar) did the total alcohol productivity exceed that of hydrocarbons. Stiles et al.[6] studied the effect of pressure in a range of 82−310 bar. The optimum operating pressure was 172 bar, on the basis of productivity ((mL alcohol/mL catalyst)/h). These pressures suppressed methanation and controlled distribution of higher alcohols for the purpose of directly adding it to gasoline as a fuel additive. It was also found that as the pressure increased, the productivity of higher alcohols increased, but to a lesser extent than methanol. Similar results were found on a Cu/Co_2O_3/ZnO/Al_2O_3 catalyst by Mahdavi et al.[43] They reported that increasing pressure from 40 to 70 bar enhanced total alcohol selectivity and decreased methane selectivity. It also increased the selectivity to higher alcohols and CO conversion.

2.6. Effect of Temperature. Higher-alcohol synthesis is usually favorable only in a narrow range of temperatures, 280−310 °C.[23,24,26,29,30,33−35,38,40−43,50] Careful investigaton of literature reveals that the best temperature range for higher-alcohol synthesis on most of the Cu-based catalysts is 280−300 °C. However, temperatures as high as 350,[46] 310−370,[92] and 375 °C[6] were found to be suitable for some catalysts. The main problems associated with the higher temperatures are (1) instability of some oxygenates at temperatures above 450 °C,[20] (2) formation of CO_2 and methane at temperatures above 280 °C,[6,23,31] and (3) deactivation of the catalyst due to sintering.[40,44,45].

In general, higher temperatures are needed for enhanced selectivity toward higher alcohols[6,26,34,40,44,45] than toward methanol.[26,34,40,44] Majocchi et al.[40] reported that the selectivity to all alcohols goes through a maximum with temperature (Figure 12) because at higher temperatures, CO_2 formation dominates. A similar maximum in higher-alcohol selectivity was reported by others.[23,31,33,48] In the range 260−330 °C, Apesteguía et al.[93,94] found that methanol selectivity decreased, isobutyl alcohol selectivity increased, and C_2^+ linear alcohol selectivity passed through a maximum. They explained these findings by assuming that methanol synthesis was close to equilibrium, isobutyl alcohol synthesis was under kinetic control, and linear alcohols were intermediates in isobutyl alcohol synthesis.

A few studies have tried to exploit the different temperature effects on the selectivities of various alcohols. Beretta et al.[95] optimized a Cs-promoted $Cu/ZnO/Cr_2O_3$ bed at 325 °C for the production of short-chain alcohols, which were then converted to isobutyl alcohol over a separate, Cs-promoted ZnO/Cr_2O_3 bed at 405 °C. The productivity of isobutyl alcohol by the double-bed arrangement was 40% higher than that obtained with an equal amount of $Cs/Cu/ZnO/Cr_2O_3$ alone. In a variation on the same work, Burcham et al.[96] used two beds of Cs-promoted $Cu/ZnO/Cr_2O_3$ maintained at different temperatures (325 and 340 °C). The setup resulted in a 42% increase of the isobutyl alcohol yield over that of Beretta et al. The improvement was ascribed to the higher activity of Cu-containing ZnO/Cr_2O_3 compared with the Cu-free catalyst, enabling operation of the second bed at lower temperature where the methanol intermediate had a higher equilibrium concentration.

Temperature control is required during an actual operation because main and side reactions during CO hydrogenation are highly exothermic ($\Delta H^\circ = -90$ to -200 kJ/mol).[7] Slurry reactors are purported to offer better heat removal and temperature control than conventional fixed-bed microreactors,[5,18,97] but only a few studies[98−100] have explored this possibility. Chaumette et al.[100] demonstrated that a Cu/Co/Zn/Al/Na catalyst gave higher selectivity to alcohols when tested in a slurry reactor than in a fixed-bed reactor, probably due to the prevention of hot spots. On $Cs/Cu/ZnO/Al_2O_3$, Breman et al.[98] showed that the presence of *n*-octacosane as slurry liquid influenced the composition of the products by increasing the C_{n+1}-to-Cn ratio for 1-alcohols with $n \geq 2$ and for 2-methyl-1-alcohols with $n \geq 4$. They mentioned excellent temperature control as a potentially important advantage of the gas−slurry process, but also suggested the product distributions were mainly influenced by interactions between adsorbed species and the liquid phase.

2.7. Effect of Space Velocity. In general, low space velocities or higher contact times were found to be favorable for higher-alcohol synthesis,[23,43,46] which indicates that higher alcohols are formed at a slower rate than methanol[33,34] or in several intermediate steps.[49,93] Low space velocities are also favorable for high conversion.[34,43]

Over a K-promoted $CuO/ZnO/Al_2O_3$ catalyst, Boz et al.[34] observed that a decrease in space velocity increased higher-alcohol, methane, and CO_2 selectivities and decreased methanol selectivity. Interestingly, the selectivity toward aldehydes goes through a maximum.

