Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas

James J. Spivey* and Adefemi Egbebi

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The selective catalytic conversion of biomass-derived syngas into ethanol is thermodynamically feasible at temperatures below roughly 350 °C at 30 bar. However, if methane is allowed as a reaction product, the conversion to ethanol (or other oxygenates) is extremely limited. Experimental results show that high selectivities to ethanol are only achieved at very low conversions, typically less than 10%. The most promising catalysts for the synthesis of ethanol are based on Rh, though some other formulations (such as modified methanol synthesis catalysts) show promise. (*Critical review*—173 references.)

1. Introduction

1.1 Biomass

Potential of biomass as an energy source. The use of biomass and other renewables to provide energy and chemicals is receiving increased attention because these resources can supplement existing supplies of raw materials and have less net environmental impact, according to some studies.[1] Worldwide, renewable energy sources (including biomass) account for about 19% of total energy usage,[2] and have the potential to supply 50% of world energy demand in the next century.[3] In the US, biomass supplied roughly 3% of a total energy demand of 98 quads in 2003,[4] and is projected to grow to at a rate of 1.5% per year through to 2025.[5,6]

Biomass gasification.Virtually all of the energy derived from biomass (98% by one estimate[7]) is currently produced by direct combustion. Gasification is an alternative that offers a number of advantages, *e.g.*, the potential for higher thermal efficiency.[8,9] Large scale biomass gasification plants ranging in size from 15–70 MW_{th}[10] are being developed in Europe, primarily for power generation.

Gasification is a thermochemical process in which biomass reacts with air (or oxygen) and steam to produce synthesis gas, a mixture consisting primarily of CO, CO_2, H_2, and H_2O (Fig. 1). This mixture can be used to produce a range of products using well-established technologies, such as fuels *via* the Fischer–Tropsch process.[11–14] However, the use of biomass-derived syngas to produce higher alcohols has received relatively little attention, despite the potential to produce valuable compounds such as ethanol.[13,15,16] Challenges that remain include novel catalytic reactor designs tailored to the typically smaller scale of biomass conversion

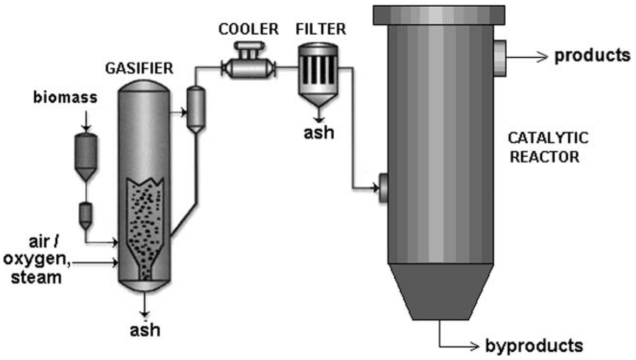


Fig. 1 Generic biomass gasification process.

Louisiana State University, Cain Department of Chemical Engineering, Baton Rouge, LA 70803, USA. E-mail: jjspivey@lsu.edu; Fax: (225) 578-1476; Tel: (225) 578-3690

James J. Spivey

James J. Spivey received BS and MS degrees in Chemical Engineering from NC State University and a PhD in the same field from Louisiana State University (1980). He is currently the James Shrivers Professor of Chemical Engineering at LSU, where his research interests focus on the use of heterogeneous catalysts for the conversion of syngas and low molecular weight hydrocarbons to both energy and higher value chemicals.

Adefemi Egbebi

Adefemi Egbebi was born in 1975 in Lagos, Nigeria. He received his BSc in Chemical Engineering from Obafemi Awolowo University, Ife, Nigeria in 1999. He moved to the Louisiana State University in Baton Rouge, USA where he his presently working on his doctoral degree on the conversion of biomass-derived syngas to oxygenated fuels under the supervision of Dr James Spivey.

processes,[17] catalysts for downstream adjustment of the H_2/CO ratio for specific end products,[18] and catalysts for the conversion of biomass-derived syngas to ethanol.

1.2 Ethanol

Ethanol as a fuel additive. Among other uses, ethanol has been used as a fuel in the US since at least 1908, although it was later displaced as a commodity fuel by petroleum-derived compounds.[19] Standard Oil marketed a 25% ethanol/gasoline mixture in the 1920's.[19] Recent incentives to use ethanol as a fuel additive in the US have led to an increase in production of about 12% per year in recent years.[19]

Current economic and process studies have shown that ethanol is an attractive end product because a widespread market exists for its use as a fuel additive,[19,20] among other applications. In fact, over 2 billion gallons of ethanol were produced in the US in 2002, mostly for use as a fuel additive,[21] with projections suggesting production of 5 billion gallons per year by 2012.[22] Although this is a small fraction of the US consumption of 134 billion gallons per year of gasoline, studies show that there is a potential to increase ethanol production to 34–75 billion gallons per year (*i.e.*, between 18 and 39% of US gasoline needs, on energy basis)—if the necessary technology can be developed.[23]

There are also clear environmental benefits of ethanol, both as a neat fuel and as a fuel additive. For example, Table 1 shows that biomass-derived ethanol transportation fuel results in lower net petroleum use and lower greenhouse gas emissions than gasoline per mile driven.[24]

Recent reports have suggested that there are advantages to higher alcohols such as 1-butanol as a blending agent with gasoline and as a neat transportation fuel. These advantages include lower solubility in water than ethanol (and therefore more easily separated from groundwater incase of a leak), higher energy content, less corrosion of existing infrastructure, and greater compatibility with gasoline.[25] However, ethanol use as a fuel additive appears to be growing due to its widespread availability and (at least in the near term), regulatory incentives. Like methanol, it can also be used as an esterifying reagent for the synthesis of biodiesel from fatty acids.[26–28] In addition, research shows that if 1-butanol is the desired product, it can be produced by the self condensation of ethanol on catalysts such as alkali zeolites[29] and $Ni/\gamma\text{-}Al_2O_3$.[30]

These facts suggest that there is a large potential market for ethanol, and that ethanol is a logical and environmentally favorable end product. Note that the catalysts used to produce ethanol from syngas typically form methanol and other higher alcohols as co-products. Thus, even though the discussion here focuses on the synthesis of ethanol, this review may be more generally applicable to the synthesis of higher alcohols (and other oxygenates) from syngas.

Table 1 Comparison of gasoline and biomass-derived ethanol[24]

Fuel	Petroleum use, Btu per mile	Greenhouse gas emissions, g per mile
Gasoline	5158	468
Bio-ethanol	258–758[a]	344–355[b]

[a] Depends on specific source of ethanol, includes petroleum use in processing and transporting. [b] For ethanol from corn grain.

Ethanol as a hydrogen carrier. Ethanol has been studied as a means of transporting hydrogen—ethanol would be produced at a central site, transported as a liquid to the point of use (*e.g.*, a fuel cell), and then used directly in a fuel cell[31–33] or reformed to produce a hydrogen-rich gas *via* steam reforming[34–39] or partial oxidation:[40,41]

$$C_2H_5OH + H_2O \rightarrow 2\ CO + 4\ H_2$$

$$\Delta H_r^\circ = +61.1\ \text{kcal mol}^{-1} \quad \Delta G_r^\circ = +29.2\ \text{kcal mol}^{-1}$$

$$C_2H_5OH + \tfrac{1}{2}\ O_2 \rightarrow 2\ CO + 3\ H_2$$

$$\Delta H_r^\circ = +3.33\ \text{kcal mol}^{-1} \quad \Delta G_r^\circ = -25.4\ \text{kcal mol}^{-1}$$

When CO_2 is allowed as a reaction product (as is the case in practice), these two reforming reactions can be combined so that the overall reaction is exothermic and favorable, *e.g.*;

$$2\ C_2H_5OH + 2\ H_2O + O_2 \rightarrow 8\ H_2 + 2\ CO_2 + 2\ CO$$

$$\Delta H_r^\circ = -13.1\ \text{kcal mol}^{-1} \quad \Delta G_r^\circ = -64.6\ \text{kcal mol}^{-1}$$

This reaction approaches autothermality ($\Delta H_r^\circ = 0$) at temperatures typical of reforming, roughly 600–750 °C[39,42]

When evaluated on a common basis, reforming of ethanol for use in fuel cells compares favorably with the reforming of methane and methanol[43]

Catalysts and reaction conditions needed for ethanol reforming have been widely studied. Most catalysts are based on Ni[42,44–47] with various modifiers and supports designed to improve activity/selectivity and to minimize coking. Analysis of studies on ethanol reforming is beyond the scope of this review, and the reader is referred to papers cited above for further information.

Gasification routes to ethanol. Although most of the current research and development efforts are focused on biochemical routes to ethanol[19,20] (and butanol[25]), thermochemical routes such as gasification can also produce these higher alcohols by conversion of the syngas produced in gasification. However there are currently no commercial plants producing ethanol or higher alcohols from syngas as an end product.[48] Among the processes being studied to produce ethanol are biomass gasification followed by:

- low-temperature fermentation to produce ethanol from CO and hydrogen,[49] or
- catalytic synthesis of mixed alcohols[50] or mixed oxygenates.[51]

Although biochemical processes are typically more selective to specific end products (including ethanol), the reaction rates of thermochemical processes are orders of magnitude higher and can be used to process a wide range of feedstocks (forest residues, animal wastes, *etc.*) into a syngas mixture of reasonably consistent composition. This can be a significant advantage in making these processes economically competitive.

