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Methanol synthesis and water-gas shift reactions on Raney copper catalysts

M.S. Wainwright [a,*], D.L. Trimm [b]

[a] *Faculty of Engineering, The University of New South Wales, Sydney 2052, Australia*

[b] *School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney 2052, Australia*

Abstract

The use of Raney copper to catalyse the synthesis of methanol and the water-gas shift reaction is reviewed. The preparation of Raney copper and Raney copper–zinc alloys together with their leaching to form active catalysts is first considered. The production of methanol is promoted by copper and the major — but not the only — role of zinc oxide involves the production of higher and more stable copper surface areas. There is some evidence that the catalytic activity of both methanol synthesis and water-gas shift may be improved by events occurring at the Cu–ZnO interface. It is now clear that carbon dioxide is the major reactant forming methanol under industrial conditions. Both in the water-gas shift and the synthesis reactions, formates appear to be the main intermediates. Raney catalysts have the advantages of high mechanical strength, of regenerability and of producing less side products during methanol synthesis — an important practical consideration. Their applicability to industrial operations would seem advantageous.

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1. Introduction

The industrial production of methanol from synthesis gas was revolutionised some years ago by the development of catalysts that could operate at relatively low pressures [1,2]. The catalysts consisted of intimate mixtures of copper and zinc oxide, mixed with either alumina or chromia [1–3]. In that the activity of the mixed oxides was significantly higher than that of the individual components, methods of catalyst preparation have been studied in some detail [3,4].

One alternative route to active catalysts is based on alkaline leaching of copper/zinc/aluminium alloys to produce zinc-promoted Raney copper [5,6]. Alloying achieves excellent mixing of the components and extraction with sodium hydroxide removes aluminium, redistributes the zinc and develops porosity and surface area [6]. The resulting catalysts have been found to be at least as active as commercial co-precipitated catalysts [6].

The role of copper and zinc oxides in methanol synthesis and water-gas shift catalysts has been the subject of much debate. Herman et al. [3] suggested that the active species for methanol synthesis was Cu^I dissolved in ZnO, an opinion shared by Kalchev et al. [7]. Andrew, on the other hand, has argued that copper is the only active species [8], the zinc oxide being present to distribute the copper and adsorb potential poisons. The importance of copper is also emphasised by many other workers [5,6,9]. Recently, however, the importance of the copper/ZnO interface has been recognised, and catalytic activity is suggested to

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* Corresponding author.

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originate from this interface [6]. This suggestion re-emphasises the need for careful preparation, even of Raney copper catalysts [5,6].

The use of copper-based catalysts for the synthesis of methanol offers significant improvement over earlier catalysts but is itself far from problem free. The possibility of catalyst poisoning, particularly as a result of traces of sulphur in the feed gases, is very real [4]. In addition, the need to adjust the ratio of carbon oxides to hydrogen from that produced usually by steam reforming to that required for methanol synthesis emphasises the importance of water-gas was shift reactions [4,10]. At low temperatures, copper-based catalysts promote these reactions.

The synthesis of methanol may also be complicated by various side reactions. The reaction between carbon monoxide and hydrogen may produce methane, methanol and higher hydrocarbons or alcohols as follows:

$$CO + 3H_2 = CH_4 + H_2O \qquad (1)$$

$$CO + 2H_2 = CH_3OH \qquad (2)$$

$$nCO + (2n+1)H_2 = C_nH_{2n+2} + nH_2O \qquad (3)$$

$$mCO + 2mH_2 = C_mH_{2m+1}OH + (m-1)H_2O \qquad (4)$$

Similar reactions can occur with carbon dioxide and, indeed there is strong evidence that methanol is produced mainly via CO_2 [11,12].

$$CO_2 + 3H_2 = CH_3OH + H_2O \qquad (5)$$

Dehydrogenation of methanol to methyl formate can also occur over copper catalysts [13].

$$2CH_3OH = HCOOCH_3 + 2H_2 \qquad (6)$$

but the high pressures of the methanol synthesis reaction do not favour the reaction. Steam reforming of methanol involving steam either from the feed gas or from reaction (5) is also not favoured at high pressures [14].

$$CH_3OH + H_2O = CO_2 + 3H_2 \qquad (7)$$

Small traces of impurities or dopants may affect the activity and selectivity of the catalysts. Thus, for example, the selectivity of reaction (4) to C_2 oxygenates has been found to pass through a maximum as a function of cesium concentration [15], while as little as $<0.1\%$ cesium was found to accelerate the water-gas shift reaction by a factor of two [16].