The effect of space velocity has been studied by Xu and Iglesia on product concentrations obtained from reaction of a $^{13}CO/H_2/^{12}CH_3OH$ mixture on a 2.9 wt % $Cs/Cu/ZnO/Al_3O_3$ catalyst (Figure 13).[101] Under the applied conditions on this catalyst, methanol concentration was far from equilibrium and increased with increasing contact time. The concentration of ethanol, which could undergo secondary condensation reactions, increased linearly at low contact times and more slowly at higher contact times. The concentration of isobutyl alcohol, a terminal product formed by secondary reactions, increased slowly at low contact times and faster at high ones.

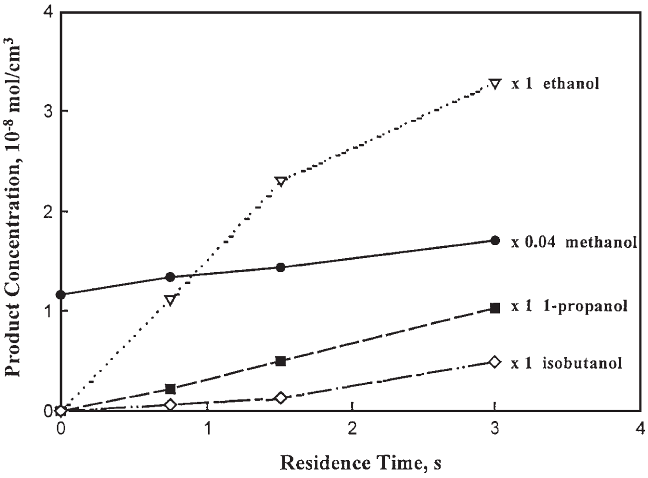


Figure 13. Effect of residence time on product concentration for 2.9 wt % $Cs/Cu/ZnO/Al_2O_3$. Operating conditions: $T = 538$ K, $P = 2.0$ MPa, $^{13}CO/H_2/^{12}CH_3OH = 100/100/1.3$[101] (reprinted from ref 101, copyright 1999, with permission from Elsevier).

2.8. Effect of CO_2 in the Feed Gas. Syngas generated from biomass contains up to 25% of CO_2. Although CO_2 can be captured using CaO,[102] it would be preferred in an industrial setting to synthesize catalysts that can covert CO_2 to higher alcohols in the presence of CO and H_2 because this would eliminate the CO_2 removal step upstream.[18]

Unfortunately, CO_2 typically has a negative impact on higher-alcohol synthesis, but has a promoting effect on methanol formation.[4,6] Evidence exists that CO hydrogenation and CO_2 hydrogenation occur by two independent pathways: the CO_2 route is preferred for methanol synthesis,[103,104] and the CO route can lead to methanol and higher alcohols.[105,106] Some proposed mechanisms are described in Section 2.10. However, in some cases, it is reported that CO_2 inhibits the formation of both methanol and higher alcohols [33,54] or of only higher alcohols.[32]

Another drawback of CO_2 addition is that it enhances methanation.[6,33] Hilmen et al.[54] ascribed this to high oxygen coverage and therefore oxidation of reduced Cu atoms available for methanol and higher-alcohol synthesis. Higher-alcohol productivity (g/kg/h) is also decreased by neutralization of basic sites (responsible for chain growth) by CO_2. Another possible explanation could be the blockage of active sites by reversible preferential adsorption of CO_2.[33]

However, on some catalysts, low levels of CO_2 (2−6%) were found to increase higher-alcohol productivity (mol/L/h),[34] yield,[45] and rate of formation (mg/g/h).[24] For example, Calverley and Smith[45] reported that CO_2 is directly involved in the synthesis of higher alcohols. Addition of CO_2 enhanced higher-alcohol yield when the loading was 0.5% K_2CO_3 but was not beneficial at higher K loading (4%). Higher-alcohol yield passed through a maximum (4% CO_2) for both unpromoted and promoted catalysts; similar behavior was observed for methanol. Because of these similarities, it can be said that CO_2 also participates in higher-alcohol synthesis, since CO_2 was already believed to participate in methanol synthesis.[107,108] It appears that copper/