2. Reaction thermodynamics

In order to understand the synthesis of ethanol from biomass-derived syngas it is necessary to examine the individual reactions leading to ethanol from the compounds present in syngas: CO, CO_2, H_2 and H_2O. A great deal of literature has been published on these reactions, which are essentially hydrogenation reactions, *i.e.* hydrogenation of CO or CO_2 to C_2^+ products. Side reactions involving these compounds such as the water-gas shift and methanation reactions also occur.

2.1 Hydrogenation of CO to ethanol

$$2CO + 4H_2 \rightarrow C_2H_5OH + H_2O$$

$$\Delta H_r^\circ = -61.20 \text{ kcal mol}^{-1}$$

$$\Delta G_r^\circ = -29.32 \text{ kcal mol}^{-1}$$

This is a highly exothermic and favorable reaction. Thermodynamic analysis of the reaction assuming a stoichiometric mixture of CO and H_2 (H_2/CO = 2.0) at 30 bar shows that ethanol and water concentrations decrease with temperature while those of the reactants increase (Fig. 2). This suggests that ethanol formation from CO hydrogenation should be done at temperatures below roughly 350 °C.

2.2 Hydrogenation of CO_2 to ethanol

$$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O$$

$$\Delta H_r^\circ = -41.54 \text{ kcal mol}^{-1}$$

$$\Delta G_r^\circ = -15.70 \text{ kcal mol}^{-1}$$

This reaction is also exothermic and thermodynamically favorable. Fig. 3 shows that the concentration trends follow those of CO hydrogenation. Ethanol and water concentrations decrease while those of CO_2 and H_2 increase with temperature. This result also suggests that ethanol synthesis from syngas should be carried at low temperatures for reasonable conversion of reactants.

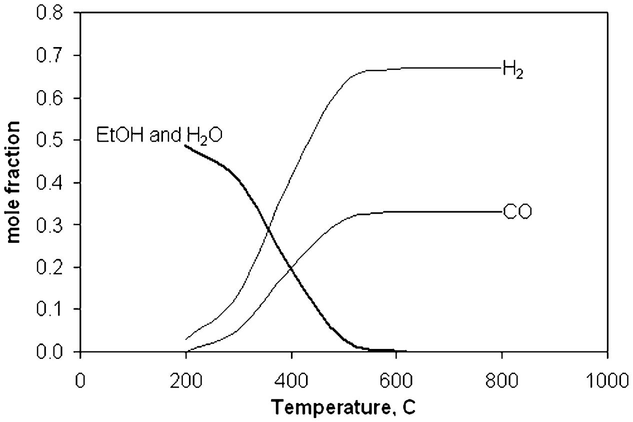


Fig. 2 Equilibrium composition for the hydrogenation of CO to ethanol. (H_2/CO = 2.0, 30 bar, calculated using AspenPlus® software.)

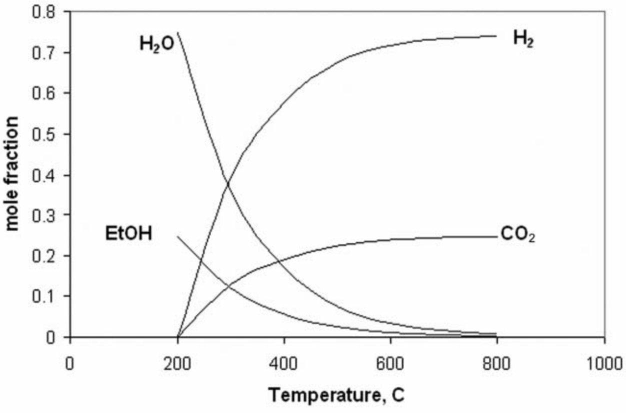


Fig. 3 Equilibrium composition for the hydrogenation of CO_2 to ethanol. (H_2/CO_2 = 3.0, at 30 bar, calculated using AspenPlus® software.)

2.3 Side reactions

The water gas shift (WGS) reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

is a very important side reaction that affects the equilibrium of both CO and CO_2 hydrogenation reactions. In the hydrogenation of CO to ethanol, the H_2O formed can readily react with CO to produce CO_2 and H_2, while in CO_2 hydrogenation the reverse WGS reaction may occur. The reverse WGS is essentially a partial reduction of CO_2 to CO, which has been identified as an elementary step involved in the synthesis of ethanol from CO_2 hydrogenation.[52,53] This suggests that the hydrogenation of both CO and CO_2 proceed through a common intermediate.

When methanation of CO and/or CO_2

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

are allowed to occur along with the hydrogenation reactions, methane is the most thermodynamically significant product.[54] Fig. 4 shows the equilibrium concentrations of an initial mixture composition corresponding to syngas produced by biomass gasification, with no methane allowed as product. Considerable concentrations of ethanol are present at equilibrium at temperatures below ~400 °C, 30 bar.

However, if methane is allowed as a product at these same conditions, the ethanol mole fraction is virtually zero at all temperatures (Fig. 5). This shows that the thermodynamically favored formation of methane must be kinetically limited if ethanol yield is to be significant.

2.4 Effect of pressure

Increasing pressure increases the equilibrium concentration of ethanol from the hydrogenation of either CO or CO_2. Fig. 6 shows the ethanol concentration as a function of pressure within the temperature range of interest (note that the low ethanol mole fractions is due to methane formation which is allowed in this calculation). Formation of ethanol is favored at

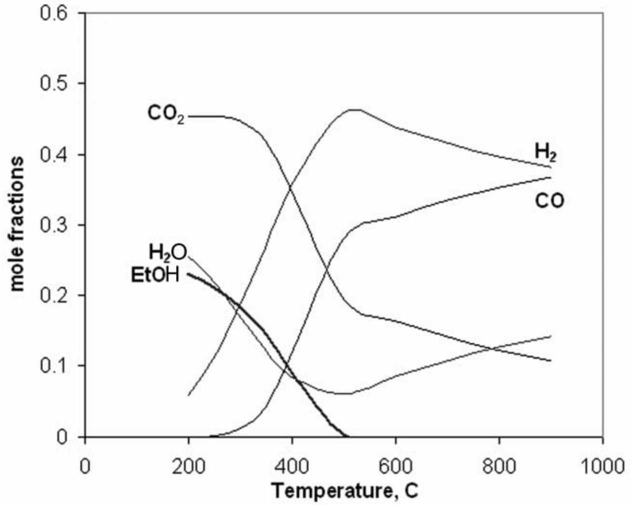


Fig. 4 Concentration profiles of the hydrogenation of CO and CO_2 to ethanol reaction at 30 bar with no methane product allowed. (Initial conditions: H_2 = 49%, CO = 26%, CO_2 = 21%, H_2O = 4%, calculated using AspenPlus® software.)

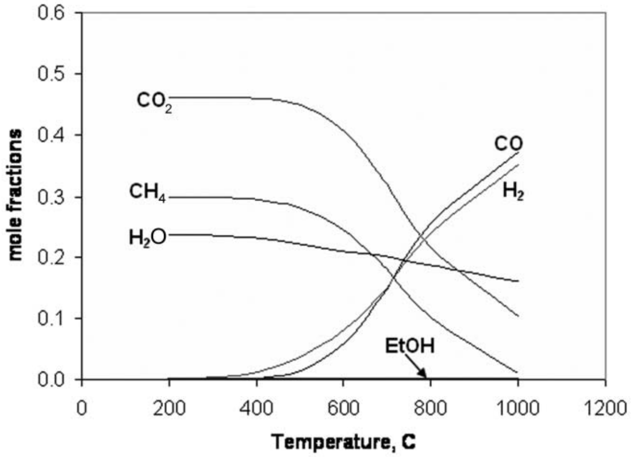


Fig. 5 Concentration profiles of the hydrogenation of CO and CO_2 to ethanol reaction at 30 bar with methane formation allowed. (H_2 = 49%, CO = 26%, CO_2 = 21%, H_2O = 4%, calculated using AspenPlus® software.)

higher pressures, but goes through a maximum at about 700 °C.

This is in qualitative agreement with experimental results. For example, Chuang *et al.* show that increasing the pressure from 1 to 10 atm resulted in an increase in ethanol formation rate from zero to 0.44 mol kg^{-1} h^{-1} at 300 °C over a Rh–TiO_2 catalyst.[55]

3. Catalyst types

We are aware of no systematic experimental studies of the catalytic synthesis of ethanol from gas mixtures that are designed to approximate those of gasified biomass. The vast majority of reported studies are based on the hydrogenation of CO. There are limited studies based on hydrogenation of CO_2, and even fewer on hydrogenation of mixtures of CO and CO_2.

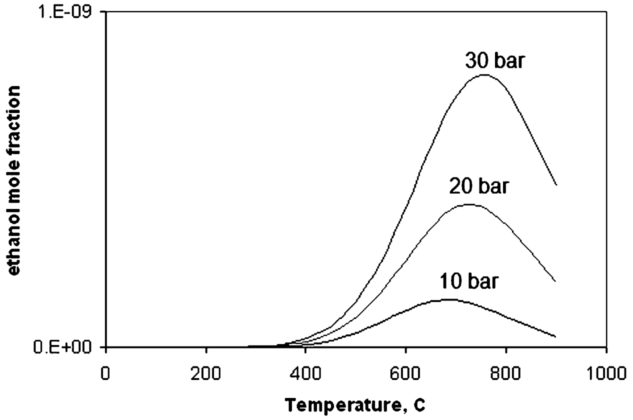


Fig. 6 Equilibrium ethanol concentration increases with pressure. (Methane formation allowed; H_2 = 49%, CO = 26%, CO_2 = 21%, H_2O = 4%; 300 °C, calculated using AspenPlus® software.)