One advantage of Raney copper catalysts is the relatively selective nature of methanol synthesis over the solids. As will be discussed, the roles of copper, zinc oxide and alumina are open to some question, but the ability to leach the catalysts to produce close contact between the various phases offers significant advantages. As a result, the preparation of Raney copper–zinc catalysts doped with zinc oxide forms an important part of this review.

Raney catalysts may also be used to promote the water-gas shift reactions (WGS). The importance of WGS was first recognised in the latter part of the nineteenth century as a means of converting carbon monoxide, produced from coke, to carbon dioxide.

$$2CO + H_2O = H_2 + CO_2 \qquad \Delta H = -41.1\ \mathrm{kJ/mol} \qquad (8)$$

The equilibrium reaction has since developed major importance in the context of adjusting carbon oxides:hydrogen:steam ratios from steam reforming and for methanol synthesis and Fischer–Tropsch reactions.

The production of hydrogen is favoured at low temperatures, with the equilibrium constant reducing from 228 at 473 K to 11.7 at 673 K [4]. However, the process was originally operated mainly at high temperatures using Fe–Cr-based catalysts [17,18]. Low-temperature copper-based catalysts came into their own in the 1960's [4]. Although difficulties with catalyst life-time were experienced, improvements in formulation and preparation has led to widespread use of the systems [4].

Improvements in the thermal stability of the catalysts resulted from inclusion of oxides of zinc and aluminium [6]. Reduction before use led to copper crystallites suspended with zinc oxide and alumina [4] but also led to the formation of α-

brass [19]. Spencer has calculated that significant (0.2–5 wt.-%) amounts of zinc in brass can be formed during reduction of the catalysts, although this amount reduces to ca. 0.005 wt.-% under typical operating conditions [19].

The nature of the active sites for WGS is still a subject of some controversy, with opinion divided as to the relative importance of copper surface area and of Cu^{I} cations dissolved in ZnO lattices. Herman et al. [3] identified the formation of a solid solution of Cu^{I} in ZnO, and suggested that these species were catalytically active. Petrini et al. [20] used XPS to identify a non-equilibrium solid solution of Cu^{II} in ZnO and found evidence for the presence of Zn^{II} in CuO. Stefanov et al. [21] also identified Cu^{II} ions in ZnO as well as a crystalline CuO phase. In all cases Cu^{I} in ZnO was suggested to play some role in catalysis.

On the other hand, Campbell [22] and many other authors [5,8,9,23] have suggested that the copper surface area is the critical factor. One role of ZnO was suggested to be to increase the dispersion of copper [23] with high copper surface areas being related to well dispersed small copper crystallites [24].

Both of these arguments lead to the conclusion that an intimate mixture of Cu and ZnO is necessary, with alumina acting mainly as a thermal stabilising agent. In these terms, it is not surprising that Raney copper catalysts, which allow the closest contact between constituents of the alloys, have been studied for both water-gas shift and methanol synthesis.

In this paper the use of zinc oxide-promoted Raney copper catalysts for both low-temperature methanol synthesis and water-gas shift reactions are considered with emphasis on the mechanism of the reactions and on the role of catalyst components in promoting both systems.

2. Preparation and characterisation of Raney copper–zinc catalysts

Murray Raney was the first to produce sponge metal catalysts by the selective leaching of silicon from a Si–Ni alloy [25] or aluminium from an Al–Ni alloy [26] resulting in high surface area nickel catalysts for hydrogenation of cotton seed oil. Raney copper catalysts were then produced by leaching of aluminium from Al–Cu alloys using aqueous sodium hydroxide. The literature on Raney copper up to 1977 was the subject of a major review by Stanfield and Robbins [27]. Raney copper catalysts were first used for selective hydrogenation of aldehydes and ketones. More recently they have been used for the liquid phase hydrolysis of nitriles [28].