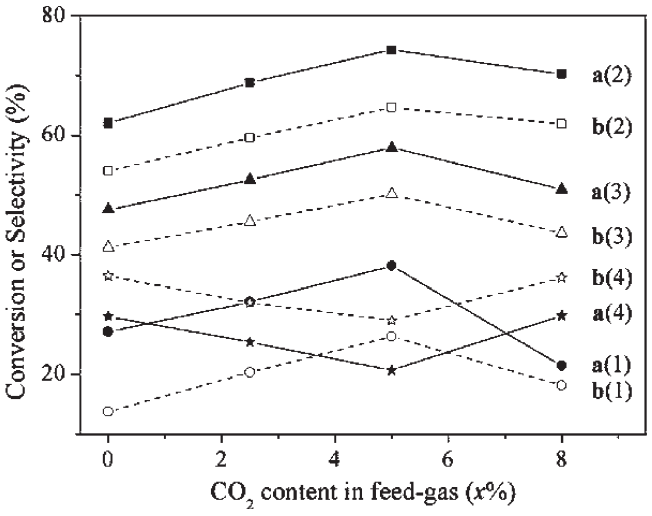


Figure 14. Effect of CO_2 content on the performance of (a) coprecipitated Co_3Cu_1 with 11% carbon nanotubes and (b) coprecipitated Co_3Cu_1. CO_2 affects (1) CO conversion, (2) total oxygenate selectivity, (3) C_2-C_8 alcohol selectivity, and (4) total hydrocarbon selectivity. Operating conditions: $T = 300$ °C, $P = 50$ bar, GHSV = 7200 mL/h/g, $V(H_2)/V(CO)/V(CO_2)/V(N_2) = (47.5 - x/2)/(47.5 - x/2)/x/5$. Selectivities are carbon-based[77] (reprinted from ref 77, copyright 2009, with permission from Elsevier).

alkali interface sites convert CO to methanol and higher alcohols, and Cu sites convert CO_2 to methanol and higher alcohols.[45]

Even if the rate of formation of higher alcohols increases in the presence of CO_2, this does not guarantee the improved *selectivity*. Sometimes the rate of hydrocarbon formation increases much more rapidly in the presence of CO_2.[32] In other cases (as in Figure 14), however, optimizing the feed composition leads to minimum hydrocarbon selectivity and maximum conversion, total oxygenate selectivity, and higher-alcohol selectivity.[77] In general, the effect of CO_2 on catalytic performance is quite complex and not easily predictable. It seems to depend not only on the CO_2 level but also on such variables as catalyst composition and reaction temperature.[105]

2.9. Role of Support. Generally speaking, the support acts to[109]

- stabilize the active species and promoters;
- promote hydrogen or oxygen donation or exchange;
- modify the dispersion, reducibility, and electron-donating or -accepting effects of metal particles .

In CO hydrogenation, interaction of support and active components can significantly alter selectivity to ethanol and higher alcohols. For example, Nunan et al.[38] showed that ethanol yield remained almost constant with Cs loading over Cu/Zn/Cr catalysts; however, it decreased[38] on Cu/Zn/Al. They also reported that a much higher level of Cs was needed for Cu/Zn/Cr catalyst than for Cu/Zn because Cr is acidic in nature, and therefore, more Cs is needed to neutralize this catalyst. $Cu/ZnO/Cr_2O_3$ produced more C_2^+ alcohols and hydrocarbons than $Cu/ZnO/Al_2O_3$, but the latter produced more total alcohols. However, at the reaction conditions used, both catalysts gave almost identical products.

In their studies of copper−cobalt catalysts (Table 3), Mouaddib et al.[91,110] found that those supported on MgO yielded predominantly methanol; those on TiO_2, CeO_2, or La_2O_3 produced mainly hydrocarbons; and those on ZrO_2 or SiO_2 were more selective than the others toward higher alcohols. By comparing the IR band areas of CO adsorbed on cobalt and on copper,[110] they explained the observed selectivities on the basis of different surface compositions induced by the different supports. For example, the surface of the CeO_2-supported catalyst was enriched in cobalt, which led to CO dissociation and chain growth to form hydrocarbons. The surface of the MgO-supported catalyst was enriched in copper and produced methanol. The ZrO_2-supported catalyst had a surface that contained both copper and cobalt, the combination of which favored CO insertion into growing hydrocarbon chains to give acyl species that could be hydrogenated to alcohols.

Table 3. Selectivities (%) at 250°C and 10 bar of Copper−Cobalt Catalysts Supported on Various Oxides[91]

	S^a		
support	hydrocarbons	methanol	C_2-C_5 alcohols
MgO	14	76	10
La_2O_3	57	35	8
CeO_2	63	22	15
TiO_2	75	12	13
ZrO_2	36	39	25
SiO_2	34	37	29

[a] S = selectivity.

Stiles et al.[6] added some of the aforementioned components (CeO_2, ZrO_2, SiO_2, and TiO_2) in the amount of 5% to CuZnMnCo catalysts stabilized by Al_2O_3 or Cr_2O_3. They observed that CeO_2, ZrO_2, SiO_2, and TiO_2 all increased methanation, but only CeO_2 and ZrO_2 also increased the higher-alcohol fraction.

Takeuchi et al.[111] also investigated the influence of support on Co/Cu/Zn catalysts. The catalysts supported on MgO or SiO_2 gave carbon selectivities to ethanol higher than 20% at 280 °C. Those on La_2O_3 (at 280 °C) and TiO_2 (at 250 °C) produced ethanol with carbon selectivities >15%. At 280 °C, Al_2O_3- and ZrO_2-supported catalysts gave high CO conversion—18% and 31%, respectively—but their ethanol selectivities were <10%. Cr_2O_3 and ZnO as supports resulted in increased selectivity to methanol and CO_2.