None of these studies contains realistic concentrations of H_2, CO, CO_2 and steam as contained in syngas from gasified biomass.

Catalysts for ethanol synthesis from the hydrogenation of CO or CO_2 can be broadly grouped into four categories:

a) Rh-based catalysts
b) Modified methanol synthesis catalysts (based on Cu)
c) Modified Fischer–Tropsch type catalysts.
d) Modified Mo-based catalysts.

3.1 Rh-based catalysts

A. CO hydrogenation. By far the most widely studied catalysts for the hydrogenation of CO to oxygenates are based on Rh. Supported Rh has been known for decades to have the ability to produce C_2^+ oxygenates such as ethanol, acetaldehyde and acetic acid selectively from syngas.[56] Rh occupies an interesting position in the periodic table because it lies between metals that easily dissociate CO to form higher hydrocarbons (*e.g.*, Fe and Co) and those which do not dissociate CO and produce methanol (*e.g.*, Pd, Pt and Ir).[57,58] Rh can form methane, alcohols, or other oxygenates, from CO hydrogenation depending on support, promoter, and reaction conditions.[57,59–63]

Reaction sequence. Despite some differences in the details, the general mechanism proposed by a number of researchers for the formation of ethanol and C_3^+ oxygenates from CO hydrogenation can be represented by the sequence of reaction steps shown in Fig. 7.[64,65]

Steps 1–4: CO and H_2 adsorption. First, in steps 1 and 2, CO and H_2 are adsorbed. The adsorbed, non-dissociated CO is then either hydrogenated to form methanol (step 3)[65,66] or dissociated (step 4). The adsorption of CO on Rh is a key step because it is thought to be rate-determining in many cases.[59,67,68] CO adsorption is strongly affected by the presence of promoters,[69–71] Rh cluster size and shape,[72–74] support[75–77] pretreatment,[78] and reaction conditions. These factors determine whether the adsorption is dissociative, non-dissociative, or both. Because a combination of both is required for ethanol synthesis (steps 4 and 7), it is not surprising that the activity and selectivity on Rh-based catalysts differ greatly depending

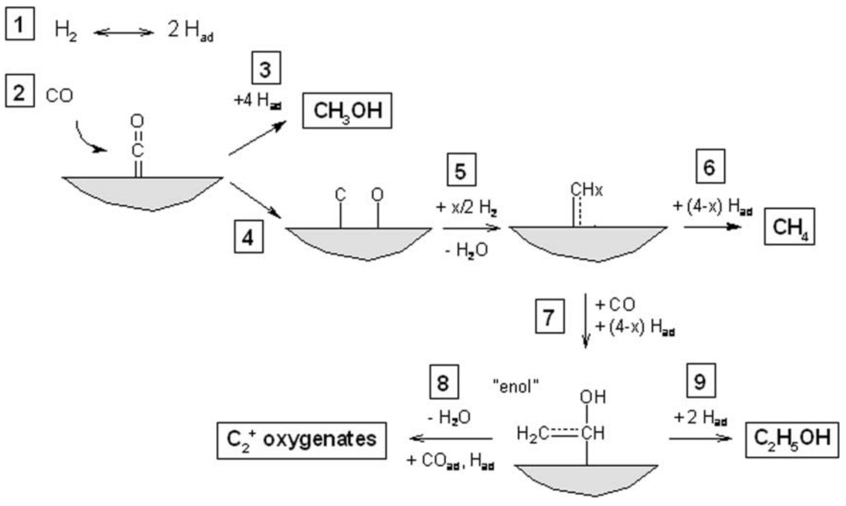


Fig. 7 A simplified sequence for ethanol formation by CO hydrogenation on Rh-based catalysts. Individual reaction steps are indicated by boxed numbers.

on the exact composition, preparation and history of the catalyst.

Several general conclusions regarding CO adsorption (steps 2 and 4) can be drawn from the literature:

(a) *Promoter effects*—transition metal promoters are thought to provide a site for interaction of the O atom in CO at the metal–promoter surface, as shown in Fig. 8.[70,71,79] During reduction, oxygen vacancies are created in the promoter, which allows for a strong (and controllable) interaction with the promoter. It seems that the most effective promoters decorate the surface of the Rh clusters, creating numerous sites for interaction between the promoter and Rh atoms. The stronger the M−O bond in Fig. 8, the more likely that CO will dissociate (*e.g.*, Kato *et al.* observed a strong correlation between the heat of formation of the promoter oxide and CO dissociation[70]).

(b) *Support effects*—the support affects the Rh dispersion, which in turn affects the nature of the CO adsorption. For example, Trautmann and Baerns found that 0.5% Rh supported on SiO_2 produced Rh crystallites that adsorbed CO non-dissociatively, whereas the same metal loading on Al_2O_3 and TiO_2 formed more dispersed clusters that adsorbed CO dissociatively.[80] Qualitatively similar effects are reported by others,[81] with TiO_2 typically being the most active support for dissociative adsorption.[75]

(c) *Cluster size effects*—CO adsorption appears to be a strong function of the Rh cluster size and morphology.[68] CO adsorption on low-index Rh stepped surfaces is non-dissociative[82–87] while dissociative adsorption takes place on both stepped and polycrystalline surfaces[88–93] and small Rh clusters.[75] However, this cluster size effect is not general—Libuda *et al.* found that CO dissociation activity increased with increasing particle size for Rh supported on an alumina film,[72] while others have seen a maximum in CO dissociation at a cluster size of about 500–1000 atoms.[94]

Steps 5–9: ethanol and by-product formation. The dissociated CO is then hydrogenated to form a surface hydrocarbon $(CH_x)_{ad}$ (x = 2 or 3; step 5). [Although not shown, another possibility is that the O_{ad} atom formed in step 4 reacts with CO to form CO_2[95].] This $(CH_x)_{ad}$ species can be hydrogenated to form methane (or higher hydrocarbons, not shown) in step 6[53,96] or an undissociated CO can be inserted into the metal–carbon bond in $(CH_x)_{ad}$[64] to form an "enol" intermediate in step 7. The resulting enol intermediate either reacts with adsorbed H atoms and CO to form higher oxygenates (step 8), or reacts only with adsorbed H atoms to form ethanol (step 9).

This reaction sequence is not intended to account for every elementary step, but does agree with most experimental results on Rh-based catalysts, and with the main features of mechanisms that have been postulated for these catalysts.[64,65] The sequence does not explicitly account for other C_2 oxygenates such as acetaldehyde or acetic acid, which are known by-products. However, these compounds can be formed as by-products in the sequence shown in Fig. 7. For example, acetaldehyde could be formed in step 7 by CO insertion into the $(CH_x)_{ad}$ species (as is required for ethanol formation), followed by mono-hydrogenation of the α- and β-carbon atoms without the formation of the hydroxyl group. Acetic acid could be formed by hydration of the enol intermediate by water formed in step 5.

Intermediates. Intermediates observed or postulated in mechanistic studies can also be explained by Fig. 7. For example, ketene ($H_2C{=}C{=}O$) has been shown to be a key intermediate.[65,97,98] Its formation is implicit in step 7, which is the sum of several single steps. Ketene can be formed by CO insertion into the $(CH_x)_{ad}$ species (x = 2), and would therefore be a precursor to the enol, which is formed by the hydrogenation of ketene. Acetyl intermediates ($H_3C{-}C{=}O$) have also been suggested.[97,98] These species can also be formed in step 7 by CO insertion into $(CH_x)_{ad}$ in the case where x = 3.

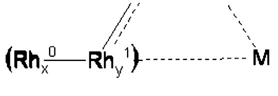


Fig. 8 Interaction of CO with Rh-promoter surface; M = reduced metal oxide promoter (from Du *et al.* ref. 79).

Formyl species (H–C=O)[99,100] are possible in step 3, but lead only to methanol in the sequence shown in Fig. 7. This does not agree with the results of Wang *et al.* on promoted Rh/SiO_2 catalysts,[100] which suggest that a formyl group is also an intermediate in ethanol synthesis. The difference may be due to the presence of the promoters in the Wang *et al.* study, which included Mn, Fe, Li, and Ti.

On virtually all catalysts on which high ethanol selectivities have been reported, CO conversions are low because hydrocarbon formation, which typically accompanies high catalyst activity, is suppressed. The observed trend is that selectivity to C_2 oxygenates decreases with increasing CO conversion. Therefore there has to be a balance between the catalyst activity and selectivity to obtain a high yield of ethanol.

Promoters. The selectivity to ethanol for unpromoted Rh catalysts is relatively low—the main products are hydrocarbons.[56,101] The formation of ethanol can be greatly enhanced by the addition of promoters.[55,79,102] The above reaction sequence (Fig. 7) suggests that Rh-based ethanol synthesis catalysts can be improved by promoters that increase CO dissociation and CO insertion activity while suppressing the hydrogenation of $(CH_x)_{ad}$ intermediate. The catalyst must dissociate only a portion of the CO molecules so that the catalyst surface contains both adsorbed molecular CO, and surface carbon species produced by dissociative adsorption.[65] There must also be a balance in hydrogenation activity—hydrogenation of the $(CH_x)_{ad}$ intermediate is undesirable, but hydrogenation of the enol is essential.