Fauconnau [29] was the first to report the preparation of Raney Cu–Zn catalysts which were used for the selective hydrogenation of aldehydes and ketones. Later, Reynolds and Mackenzie [30] described the preparation of Raney Cu–Zn catalysts by acid leaching of zinc from a Cu–Zn alloy. The foraminate catalysts so formed were used for the selective hydrogenation of furfural and acetone.

Wainwright and co-workers at the University of New South Wales (UNSW) were the first to report the potential use of Raney copper and Raney Cu–Zn catalysts for the production of methanol for use as a synthetic liquid fuel [31,32]. Over the past 15 years the group has made a systematic study of all aspects of preparation and characterisation of Raney Cu–Zn catalysts including the precursor alloys and leaching conditions.

3. Precursor alloys

The initial study of methanol synthesis over Raney Cu–Zn catalysts involved the caustic leaching of a Cu–Zn–Al alloy [32]. Following this work it was found that the composition of the precursor alloy had a marked effect on the leachability thereby influencing the physical and chemical properties of the resulting catalysts. The Cu–Zn–Al system is a complex one as can be seen from Fig. 1 which is the liquidus projection showing the phases that are formed during the cooling of Cu–Zn–Al melts [33].

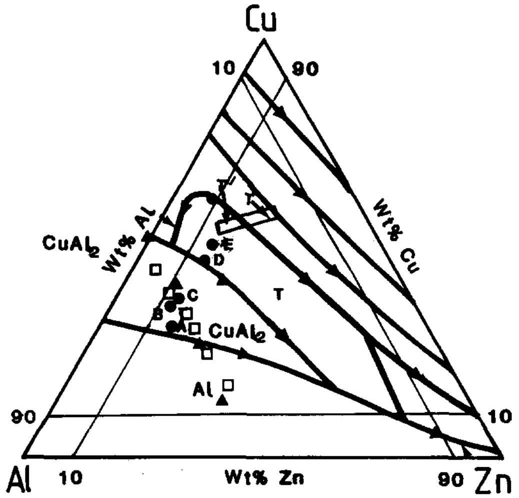


Fig. 1. A; -Cu–Zn phase diagram, liquidus projection [33]. (●) Alloys investigated by Bridgewater et al. [5]. (□) Alloys investigated by Friedrich et al. [37]. (▲) Alloys investigated by Mellor [16].

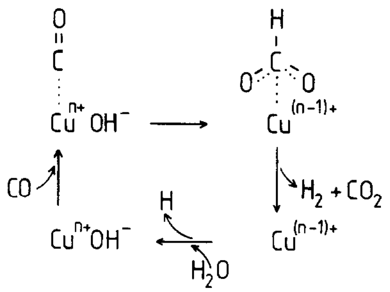
Electron microprobe studies of Cu–Al (50:50 wt.-%), Cu–Al–Zn (45:50:5 wt.-%) and Cu–Al–Zn (47:50:3 wt.-%) alloys by Nadirov and co-workers [34] showed that the Cu–Al alloy contained a $CuAl_2$ phase and a eutectic of Al and $CuAl_2$. This result was later confirmed by Young et al. [35]. Nadirov et al. [34] showed that the Cu–Al–Zn alloys comprised a $CuAl_2$ phase (50 wt.-% Cu, 49.5 wt.-% Al with 0.5 wt.-% dissolved Zn) and a eutectic of composition 29 wt.-% Cu, 63 wt.-% Al and 9 wt.-% Zn.

Friedrich et al. [36,37] made an extensive study of precursor alloys containing 50 wt.-% Al and 0 to 50 wt.-% Zn with the balance Cu. These alloy compositions are shown by the □ symbols in Fig. 1. For alloys containing 0 to 17% Zn, the primary precipitate is Cu $(Zn)Al_2$ ($CuAl_2$ containing dissolved zinc) as reported earlier by Nadirov et al. [34]. As the Zn content of the melt is increased, the Zn content of the $Cu(Zn)Al_2$ phase increases. It has been reported [33] that $CuAl_2$ can dissolve up to around 3 wt.-% Zn without significant change to the lattice parameter. For melts containing more than 17 wt.-% Zn the primary precipitate is an aluminium-based solution.