2.10. Reaction Pathways. There can be several reactions occurring in parallel during CO hydrogenation. Table 4 shows some of the main reactions.[7] Reaction "a" shows that a specific stochiometric combination of CO and H_2 produces alcohols and also the side product H_2O. Reaction "b" shows another stoichiometry produces alcohol and the side product CO_2. Reaction "c" is the water−gas shift reaction. Reactions "d" and "e" produce hydrocarbons. Reaction "f" produces aldehydes. The consecutive reactions "g", "h", and "i" produce esters, ketones, and β-alkyl oxygenated compounds. These consecutive reactions are favored at low H_2/CO ratios. None of the individual main and side reactions are thermodynamically limited in the operating temerature range (250−350 °C) other than methanol and the water−gas shift reaction.

Several mechanisms for the formation of ethanol and higher alcohols have been suggested in the literature,[4,18−20] and some of the main reaction mechanisms are discussed here. To find if the formation of methanol and higher alcohols are related, Elliott et al.[24,112] poisoned the methanol synthesis sites by adding cobalt. The poisoning reduced the activity of the catalyst by more than an order of magnitude. It also inhibited the formation of both methanol and higher alcohols, indicating that

Table 4. Reactions Occurring during CO Hydrogenation.[7]

Main Reactions

a. $nCO + 2nH_2 \longrightarrow C_nH_{2n+1}OH + (n-1)H_2O$

b. $(2n-1)CO + (n+1)H_2 \longrightarrow C_nH_{2n+1}OH + (n-1)CO_2$

difference (b-a):

c. $(n-1)CO + (n-1)H_2O \longrightarrow (n-1)CO_2 + (n-1)H_2$

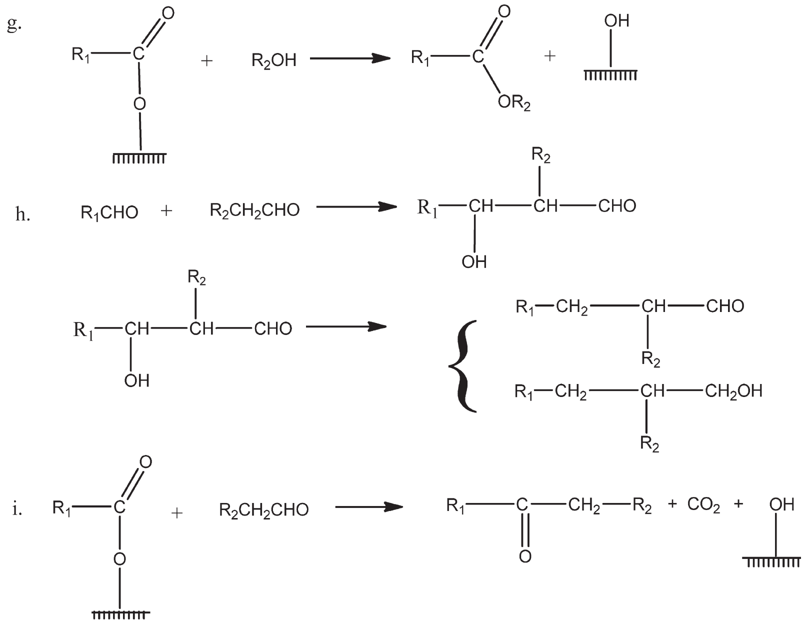
Side Reactions

d. $nCO + (2n+1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O$

e. $nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$

f. $nCO + (2n-1)H_2 \longrightarrow C_{n-1}H_{2n-1}CHO + (n-1)H_2O$

Consecutive Reactions



$R_1, R_2 = C_nH_{2n+1}$

their formation is related. Using these results alone, it could not be verified whether the decrease in formation of higher alcohols was due to (a) poisoning of catalytic sites that are active only for higher alcohols or (b) poisoning of sites responsible for methanol formation, with higher alcohols being then formed from a methanol intermediate. To determine this, they added methanol to the feed on a poisoned (with Co) catalyst. Still, the formation of higher alcohols on the poisoned catalyst was much lower than the unpoisoned one, suggesting that a decrease in the formation of higher alcohols was directly due to the poisoning of sites active for higher alcohols and not due to depleted methanol. This showed that syntheses of methanol and higher alcohols share a common active site or perhaps have the same intermediate.