A variety of promoters including, transition metal oxides,[53,56,64,101,103] rare earth oxides[79] (and combinations thereof[104]), alkalis[55] and noble metals[105] have been studied and found to exhibit significant enhancement of the ethanol yield. The effect of these promoters can be dramatic. For example, Fig. 9 shows the effect of Fe promotion on the selectivity to ethanol and other reaction products for a 2% Rh/Al_2O_3 catalyst.[106] The results show a substantial increase in ethanol selectivity with Fe addition up to 10% Fe. The authors of this study point out that the increase in ethanol selectivity corresponds directly to a decrease in methane selectivity, suggesting that one is at the expense of the other. This is consistent with the reaction scheme of Fig. 7 : Fe promotes CO insertion (step 7) rather than hydrogenation of the $(CH_x)_{ad}$ species (step 6). A similar suppression of hydrogenation has been ascribed to the effect of alkali addition to a Rh/TiO_2 catalyst, leading to an increase in ethanol selectivity.[55]

Similar increases in ethanol selectivity compared to an unpromoted supported Rh catalyst have been reported for lanthanides,[79] and vanadium,[53,104] manganese,[104] silver,[105] ceria,[107] and combinations of Ti, Fe, and Ir.[108]

Supports. The support can also greatly affect the activity and selectivity of the reaction. The effect can be direct—*e.g.*, when the support interacts directly with the metal in the catalytic reaction or indirect—*e.g.*, when the support affects the dispersion of the Rh or promoters, which then affects the reaction.

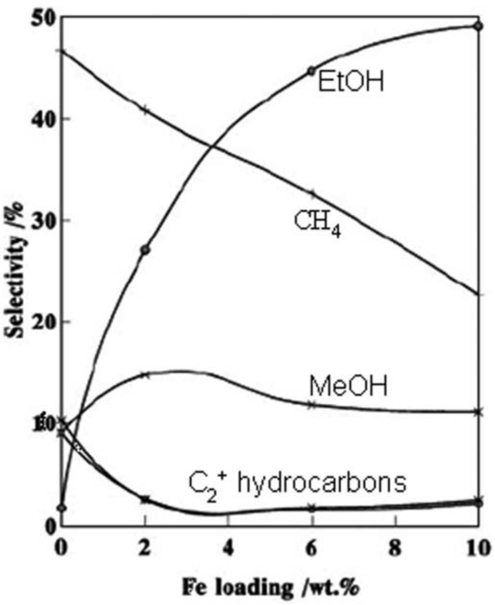


Fig. 9 Effect of Fe promotion on product selectivity in CO hydrogenation; 10 bar, H_2/CO = 1/1, 270 C, 133 cc per min-g cat.; CO conversion <3.8%; 2% Rh/γ-Al_2O_3. (Reproduced with permission from ref. 106. Copyright 1997 Elsevier.)

Most studies of supported Rh catalysts for CO hydrogenation to oxygenates use SiO_2 as a support, to which various promoters are added. There are relatively few studies of unpromoted Rh on other supports in which oxygenates are formed, and fewer still in which a direct comparison among supports is made. As discussed above, this is because unpromoted Rh seems to produce hydrocarbons only, essentially independent of the support.[109–112] This is likely due to the fact that CO adsorption on these unpromoted catalysts is almost entirely dissociative, which precludes the CO insertion reaction needed to produce C_2^+ oxygenates.[113]

Gronchi *et al.*[53] have studied 1% Rh on La_2O_3, ThO_2, ZrO_2, and V_2O_3. They found that V_2O_3 gave the highest yield of ethanol, but differing conversions among the runs on each catalyst make direct comparisons with the other supports difficult. The effect of the support on ethanol selectivity among the catalysts is not discussed in detail. Guglielminotti *et al.* show that small Rh clusters prepared by carbonyl decomposition interact strongly with a ZrO_2 support *via* the surface hydroxyls, which increases CO chemisorption.[67] However, the effect on ethanol formation is not discussed.

B. Rh-based catalysts—CO_2 hydrogenation. Because biomass-derived syngas contains CO_2 as well as CO, the hydrogenation of CO_2 to ethanol is also of interest. Hydrogenation of CO_2 to the products of interest here can, of course, proceed *via* the reverse water gas shift (r-WGS) reaction, followed by hydrogenation of CO to final products. Thermodynamic analysis shows that the ethanol concentration decreases with temperature, and is less than 10% above ~350 °C.

If so, then the reaction scheme in Fig. 7 would be modified only to account for the formation of surface C and O from CO_2 rather than CO, with the remaining steps being the same. There is experimental evidence to support this: adsorption of CO_2 results in the formation of linearly and bridge-bonded CO, which has been identified by IR spectroscopy on Rh–Mo/ZrO_2,[67] Rh/Al_2O_3,[114] and Rh–Li/Y.[115] In one of these

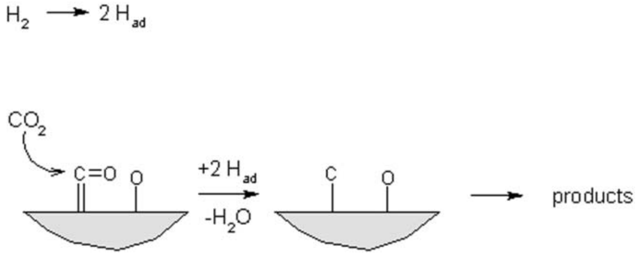


Fig. 10 Initial steps in the hydrogenation of CO_2, based on ref. 109 and 116. Steps leading to the formation of final products are shown in Fig. 7.

studies,[114] the presence of hydrogen strongly enhanced the formation of CO, possibly by reacting with the surface O atom formed in the initial adsorption of CO_2 and driving the adsorption process forward. As shown in Fig. 10, this suggests that CO_2 hydrogenation proceeds *via* the dissociative adsorption of CO_2 to form CO and O atoms on the surface.[109,116] CO then dissociates to adsorbed C and O atoms, with final products being formed as shown in Fig. 7.

Essentially the same mechanism is proposed by Bando *et al.*, who also studied the effect of Li promoters on CO_2 hydrogenation over a 5% Rh/Y catalyst.[115] Fig. 11 shows that the addition of Li monotonically increased the yield of methanol and ethanol, but also increased the yield of CO, probably by the desorption of CO formed in the dissociative adsorption of CO_2 in Fig. 10.

Consistent with other studies,[109,110,117] Fig. 11 shows that unpromoted Rh forms only methane. This agrees with a comprehensive study of 28 promoters for a 5% Rh/SiO_2 catalyst, which showed that the selectivity to ethanol was significant only for Li.[117] Methane was the primary product for most other promoters in this study, with significant levels of CO being formed (along with methane) in the case of Pt, Cu, Ag, Zn, and Sn promoters.

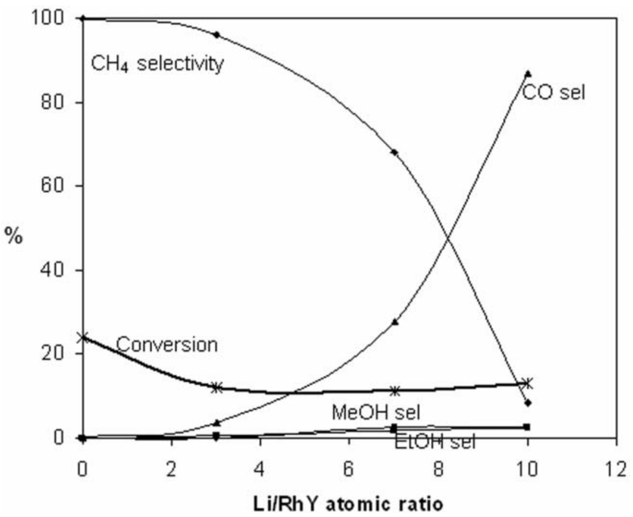


Fig. 11 CO_2 hydrogenation over Li/RhY. (Experimental conditions: H_2/CO_2 = 3/1; 3 MPa; 250 °C; 100 cc per min-g cat.)[115]

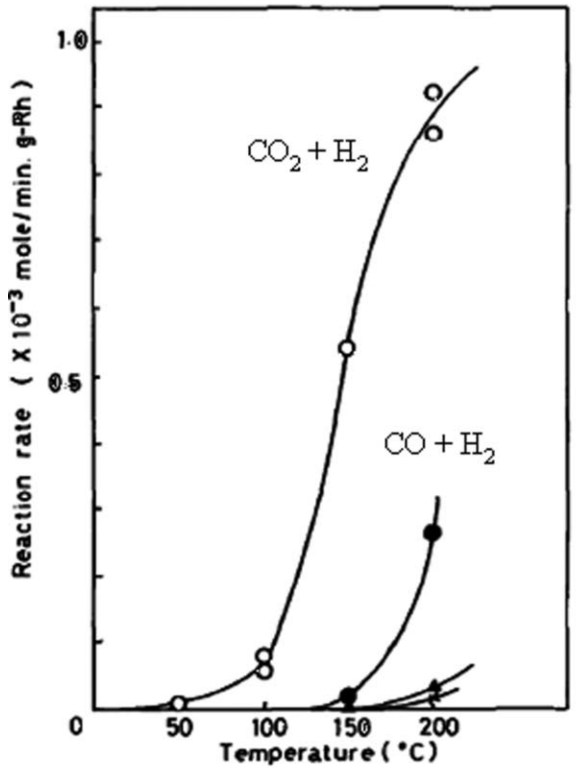


Fig. 12 Methane formation rates for CO + H_2 and CO_2 + H_2 reactions; 2.3% Rh/ZrO_2; recirculation reactor; 60 Torr H_2, 15 Torr CO; 0.25 g cat. (Reproduced with permission from ref. 109. Copyright 1982 Elsevier.)