The study by Friedrich et al. showed that the phase formed as a secondary precipitate depends on the Zn content of the melt. With no Zn present the binary Al–$CuAl_2$ eutectic forms, as reported by Nadirov et al. [34] and Young et al. [35]. For Zn levels less than 17 wt.-% an aluminium-based solid solution is the secondary phase. At higher levels of Zn the $Cu(Zn)Al_2$ phase forms as the secondary precipitate; Friedrich et al. [36] found that the final solidification was the ternary phase T and that in some cases $CuZn_5$ is formed. It has been reported [33] that $Cu_5Al_3Zn_2$ is formed at the low Al end of the ternary phase region whilst Cu_3Al_3Zn forms at the high Al end.

Following a detailed analysis the liquidus projection diagram (Fig. 1) Bridgewater et al. [15] made a systematic study of alloys produced from melts containing 14 wt.-% Zn, 30 to 50 wt.-% Cu with the balance Al. These are shown as compositions A to E in Fig. 1. Melts A, B and C containing 31–38 wt.-% Cu formed $Cu(Zn)Al_2$ as the primary precipitate. Only small quantities of ternary phase were formed as a result of the peritectic reaction being stopped due to the rapid quench cooling used in the alloy preparation. As the Cu content of the melt was increased the amount of the primary $Cu(Zn)Al_2$ phase increased and the amount of the secondary Al(Zn) phase decreased. Melts D and E which contained greater than 38 wt.-% were in the ternary phase region of the liquidus projection (Fig. 1) and large amounts of this phase were detected in the quenched product.

Recently Andreev and co-workers [38] have made an extensive study of Raney Cu–Zn–Al catalysts for the water-gas shift reaction. The catalysts were prepared from a melt containing Cu: 42 wt.-%, Zn: 14.3 wt.-% and Al: 43.5 wt.-% that was rapidly quenched. Mellor [16] used catalysts prepared from melts containing Al: 50 wt.-%, Cu: 10–50 wt.-% and Zn: 0–40 wt.-% Cu for the WGS reaction. He also investigated catalysts prepared from a melt containing Al: 39 wt.-%, Cu: 43 wt.-% and Zn: 18 wt.-%. The melts were rapidly quenched in cold water.



Mechanism of Andreev.

4. Leaching of Cu–Zn–Al alloys

Raney Cu–Zn catalysts for methanol synthesis and WGS reactions are prepared by leaching of the precursor alloys in aqueous caustic solutions [32,38]. The chemical reactions that occur during the leaching of Cu–Zn–Al alloys are as follows:

$$Al + OH^- + 3H_2O \rightleftharpoons Al(OH) + \tfrac{3}{2}H_2 \tag{9}$$

$$Zn + 2OH^- + 2H_2O \rightleftharpoons Zn(OH) + H_2 \tag{10}$$

The leached structures that result are influenced by a number of factors. Friedrich et al. [36] found that the microstructure of the Cu–Al–Zn alloy was reproduced in the leached material. The size of the $Cu(Zn)Al_2$ grain, which decreased from 11.2 nm to 6.2 nm as the Zn content of melt increased and the Cu content decreased, was retained after leaching. Electron microprobe analysis showed that the resultant porous copper grains contained significant levels of Al_2O_3 and ZnO. The intergranular material leached completely leaving large pores, typically several microns wide, between the grains. The zinc content of the intergranular material increased with increasing zinc content of the melt and became increasingly resistant to leaching.

Bridgewater et al. [5] found that as the amount of intergranular material increased in alloys formed from melts of composition A to E in Fig. 1, the void volume and pore dimensions increased in the leached product which became increasingly friable. They also found that the ternary phase present in alloys D and E was not leached by caustic. Using electron microprobe analysis they found zinc and aluminium profiles in the porous copper grains similar to those observed by Friedrich et al. [37]. The high concentrations of zinc, which were well in excess of the 3 wt.-% solubility of Zn in $CuAl_2$, resulted from reprecipitation of $Zn(OH)_2$ from the leachate which contained high levels of sodium zincate as a result of leaching of the intergranular material and the Zn within the grains. A similar explanation was given for the precipitation of $Al(OH)_3$. The reprecipitation process occurs due to a lowering of the pH at the leached alloy interface as a result of hydroxyl ion consumption at the interface.