In another study, over a $CuO/ZnO/Al_2O_3$ catalyst, Elliott and Pennella[50] suggested on the basis of experimental results in which they used labeled methanol that the precursor for the formation of methanol and ethanol is the same. The mechanism they suggested is shown in Figure 15. It shows that syngas (CO and H_2) or methanol could form an adsorbed C_1 species that serves as a common precursor for both methanol and ethanol, consistent with their previous study.[24]

$$\begin{tikzcd}
CO + H_2 \arrow[r, leftrightarrow] & I \arrow[r, leftrightarrow] \arrow[d] & CH_3OH \\
 & CH_3CH_2OH &
\end{tikzcd}$$

Figure 15. Paths for the formation of methanol and ethanol.[50]

Higher alcohols can form directly from methanol, as shown using labeled methanol with syngas over an alkali-promoted Cu-based catalyst.[27] Ethanol formation was studied by feeding ^{13}C-enriched syngas over Cs/Cu/ZnO. The results showed that methanol is a major source of both carbons of ethanol. This can be explained by the reaction sequences shown in Figures 16 and 17. CO activation occurs by Cs^+ and its OH^- ion forming an adsorbed formate species. Then, in the second step (rate-limiting), hydrogenation occurs to produce an adsorbed formyl intermediate. Hydrogenation of this formyl group results in formaldehyde in the third step, which then transforms to methoxide in step 4. Finally, hydration produces methanol and regenerates the surface hydroxyl in step 5.

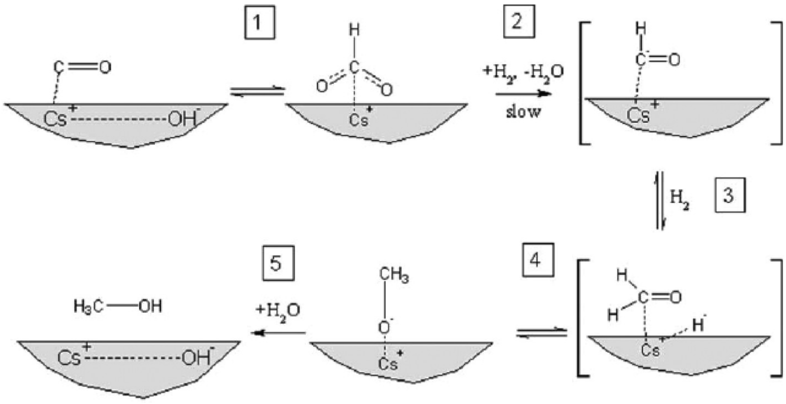


Figure 16. Mechanism for methanol formation from CO hydrogenation on Cu-based catalysts[4,27] (ref 4, reproduced by permission of The Royal Society of Chemistry).

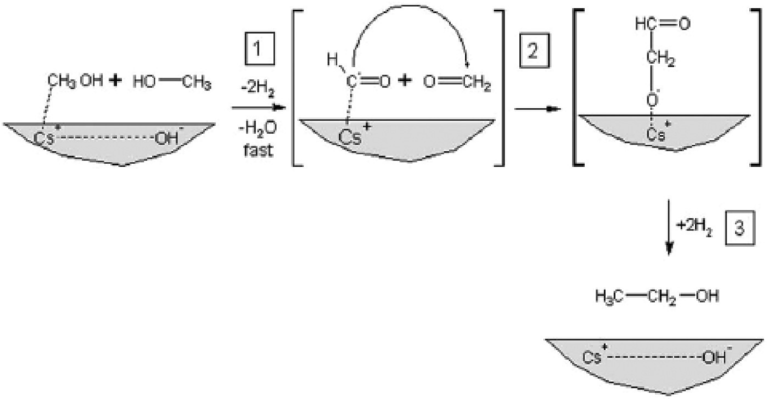


Figure 17. Mechanism for ethanol formation from CO hydrogenation on Cu-based catalysts[4,27] (ref 4, reproduced by permission of The Royal Society of Chemistry).

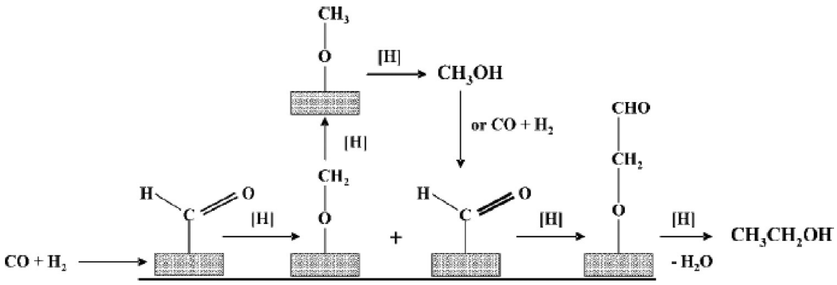


Figure 18. Ethanol formation by CO hydrogenation via a chain-growth mechanism over modified methanol synthesis catalysts[18] (reprinted with permission from ref 18, copyright 2008, American Chemical Society).