C. Rh-based catalysts—Comparison of CO *versus* CO_2 hydrogenation. Mechanistic studies comparing CO + H_2 *versus* CO_2 + H_2 over Rh-based catalysts show substantial differences in these two reactions.[88,109,118,119] Specifically, CO_2 hydrogenation seems to take place at lower temperatures. Fig. 12 compares the two reactions for a 2.3% Rh/ZrO_2 catalyst.[109] The results show that only methane is formed in significant levels for both reactions, and that the rate of CO_2 hydrogenation is substantially greater than CO hydrogenation. For identical levels of Rh (2.3%) supported on ZrO_2, Al_2O_3, SiO_2, and MgO, the activation energy for CO_2 hydrogenation was always less than for CO hydrogenation[109]—suggesting that dissociation of CO_2 is faster at a given temperature on all supports. Reaction orders were near zero in CO (consistent with Marengo *et al.*[120]) and near 0.4 for CO_2, which means that CO can act as a poison for H_2 adsorption and limit the observed reaction rate.

D. Rh-based catalysts—hydrogenation of CO + CO_2 mixtures. Virtually all the available relevant literature has focused on the hydrogenation of either CO or CO_2, rather than mixtures of the two. The effect of the mixture composition on the hydrogenation reaction is important, however, because biomass-derived syngas (as well as syngas from other sources) will contain significant levels of both. In addition, the high levels of steam in syngas will also affect the reaction, but we are aware of no literature in which the effects of varying levels of CO, CO_2, H_2 and H_2O on the synthesis of ethanol on Rh-based catalysts have been studied. Fig. 13 shows the effect of replacing a portion of CO in the feed with increasing

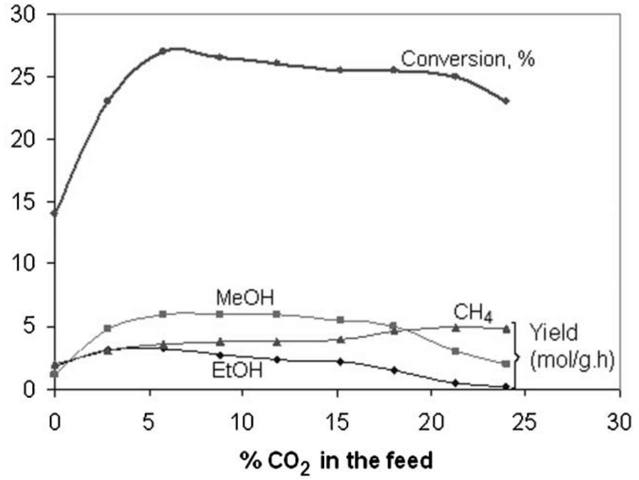


Fig. 13 Effect of CO_2 on CO hydrogenation to methanol and ethanol; 1% Rh–Mo/ZrO_2 (Rh/Mo = 1/1 atomic ratio); 503 K, 2 MPa, GHSV 2400 h^{-1}.[120]

concentrations of CO_2 on 1% Rh–Mo/ZrO_2 (Rh/Mo atomic ratio = 1/1).[120]

The yields of methanol and ethanol behave similarly—increasing at low levels of CO_2, reaching a maximum at about 5–10% CO_2, then declining steadily. The authors attribute this to the r-WGS reaction,[120] which presumably produces additional CO that is converted to the alcohols. Methane yield increases continuously over the range of CO_2 concentrations studied, however. The decline in alcohol yield at higher levels of CO_2 is attributed to strong adsorption on sites that lead to the alcohols, with the reaction then being shifted toward methanation. An alternative explanation is that CO_2 reacts more readily to form methane than CO over the entire range of CO_2 concentrations (Fig. 12[109]), causing the monotonic increase in methane yield with CO_2 content. Up to about 20% CO_2, the combined yields of methanol and ethanol follow the conversion quantitatively, meaning that the alcohol selectivity over this range is more constant than the yield alone would suggest. At CO_2 concentrations above ~20%, the r-WGS reaction may indeed produce sufficient strongly-adsorbing CO[109] to inhibit the reactions leading to the alcohols.

Bando *et al.* added 1.8% CO to a $CO_2 + H_2$ mixture (H_2/CO = 3/1) and saw significant increases in methane selectivity (from 15 to 40%) and ethanol selectivity (~0 to 13%) over 5% Rh–Li/Y.[115] This can be explained by the strong adsorption and surface coverage of CO compared to CO_2. From Fig. 7, this could provide more surface coverage of C and O atoms, leading to an increase in both methanation (step 6) and CO insertion, step 7. A subsequent study by these same authors shows that Li stabilizes the Rh clusters compared to an identical catalyst without Li.[121] This apparently causes these changes in selectivity.

3.2. Modified methanol synthesis catalysts

A. Modified methanol synthesis catalysts—CO hydrogenation. It was noted as early as the 1920's that the yield of higher alcohols increases during methanol synthesis on catalysts precipitated with alkali (as a result of the traces of alkali left on the catalyst during preparation).[122] This observation led to the use of alkali-doped Cu/Zn methanol catalysts for higher alcohol synthesis. The distribution of the higher alcohol mixtures obtained on these catalysts depends on the promoter concentration, feed concentration (H_2/CO ratio) and the reaction conditions. However, no matter what the choice of catalyst or conditions, methanol remains the dominant product on these catalysts.[123] Most of the work reported on modified methanol catalysts for CO hydrogenation to higher alcohols has been on Cu-based catalysts. Alkali-doped binary Cu/Zn system and ternary Cu/Zn/Al or Cu/Zn/Cr (this third component, either Al or Cr, is always added to stabilize Cu/Zn against sintering[124]) system have been extensively studied by Smith *et al.*[122,125] and Nunan *et al.*[126–128]

Reaction sequence/mechanism. A chain growth mechanism has been proposed for the formation of higher alcohols on modified Cu/Zn catalysts. The chain growth mechanism was first proposed by Frohlich and Cryder,[129] who reported that higher alcohols are formed by the successive condensations of two lower alcohols with H loss from either the hydroxylated (α) carbon or adjacent (β) carbon atoms. It was assumed that hydrogen loss from the β-carbon is faster than the α-carbon.[130] This mechanism suggests that methanol with only an α-carbon will slowly react to form ethanol, while ethanol which has both α- and β- carbons, reacts to form propanol at a faster rate. The effect is that large amounts of methanol and small amounts of ethanol are formed on these catalysts.

Different modifications have been made to this mechanism to account for branched and linear alcohols found in the product stream. Smith and Anderson,[122] working with K/Cu/Zn/Al, assumed the simple case of a single carbon addition with no α-addition beyond the first step and no addition to a –CH group. This mechanism is limited because it predicts only methanol, ethanol and 1-propanol with a chain termination at 2-methyl-1-propanol because β-addition cannot occur.[122] They later modified this scheme to include α-addition beyond the first step but no more than two-carbon addition.[125]

While there are various reports that describe the chain growth schemes to account for linear and branched alcohols,[124,127,131] we shall limit the review here to the mechanism of the formation of the initial C–C bond and ethanol only. The coupling reaction of two methanol molecules was identified as the predominant mechanism to form ethanol over Cu/ZnO catalyst (doped with Cs) after isotopic labeling and NMR studies eliminated the other possible routes from CO hydrogenation to ethanol.[126] Schematically, the proposed mechanism of ethanol formation over Cs doped Cu/ZnO catalyst is shown in Fig. 14. The coupling reaction of two methanol molecules to form ethanol involves a nucleophilic attack of an adsorbed formyl on formaldehyde[126] to generate the C_2 precursor with two oxygen atoms (step 2). Both the adsorbed formyl and formaldehyde are believed to be formed preferentially from methanol[132] (step 1). An alternative methanol coupling mechanism that also involved an adsorbed formyl was proposed[126] as well, but was considered as less likely because of steric hindrance.

The proposed mechanism of methanol formation on this catalyst as presented by these same authors is depicted in

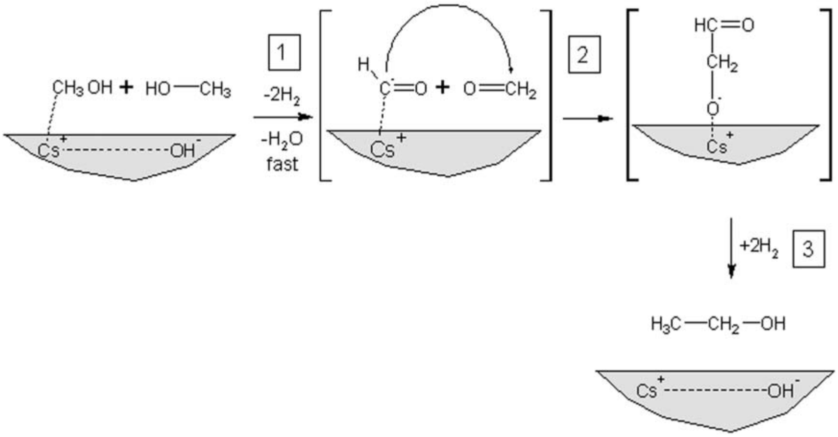
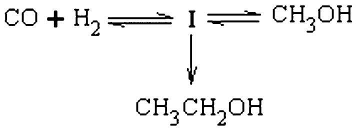


Fig. 14 Mechanism for ethanol formation from methanol condensation on Cu-based catalysts. Adapted from ref. 126. Boxed numbers refer to reaction steps.