Leaching of Al and Zn from the $Cu(Zn)Al_2$ from the $Cu(Zn)Al_2$ grains leads to the formation of mesopores with diameters typically 3 to 100 nm whereas leaching of the intergranular material leads to macropores of micron dimensions. A typical Raney Cu–Zn catalyst is the one reported by Curry-Hyde et al. [39] which was prepared by leaching alloy pellets containing Cu: 43.2 wt.-%, Zn: 17.8 wt.-% and Al 39.0 wt.-%. Pore size distributions were measured using mercury intrusion porosimetry on samples that had been passivated using nitrous oxide according to the procedure described by Tomsett et al. [40]. The leached pellets displayed a well separated biomodal pore size distribution, one appearing as a narrow distribution in the mesopore range (3 to 100 nm) and the other as a broad distribution in the macropore range (100 to 2100 nm) with a mean of 1300 nm.

The size of the copper crystallites that form the copper grains determines the mesopore sizes and thus the surface area of the leached material. Friedrich et al. [36] have studied the variation in crystallite size with Zn content on the precursor alloy using X-ray line broadening and have shown that increasing the Zn content in the alloy decreased the Cu crystallite sizes of the leached product.

The leaching temperature also affects the surface area and crystallite size. Kagan et al. [41] found that, by leaching at 291 K, crystallite sizes between 14 and 34 nm were obtained and at 353 K the size range was 16 to 80 nm. A study by Pearce and Lewis [42] confirmed that crystallite sizes increase with increasing leach temperature. Tomsett et al. [43] studied structural changes during the leaching of copper-based Raney catalysts using pellets of Cu: 50 wt.-%, Al: 50 wt.-% and Cu: 43 wt.-%, Zn: 18 wt.-%, Al: 39 wt.-% leached in 20 wt.-% NaOH solutions at temperatures from 274 to 323 K. It was found that prolonged contact of the leached porous copper with the caustic solution resulted in decreased BET surface areas, increased pore diameters and increased copper crystallite sizes whilst the pore volume of the material remained constant. The study showed that the degradation of surface area with prolonged leaching of pellets is due to a rearrangement of the copper structure through a dissolution — reprecipitation process which was discussed in greater detail in a subsequent paper [44]. It also showed that there is an optimal leach depth for Raney copper catalyst pellets as had been found earlier for Raney Cu–Zn catalysts [45].

Tomsett et al. [46] studied pore development during leaching of a Cu: 50 wt.-%, Al: 50 wt.-% alloy in aqueous sodium hydroxide. They found that the rate of leaching of the alloy was controlled by liquid phase diffusion in the pores of the leached product. At constant temperature the copper crystallite size was found to increase as the leach rate decreased. When the temperature was increased so did the crystallite size and pore spacing. More recent electron microscopy studies [44] have shown that the resulting copper structures consist of very fine copper rods or fibres having diameters from 1 to 10 nm [44]. These rods are regularly spaced and are aligned approximately parallel to the direction in which the leach reaction advances through the alloy.

Curry-Hyde et al. [47] have shown that significant improvements can be made to the performance of Raney Cu–Zn methanol synthesis through zinc impregnation during the leaching process. Both Cu: 53 wt.-%, Al: 47 wt.-% and Cu: 43.2 wt.-%, Zn: 17.7 wt.-%, Al: 39 wt.-% alloys have been studied using 0.62 M sodium zincate in 6.1 M sodium hydroxide leach solutions at temperatures of 274 and 303 K [47]. It was found that the addition of zincate to the sodium hydroxide solution slows the leaching rate of both alloys, the greatest effect being observed for the Cu–Zn–Al alloy. The decrease in leaching rate results in increased surface area.