Figure 17 shows the reaction scheme for ethanol synthesis. The C−C bond in ethanol forms via coupling of the C_1 intermediates originating from methanol. First, one methanol molecule interacts with Cs^+ to form an adsorbed formyl group, and a second one forms formaldehyde after dehydrogenation via a surface hydroxyl. Then a nucleophilic attack of the adsorbed formyl on formaldehyde produces a C_2 precursor, and finally, this precursor leads to ethanol after hydrogenation.

The addition of probe molecules to a $CO + 2H_2$ flow over a Cu/ZnO/Al_2O_3 catalyst led Kiennemann et al.[113] to concur, for the most part, with the mechanism of Figure 17 for initial C−C bond formation. Addition of methanol yielded, in decreasing amounts, isobutyl alcohol, ethanol, and propanol. Addition of formaldehyde gave similar products, but the principal one was ethanol. Kiennemann et al. expressed one doubt regarding the mechanism of Figure 17: they suggested that formates should also be considered as intermediates, possibly through equilibrium with formyls.

A closely related mechanism for the formation of ethanol on modified Cu-based catalysts involves the formation of an adsorbed formyl species from adsorbed CO and H_2[18] (Figure 18). Then formaldehyde forms via the hydrogenation of this formyl species, with further hydrogenation producing methanol. Then

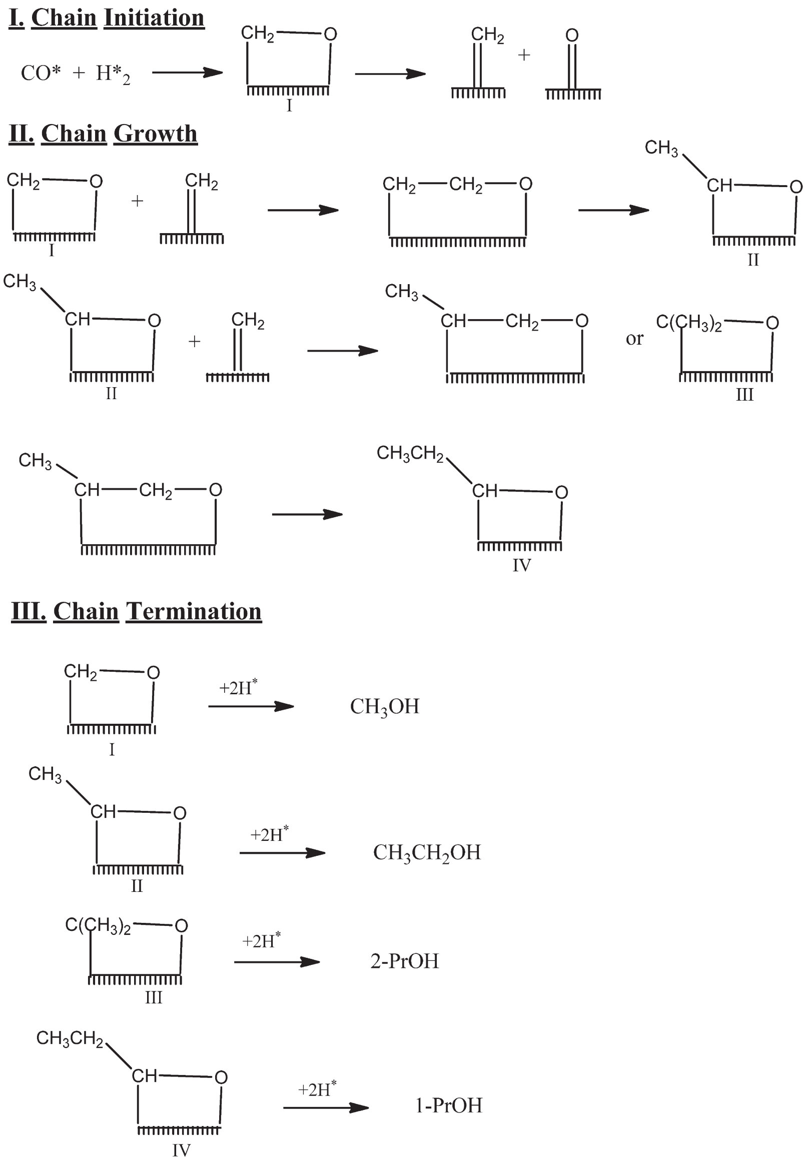


Figure 19. Mechanism for the formation of alcohols.[6,116]

the two adsorbed formyl species react to form a C—C bond, yielding an adsorbed acetyl species. Finally, ethanol is formed after the hydrogenation of the acetyl species.

On the basis of their isotopic tracer experiments using $^{12}CH_3OH/^{13}CO/H_2$, Xu and Iglesia[101] also concluded that ethanol forms by coupling of two methanol-derived intermediates on $Cs/Cu/ZnO/Al_2O_3$. On a $K/CuMgCeO_x$ catalyst, however, the predominant route to ethanol was hydrogenolysis of methyl acetate containing a methyl group from $^{12}CH_3OH$ and a doubly labeled (from ^{13}CO) acetate group. Thus, the C—C bond-forming step involved reaction of species formed directly from ^{13}CO (and H_2); methanol was initially much less involved.[101,114] These results underscore the important role of the catalyst in directing the reaction mechanism.