Fig. 15.[126] CO is activated by Cs^+ and its associated OH^- ions to form an adsorbed formate species (step 1). This is followed by slow hydrogenation/dehydration (step 2) to produce an adsorbed formyl, further hydrogenation to formaldehyde (step 3) and transformation to a methoxide (step 4) and finally hydration of the adsorbed methoxide leading to methanol. Interestingly, formaldehyde and adsorbed formyl are also intermediates in the methanol coupling reaction to ethanol (Fig. 14). Methanol has been shown to decompose to formaldehyde *via* a methoxide intermediate on various metals.[133–135] This is therefore a likely pathway through which the adsorbed formyl and formaldehyde intermediates are formed in the first step of the ethanol-forming reaction (Fig. 14). These intermediates can also be formed directly from CO and H_2, but it is a very slow step compared to their formation from the condensation of two methanol molecules.[126]

An alternative explanation is provided by Elliot and Pennella[123] who argued that the ethanol does not form from a methanol intermediate but from a surface-bound C_1 precursor (**I** below) which can be formed from either syngas ($CO + H_2$) or methanol. Such a precursor can also be the intermediate for methanol formation from syngas:



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

This pathway shows that the C_1 intermediate (**I**) could be the adsorbed formyl or formaldehyde, shown in Fig. 14 and 15 to be intermediates for both methanol and ethanol. These intermediates can also be formed from either syngas or methanol.

Promoters and their effects. Alkali promotion of Cu-based catalysts has been found to increase higher alcohol synthesis with increasing alkali atomic size, in the order Li < Na < K < Rb < Cs.[136] K and Cs have been extensively used on these catalysts and their functions have been suggested to be dual in nature: the first is the suppression of surface acidity by the titration of acid sites that leads to dimethyl ether (DME).[131] Reducing DME selectivity effectively leads to higher alcohol selectivity because DME is formed by the condensation reaction of methanol. The second function is to provide basic sites (in association with its counter-ion) necessary for the various C–C and C–O bond-forming reactions.[128] The optimum degree

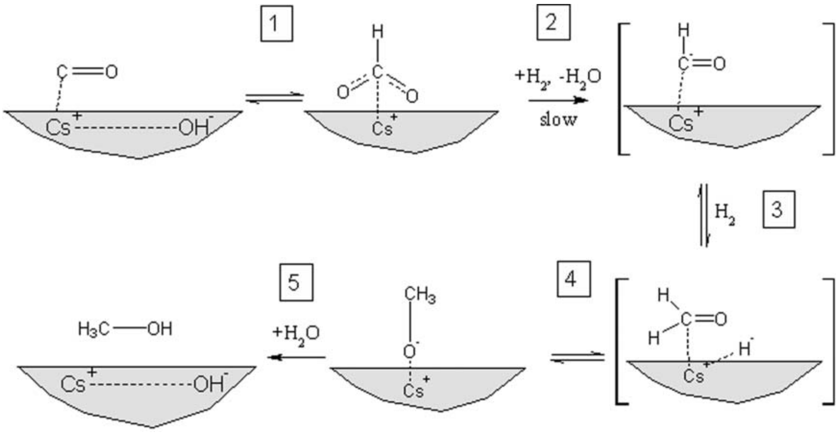


Fig. 15 Mechanism for methanol formation from CO hydrogenation on Cu-based catalysts. Adapted from ref. 126. Boxed numbers refer to reaction steps.

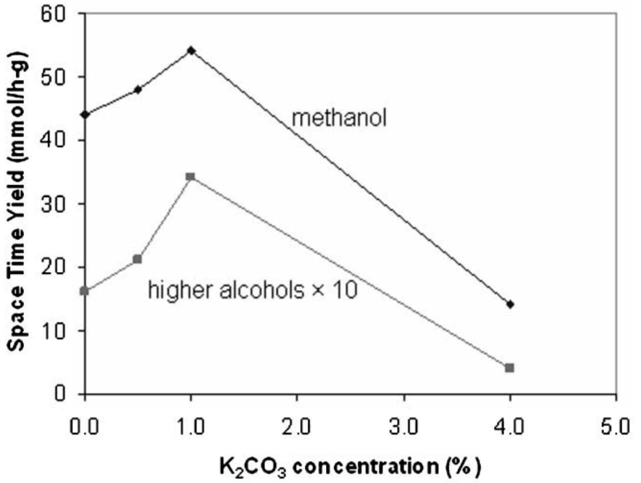


Fig. 16 Effect of K promoter concentration on methanol and higher alcohol yield (285 °C, CO/H_2 = 2/1, 10 MPa).[137]

of promotion is however dependent on the promoter type, concentration, and catalyst support, among other factors.

The yield of higher alcohols has been shown to go through a maximum as the promoter concentration is increased.[128,137] This is because as the promoter concentration increases, more alkali sites are created thereby increasing the yield of higher alcohols but eventually the promoter blocks the Cu/Zn sites that are required for methanol synthesis. When this occurs, it hinders methanol formation thereby reducing the driving force for higher alcohol synthesis.[137] However, methanol yield has also been found to pass through a maximum as promoter concentration increases, in the same manner as for higher alcohols.[126,137] Fig. 16 shows that the yield of methanol and higher alcohols follow the same trend as K concentration increases. This suggests that methanol and higher alcohols are likely formed at same sites (alkali–Cu interfaces) on the catalyst[137] and contradicts an earlier proposal[137] that methanol and higher alcohol synthesis require different sites.

Even though alkalis promote the formation higher alcohols on Cu catalysts, the effect of alkali doping on ethanol yield is not significant. Table 2 shows the product yield of CO hydrogenation over Cs doped Cu/ZnO. The addition of 0.25 mol% Cs to unpromoted Cu/ZnO leads to an insignificant increase in ethanol yield, but 1-propanol and isobutanol yields increase considerably. Ethanol yield decreases while other higher alcohols yields increase at higher levels of Cs doping.

Cu/Zn/Cr has been shown to require more Cs (or alkali) doping than Cu/Zn/Al and binary Cu/Zn for optimal higher alcohol synthesis because the chromia content introduces acidity to the catalyst which leads to DME.[128]

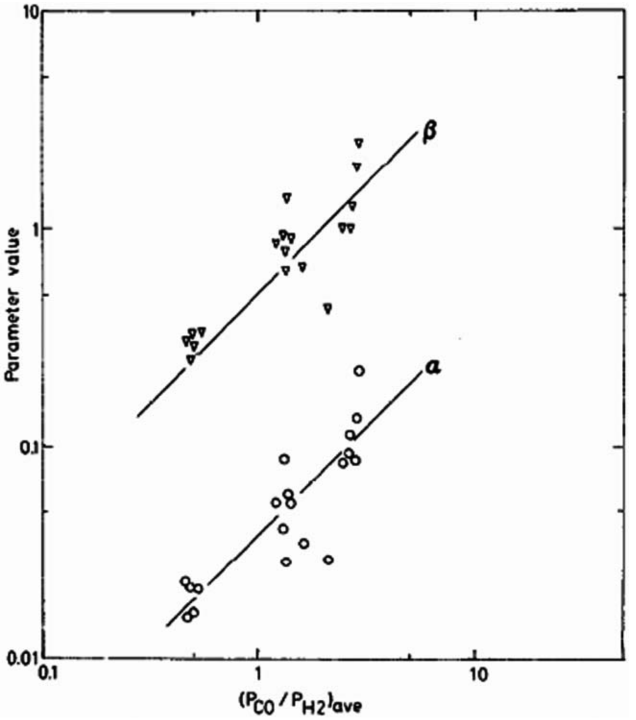


Fig. 17 Chain growth parameters, α and β, increase with CO/H_2 ratio; catalyst 0.5% K_2CO_3–Cu/ZnO; reaction conditions: 285 °C, 10.4 MPa. (Reproduced with permission from ref. 125. Copyright 1984 Elsevier.)