Baysar and Schrader[115] performed infrared spectroscopy of species adsorbed on unpromoted and K_2CO_3-promoted Zn/Cu/Cr oxide catalysts. At 285 °C and atmospheric pressure, adsorption of a CO/H_2 mixture, formaldehyde, or methanol resulted in methoxy and formate species on the surface. Adsorption of ethanol or acetaldehyde produced ethoxy and acetate species. The same surface species were observed whether the catalyst was promoted or unpromoted. However, the methoxy and formate species decomposed quickly in the presence of K_2CO_3, but the ethoxy and acetate species remained stable. The authors judged that ethoxy and acetate groups are probably intermediates in ethanol formation and that the latter might be assembled by interaction of a formate with a methyl group derived from a surface methoxy.

In studies of CO/H_2 and CO_2/H_2 reactions on Cu/Zn, trapping of surface species by Me_2SO_4[47] confirmed the presence of the following species, with their amounts in micromoles per gram:

- in $CO + 2H_2$: formate (2), acetyl (0.5), and acetate (0.5)
- in $CO_2 + 3H_2$: formate (5), acetyl (<0.1), and acetate (<0.1).

The chemical trapping study concluded that

- The CO pathway involves reduction of formate or formyl species through methoxy species to methanol. Insertion of

  CO into the methoxy species yields an acetate that can be hydrogenated to acetyl, then ethanol. (It should be noted that some authors contributing to this work later[113] rejected CO insertion into methoxy species as a mechanism for ethanol formation on Cu/Zn catalysts.)
- The CO_2 route proceeds by reduction of formate via methoxy intermediates to methanol. CO_2, due to its inability to undergo insertion and contribute to chain growth, typically leads to C_1 products, as discussed in Section 2.8.

On Mn-, Cr-, or Th-promoted $Cu/ZnO/Al_2O_3$ catalysts, Hofstadt et al.[46] suggested that a Cu^+/ZnO phase favors the formation of an oxygen-containing species (e.g., CH_3O), whereas metallic copper favors the formation of a methylene structure (CH_2). They assumed that promoters such as Mn, Cr, and Th can affect the Cu^+/Cu^0 ratio and thus favor the formation of C_2^+ alcohols by creating a balance between methylene and oxygen-containing surface species, both of which must be present. They suggested that methanol is formed by hydrogenation of CH_3O species, while CH_3O and CH_2 species combine to form a C_2 precursor, which is hydrogenated to produce ethanol.

An alternative scheme was suggested by Stiles et al.[6,116] and is shown in Figure 19. According to them, the active sites are lattice-deformity sites rather than metallic. In the chain initiation step, hydrogenation of CO forms an adsorbed formaldehyde. In the chain termination step, further hydrogenation of formaldehyde produces methanol. But if chain growth takes place, then acetaldehyde forms from the incorporation of a methylene radical into the formaldehyde, and then immediate hydrogenation of acetaldehyde produces ethanol. Methane is formed from hydrogenation of methylene radical (CH_2*).

On CuCoMoZn[117,118] and CuCoAlZnNa[119] catalysts, higher alcohols formed by addition of a C_1 oxygenated species (CO, formyl, or formate) to a surface hydrocarbon group to form an acyl or carboxylate intermediate, followed by hydrogenation (Figure 20). These catalysts did not incorporate C_2 oxygenates in the formation of higher primary alcohols. These mechanistic observations were based on addition of probe molecules, chemical trapping of surface species, and coupling experiments (e.g., C_1 oxygenate compounds with dichloro- or diiodoalkanes).

On Cs-promoted Cu/ZnO, Nunan et al.[41,120] found that lower alcohols were involved in the synthesis of higher alcohols. In particular, experiments involving ^{13}C-labeled methanol or ethanol (Figure 21) showed the effect of Cs on the mechanism of 1-propanol formation. On Cu/ZnO, this took place principally by linear chain growth of ethanol. Linear growth, instead of occurring by CO insertion reactions, involved nucleophilic attack by a formyl species on the α (C1) carbon of an adsorbed alcohol or aldehyde. Addition of Cs accelerated linear chain growth but also introduced a new, dominant path involving addition of a C_1 intermediate to the β (C2) carbon of ethanol, with retention of oxygen by the C_1 intermediate and loss of oxygen by ethanol. Isobutyl alcohol synthesis occurred by β addition of the C_1 intermediate to 1-propanol; oxygen could be retained by either the C_1 intermediate or the propanol reactant in this step.

Smith et al.[121] arrived at a kinetic model for Cs/Cu/ZnO catalysts that was consistent with the above mechanism.[41,120] The kinetic results of Breman et al.[122] on similar catalysts led to the conclusion that different mechanisms might be responsible for ethanol formation and subsequent linear chain growth.

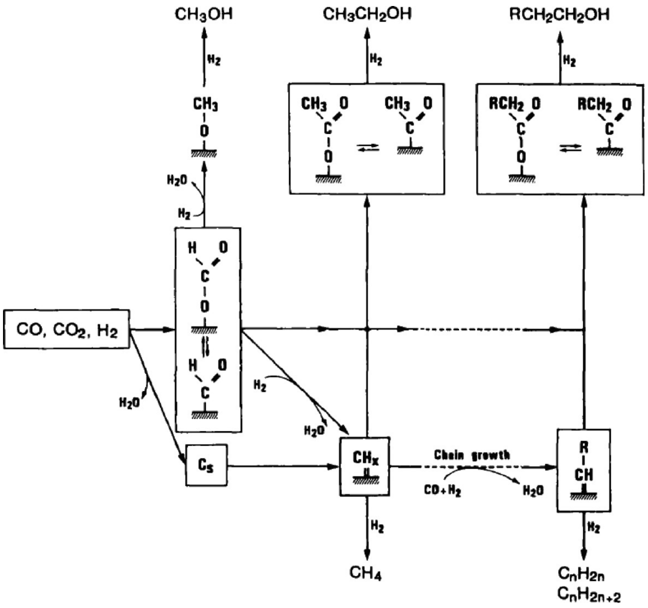


Figure 20. Mechanism of higher-alcohol synthesis on copper−cobalt-based catalysts[118] (with kind permission from Springer Science + Business Media, ref 118).

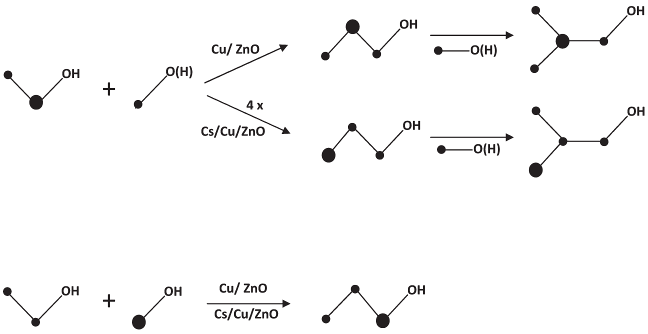


Figure 21. Synthesis of 1-propanol and isobutyl alcohol, investigated by ^{13}C labeling experiments (bold markers represent labeled carbons, identified in the products by ^{13}C NMR).[120].

Many of the foregoing mechanisms involve unpromoted or alkali-promoted Cu/ZnO-based catalysts. For these catalysts at least, conversion to C_2 species seems to be the limiting step in the higher-alcohol synthesis; conversion to C_3^+ species is more rapid.[4,18,87,123,124] However, the mechanism governing higher-alcohol synthesis depends greatly on the choice of promoters and additives, as evidenced by the different product distributions observed on different catalysts. Alkali-promoted methanol synthesis catalysts lead to branched alcohols, especially isobutyl alcohol,[87,125] whereas catalysts containing Co produce essentially linear alcohols that follow the Schulz−Flory distribution.[20,25,33,35,43,49,62]

3. CONCLUSIONS

The conversion of syngas to ethanol and higher alcohols is thermodynamically favorable but kinetically limited. Ethanol and higher-alcohol synthesis seems to be favored by a low H_2/CO ratio, low space velocity, temperatures in the range 280−310 °C, and pressures in the range 55−70 bar. CO_2 in the feed usually encourages the formation of methane and methanol at the expense of higher alcohols, although this is not always the case.

The choice of promoter plays an important role in determining whether ethanol is formed by, for example, coupling of methanol-derived C_1 intermediates or coupling of C_1 oxygenated entities with methylene species. Ethanol is believed to form via different mechanisms. Several authors believe that on alkali-promoted Cu/ZnO-based catalysts, methanol or a C_1 intermediate from methanol is a major source of both carbons in ethanol. It is also reported that methanol and higher alcohols have a common site and probably a common intermediate. Some believe ethoxy and acetate species are the intermediates for ethanol. It seems that on Mn-, Cr-, or Th-promoted Cu/ZnO/Al_2O_3 catalysts, Cu^+ favors the formation of CH_3O species, and metallic Cu favors CH_2 species. CH_3O and CH_2 species combine, leading to ethanol.

Because formation of appropriate reactive sites is critical, novel preparation methods giving improved control of particle size, catalyst dispersion, and morphology appear to be promising alternatives. These methods include plasma post-treatment, electrochemical, sol−gel, microemulsion, and wet chemical synthesis. However, more research is needed to fully understand how new methods change the atomic environment and reactive sites of a catalyst and, therefore, the activity and selectivity toward ethanol and higher alcohols.

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