Effect of CO/H_2 ratio. Besides process conditions like temperature, pressure and space velocity, the feed H_2/CO ratio also affects the higher alcohol selectivity over alkali-doped Cu-based catalysts. Higher alcohols are favored by CO-rich feed mixtures because the rate of chain growth increases with increasing partial pressure of CO while termination rate varied increased with increasing H_2 partial pressure.[122,125] Fig. 17 shows chain growth parameters, α and β increase with CO/H_2 ratio (where α and β are ratios of a growth rate constant and a desorption rate constant). High H_2 partial pressures have the effect of inhibiting the rate of C_1–C_2 chain growth step by enhancing the conversion of C_1 intermediates to methanol.[138]

B. Modified methanol synthesis catalysts—Hydrogenation of CO + CO_2 mixtures. Few reports are available on the

Table 2 Product yields of CO hydrogenation over Cs doped Cu/ZnO[127,a]

	Product yield (g kg-cat^{-1} h^{-1})						
Catalyst	CO_2	Water	Alkanes	Methanol	Ethanol	1-Propanol	1-Butanol
Undoped Cu/ZnO	367	1.3	16.8	204	22.6	10.1	3.4
0.25 mol% Cs/Cu/ZnO	412	1.3	16.2	181	22.7	29.6	8.6
0.34 mol% Cs/Cu/ZnO	403	1.7	13.4	157	17.0	38.1	8.2
0.43 mol% Cs/Cu/ZnO	430	1.3	14.0	162	18.2	24.1	4.6
1.5 mol% Cs/Cu/ZnO	403	0.04	4.3	213	8.1	18.0	—

[a] 583 K, 7.6 MPa, H_2/CO = 0.45, GHSV = 3260 L kg-cat^{-1} h^{-1}.

hydrogenation of CO_2 to ethanol on modified methanol synthesis catalysts. However, CO_2 has been co-fed with syngas mixtures to probe its effect on catalyst activity and selectivity on these catalysts. CO_2 when co-fed with CO and H_2 has a promoting effect on methanol synthesis on Cu/ZnO. Klier *et al.* report a peak in methanol synthesis rate at CO_2 concentration of 2% and a monotonic decrease in the promotion effect as CO_2 gradually replaces CO in the feed mixture[139] (Fig. 18). Even at 20% CO_2 concentration, the methanol selectivity is more than that for CO_2-free syngas feed. Klier *et al.* claim that this effect is mainly promotional because CO hydrogenation is the primary source of methanol in a $CO/CO_2/H_2$ feed mix and that CO_2 only becomes a significant source of carbon when the syngas feed is CO_2-rich.[139] However Chinchen *et al.*[140] arrived at a different conclusion using ^{14}C tracer studies: that on $Cu/ZnO/Al_2O_3$ methanol is made predominantly from CO_2 hydrogenation for all mixtures tested.

The explanation given for the promotional effect of CO_2 is that a surface formate intermediate is formed by either CO_2 and H or CO and H_2O (suggesting that CO_2 and H_2O probably have the same effect on methanol synthesis).[139] Without CO_2 in the feed the formate would not be formed and with high CO_2 concentrations, the active catalyst surface is blocked by the strongly adsorbed CO_2, retarding surface formate formation.[139] This formation of a surface formate species in methanol synthesis from CO_2 hydrogenation is consistent with Chinchen *et al.*[141] as shown in the following reaction sequence:

$$H_2 \rightarrow 2H_{(ad)}$$

$$CO_2 \rightarrow CO_{2(ad)}$$

$$H_{(ad)} + CO_{2(ad)} \rightarrow HCO_{2(ad)}$$

$$HCO_{2(ad)} + H_{(ad)} \rightarrow H_2CO_{(ad)} + O_{(ad)}$$

$$H_2CO_{(ad)} + H_{(ad)} \rightarrow H_3CO_{(ad)}$$

$$H_3CO_{(ad)} + H_{(ad)} \rightarrow CH_3OH$$

$$CO + O_{(ad)} \rightarrow CO_2$$

$$H_2 + O_{(ad)} \rightarrow H_2O$$

Elliot also reported an increase in both methanol and higher alcohols synthesis rate using a CO + H_2 feed containing 6% CO_2.[142] Conversely, over alkali promoted catalysts, Hilmen *et al.*[131] reported inhibition effects of CO_2 on both methanol and higher alcohols synthesis by increasing the oxygen coverage on Cu surfaces and titrating the basic sites necessary for condensation reactions. The degree of inhibition depended on the concentration of Cu sites on the catalyst—the inhibition for methanol synthesis is weaker on catalysts with high Cu sites density while those with lower Cu sites densities are more affected. Calverley and Smith[137] on the other hand reported that the effect of CO_2 added to CO + H_2 depended on the alkali concentration for K_2CO_3-promoted $Cu/ZnO/Cr_2O_3$. At a 0.5% K_2CO_3 loading, CO_2 in the feed enhanced methanol formation while at 4.0% K_2CO_3 the yield of methanol was depressed.

In summary, CO_2 seems to have a promoting effect for methanol synthesis, but it inhibits higher alcohol formation on modified methanol catalysts. For example, no higher alcohols were formed on Cu/ZnO when a feed mix containing only CO_2 and H_2 (with no CO) was used.[143]

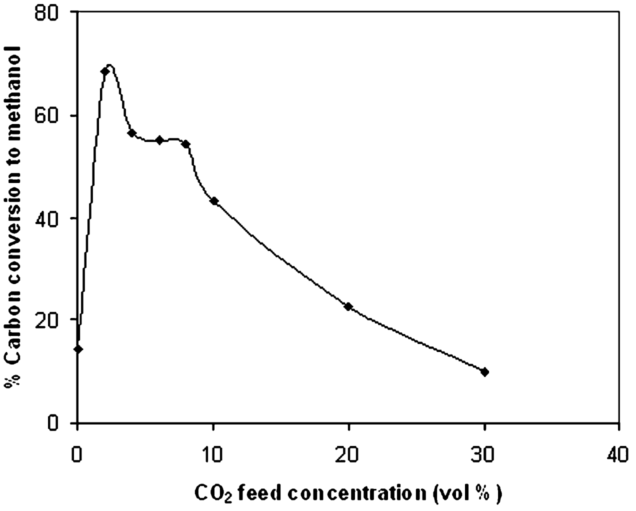


Fig. 18 Effect of CO_2 feed concentration on syngas conversion to methanol over Cu/ZnO catalysts (molar ratio 30/70); T = 225–250 °C, P = 75 atm. Data extracted from Table 1 in ref 139.

3.3 Modified Fischer–Tropsch catalysts

A. Modified Fischer–Tropsch catalysts—CO hydrogenation. Evidence that alcohols, with ethanol present in the largest proportion, are precursors to the formation of hydrocarbons on Fischer–Tropsch type catalysts has been presented since 1952.[144] These types of catalysts, based on Co, Ru and Fe, have been reported to give higher alcohols when suitably modified with additives.[145–149] Some authors reported that the synthesis of higher alcohols on Ir/Ru–SiO_2[150] and Ir/Co–SiO_2[151] might be caused by a synergistic interaction between metals that readily dissociate CO (Ru and Co) and Ir, which does not dissociate CO. A combination of two such metals might produce a catalyst that has the proper combination of CO dissociation and CO insertion, which are necessary for higher alcohol formation on some catalysts (Fig. 7).

Reaction sequence. The mechanism for alcohol formation on modified Fisher Tropsch catalysts is essentially same as the one described for Rh catalysts. It starts with CO dissociation and hydrogenation of the adsorbed carbon into CH_x surface species, followed by CO insertion into the CH_x species as shown in Fig. 7.[152]

Promoters and effects. Kintaichi *et al.*[153] tested a series of bimetallic catalysts containing a pair of group VIII metals; one which dissociates CO and one which does not. They reported that Ir–Ru/SiO_2 gives the highest CO conversion, least methanol selectivity and the highest selectivity for higher alcohols. The addition of alkali improved C_2-oxygenate selectivity. The properties of these catalysts are said to be largely affected by the preparation procedure, especially factors like impregnation sequence,[153] precursors,[148,149,154] metal and promoter loading.[153] A close interaction between

Table 3 Effects of cobalt and strontium precursors on Co-Re-Sr/SiO_2 catalysts for CO hydrogenation. Extracted from ref. 154[a]

Catalyst[b]	CO Conv. (%)	Selectivity (%)					
		CO_2	CH_4	C_2+	MeOH	EtOH	C_2-oxy
Co(N)–Re–Sr(N)/SiO_2	11.0	7	14	71	0.7	1.3	4.1
Co(N)–Re–Sr(A)/SiO_2	11.0	8	16	70	0.9	2.7	3.6
Co(Cl)–Re–Sr(A)/SiO_2	5.1	6	34	50	2.2	5.3	7.1
Co(A)–Re–Sr(N)/SiO_2	6.0	9	23	44	2.4	8.0	19.0
Co(A)–Re–Sr(Cl)/SiO_2	5.5	8	34	45	2.4	3.1	7.0
Co(A)–Re–Sr(A)/SiO_2	5.0	6	18	48	2.8	20.4	25.2

[a] Reaction conditions; $CO/H_2/Ar$ = 30/60/10; 2.1 MPa; 523 K, GHSV 2000 h^{-1}. [b] Precursors; Co(N): $Co(NO_3)_2.6H_2O$, Co(Cl): $CoCl_2.6H_2.O$, Co(A): $Co(CH_3COO)_2.4H_2O$Re-Sr(N)/SiO_2; Sr(N): $Sr(NO_3)_2$, Sr(Cl): $SrCl_2.6H_2O$, Sr(A): $Sr(CH_3COO)_2.½H_2O$.

the catalysts and promoter is important for higher alcohol yield—TPR profiles of a co-impregnated Ir–Ru/SiO_2 showed[153] a single Ir–Ru reduction peak, indicating a close interaction. A similar, single Pd–Co reduction peak is shown for Pd–Co/CeO_2.[155] A co-impregnated Ir–Ru/SiO_2 catalyst showed greater higher alcohol selectivity than those in which Ir and Ru were sequentially impregnated.

Matsuzaki *et al.*[154] reported the effects of Co and promoter precursors on the catalysts performance—they showed (Table 3) that ethanol selectivity on Co–Re–Sr/SiO_2 prepared from nitrates increased from 1.3% to 20% with the use of acetate precursors. Interestingly, unpromoted Co/SiO_2 catalyst from an acetate precursor, and those promoted with Sr prepared from chlorides, nitrates or carbonyl precursors were largely inactive for ethanol synthesis. This clearly shows the importance of preparation materials and procedure.

Different promoters have been shown to have different effects on Fischer–Tropsch type catalysts. On a Co/SiO_2 catalyst promoted with Re–Sr.[149] and Sr,[156] Takeuchi *et al.* reported deviations from the Schulz–Flory distribution of C_2 hydrocarbon and C_2 oxygenates (Fig. 19) They witnessed a deficit in C_2 hydrocarbon and an excess in C_2 oxygenates and suggested a mechanism in which oxygenates and hydrocarbons are formed through the same intermediates. This is consistent with the mechanism of Fig. 7. The effect of the promoters therefore would be the preferential conversion of the intermediate to ethanol at the expense of C_2 hydrocarbons.

Alkali dopants promote activity and selectivity to C_2^+ oxygenates by depressing hydrocarbon formation.[153] Transition metals like Ir, Re, Pt and Os help to reduce inactive Co(II) acetate species to the active metallic state by activating H_2 (during pretreatment) while keeping it highly dispersed. High Co dispersion is absolutely necessary for oxygenate synthesis; agglomeration of Co particles tends to catalyze hydrocarbon formation.[154] Although the promoted Co catalysts showed enhanced selectivity towards ethanol, hydrocarbon selectivities remain high (above 60%) in virtually all reported studies.[145,148–150,157]

B. Modified Fischer–Tropsch catalysts—CO_2 hydrogenation. Inui and co-workers report the synthesis of ethanol *via* CO_2 hydrogenation using multifunctional catalysts.[52,158–161] These catalysts are a mixture of Rh, Fe and Cu designed to partially reduce CO_2 to CO, propagate chain growth (C–C bond formation), and insert an –OH group. The Fischer–Tropsch type Fe–Cu–Al–K catalyst gave 8% ethanol selectivity from a CO_2/H_2 (25 : 75) mixture. The selectivity increased to 11% when 3% CO was substituted for CO_2. While the increase in CO concentration increased the ethanol yield, a CO-rich gas reduced ethanol selectivity because CO_2 was formed (rather than ethanol) *via* the shift reaction. The performance of this catalyst is said to be dependent on the oxidation–reduction state of the Fe catalyst during reaction—the active phase for CO_2 hydrogenation to ethanol is Fe_3O_4 and is a function of the reduction temperature. Reduction at about 450 °C gives Fe_3O_4, insufficient reduction leaves Fe in the inactive Fe_2O_3 phase and over-reduction leads to the metallic Fe. Combining Fe with other catalysts and suitable promotion from metals like Pd and Ga (which have the H_2 spillover and reverse-spillover, respectively) maintains the oxidation state of the catalysts during reaction conditions.[52]

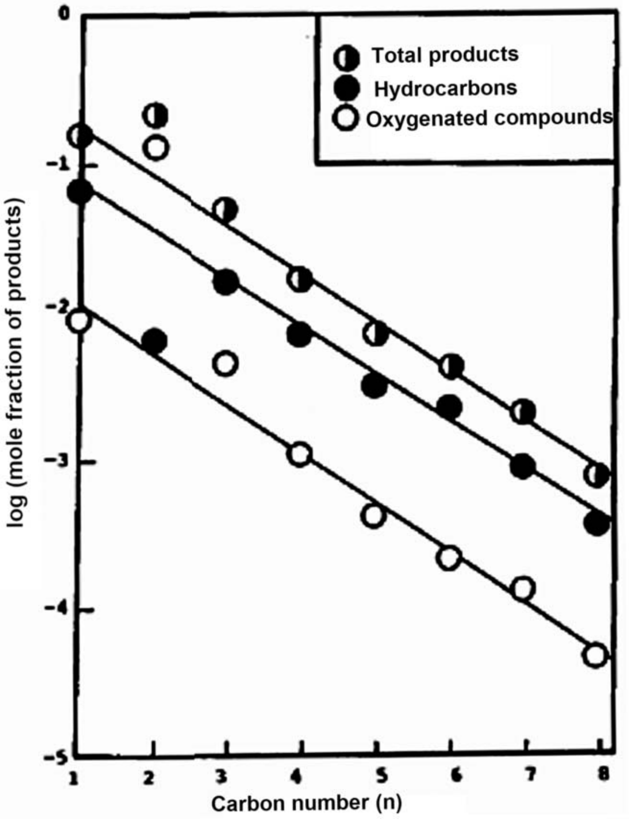


Fig. 19 Schultz–Flory plots of product generation over Co–Sr/SiO_2, catalysts. Reaction conditions: CO : H : Ar = 3 : 6 : l; pressure, 2.1 MPa; temperature, 523 K; GHSV, 2000 h^{-1}. (Reproduced with permission from ref. 156. Copyright 1989 Elsevier.)

Table 4 Catalytic performance of K/MoS_2 catalysts in CO hydrogenation[166,a]

Catalyst	CO conv. (%)	Selectivity (C-atom%)		Alcohol distribution (wt%)				
		Alcohols	CH_x[b]	C_1	C_2	C_3	C_4	C_5
K/MoS_2	11.4	55.20	44.80	71.6	18.8	7.4	2.0	0.2
$Ni/K/MoS_2$	23.3	59.98	40.02	56.3	26.9	11.6	4.5	0.7
$Ni/Mn/K/MoS_2$	17.8	81.72	18.82	45.8	32.9	15.4	5.0	0.9

[a] T = 588 K; P = 9.5 MPa; H2/CO = 2.0; GHSV = 6000h^{-1}. [b] CH_x = hydrocarbons

The importance of choice of precursors for oxygenates formation (as shown in Table 3 for CO hydrogenation) was also mirrored by Okabe *et al.* for CO_2 hydrogenation—acetate-derived $Co(A)/SiO_2$ promoted with Ir and Na from acetate precursors showed improved alcohol selectivity over nitrate-derived $Co(N)/SiO_2$.[162]

3.4 Modified Mo-based catalysts

A. Modified Mo-based catalysts—CO hydrogenation. When alkali metals are added to Mo-based catalysts, the selectivity for CO hydrogenation has been shown to shift from hydrocarbons to alcohols.[163] The promoting effect of alkalis (on MoS_2) for alcohol formation was found to increase in the order Li < Na < Cs < Rb < K, suggesting that moderate basic promotion is desired.[164] Muramatsu *et al.* claimed that the role of K on Mo/SiO_2 is to preserve the surface MoO_2 species which is active for alcohols by retarding the reduction of Mo to metal.[165] Selectivity to alcohols on alkali promoted Mo catalysts normally follows the Schulz–Flory distribution, which limits higher alcohol formation. However, further promotion with transition metals like Co and Ni has been shown to improve C_2^+ alcohol selectivity.[166–168] When K/MoS_2 catalyst is co-modified with Ni and Mn, the synergistic effect of both promoters is said to enhance the catalytic activity and the formation of C_2–C_3 alcohols. Table 4 shows the catalytic performance of K/MoS_2 catalyst in which the addition of Ni improved catalyst activity and selectivity to alcohols. Ni is thought to enhance the $C_1 \rightarrow C_2$ homologation step, which might explain the high ethanol selectivity. The further addition of Mn inhibits the enrichment of Ni, leading to the suppression of methanation functions of Ni while improving the dispersion of the catalyst.[166] The main mechanism for ethanol formation on alkali promoted Mo-based catalyst is *via* the insertion of CO into the metal–CH_x bond as depicted in Fig. 7.[169,170]

Preparation techniques have been reported by a number of authors to affect the selectivity and activity of Mo catalysts. KCl promoted Mo/SiO_2, which was prepared by the successive impregnation method in which K was added to silica gel followed by impregnation with Mo solution, was found to give higher activity and selectivity for alcohol formation than when Mo was added first. The sequence was found to greatly affect the activity and selectivity because certain interactions between Mo and SiO_2, which inhibit higher alcohol formation, are said to be less pronounced when K was added first.[171] A rapid drying procedure instead of a slow one was found to improve alcohol selectivity and activity on K–Mo/C catalyst.[172] A modified Mo/SiO_2 catalyst prepared using the metal oxide vapor synthesis (MOVS) exhibited much higher activity and selectivity to higher alcohols than a nominally similar catalyst prepared by the conventional impregnation method.[167] These improved activities and selectivities result from higher dispersion of active species.

B. Modified Mo-based catalysts—CO + CO_2 hydrogenation. Significant amounts of CO_2 are formed on MoS_2 catalyst when the feed is CO_2-free because of its high activity for the water–gas shift (WGS) reaction.[172,173] However the inclusion of CO_2 in a syngas feed shifts the WGS reaction equilibrium toward H_2O formation causing large amounts of water to be formed instead of CO_2. CO_2 in feed also reduces the formation of higher alcohols, possibly due to the inhibition of the chain growth process by CO_2 or by H_2O produced by the r-WGS reaction.[172]

4. Conclusion

Modified methanol synthesis catalysts give the highest activity for ethanol formation in terms of CO conversion, but methanol remains the dominant alcohol product. Ethanol selectivities are very low on these catalysts because of the chain growth mechanism for the formation of higher alcohols. While ethanol is formed from methanol *via* a slow difficult reaction, ethanol is quickly converted to higher alcohols *via* a faster chain growth mechanism. Rh-based catalysts give the best ethanol selectivities, albeit at lower CO conversions. Methanol formation is very low but high CH_4 formation is thermodynamically favorable and seems inevitable on these catalysts. Modified Fischer–Tropsch catalysts give moderate ethanol selectivities but methane formation is dominant and methanol selectivities are high.

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