Electron microprobe analysis [48] on the catalyst produced by leaching in sodium zincate enriched sodium hydroxide solutions revealed that the ZnO concentration profile in the leached Cu–Zn–Al is far superior to that for the same alloy leached in sodium hydroxide solution alone. Furthermore, significant amounts of ZnO can be deposited in the porous copper produced from leaching a Cu–Al alloy containing no zinc. In the case of the Cu–Zn–Al alloy, leaching in pure or zincate enriched sodium hydroxide solutions gave similar total amounts of zinc in the leached product. However, the aluminium levels were significantly lower for the solution containing zincate.

Mellor [16] has used both pure sodium hydroxide and sodium zincate doped sodium hydroxide solutions to produce Raney Cu–Zn catalysts for the WGS reaction. The methods of preparation were almost identical to those employed previously for Raney Cu–Zn methanol synthesis catalysts [37]. He also prepared catalysts by leaching the same Cu–Zn–Al alloy with nitric acid and perchloric acid. These catalysts were less active for the WGS reaction than those prepared using alkali leaching. He also used the methanol synthesis catalyst of Klier [2] that was developed to promote higher alcohol formation in co-precipitated Cu–ZnO methanol synthesis catalysts to produce alkali-promoted Raney Cu–Zn catalysts for the WGS reaction. Doping of the optimal Raney Cu–Zn WGS catalyst was conducted using CsOH, RbOH or KOH.

Mellor [16] also investigated zinc ion implantation in a passivated Raney copper catalyst that had been prepared by leaching a Cu: 50 wt.-%, Al: 50 wt.-% alloy in aqueous sodium hydroxide.

Andreev et al. [38] prepared their Raney Cu–Zn WGS catalysts by leaching an alloy of composition Cu: 42 wt.-%, Zn: 14.3 wt.-%, Al: 43.5 wt.-% in 6 M NaOH at 303 K for 16 hours, a method of preparation very similar to that as used earlier by Marsden et al. [32] for methanol synthesis catalysts.

5. Methanol synthesis

Research using Raney copper–zinc catalysts has not only been concerned with their possible applications as alternative catalysts to co-precipitated low-temperature methanol synthesis catalysts [47,49] but has also been the basis of fundamental studies leading to a greater understanding of the mechanism of the methanol synthesis reaction [50]. In this section the potential use of Raney copper–zinc catalysts in both conventional fixed-bed reactors and alternative liquid phase processes is discussed. Studies using Raney copper catalysts to investigate fundamental aspects of methanol synthesis including the roles of Cu and ZnO are then discussed. Finally the vexed question of whether CO_2 or CO is the active species in methanol synthesis is addressed.

5.1. *Catalyst activity and selectivity*

Marsden et al. [32] were the first to show that catalysts prepared by caustic leaching of alloys prepared from melts of Cu–Zn–Al (the Raney method) were both active and highly selective for methanol synthesis. It was apparent from that research that there was great potential for catalysts prepared by this method for use in industrial reactors. For this reason activity testing at UNSW has used reaction conditions typical of those used in industry in terms of temperature, pressure and synthesis gas composition. Furthermore, comparative testing of commercial co-precipitated low-temperature methanol synthesis catalysts has been performed [47,48,51]. The earliest comprehensive comparison was reported by Bridgewater et al. [51] using a Raney catalyst prepared from an alloy consisting of 43 wt.-% Cu, 39 wt.-% Al and 18 wt.-% Zn and a co-precipitated catalyst C79-4 supplied by United Catalysts Inc. that had been used in the earlier study by Marsden et al. [32]. The experimental conditions employed (430–530 K, 5 MPa and syngas containing 15 to 20% carbon oxides) were typical of those used in subsequent studies. The gas hourly space velocity (GHSV) employed was 10 000 h^{-1} which was somewhat lower than those used in industry and later studies at UNSW.

Bridgewater et al. [51] found that the two catalysts had almost identical activities per unit surface area of copper (based on measurements made using the technique of Evans et al. [52]) and showed almost the same responses to changes to process conditions such as synthesis gas composition and temperature despite the different morphologies resulting from the two very different methods of catalyst preparation. The study also showed that zinc free Raney copper is capable of catalysing the methanol synthesis reaction at a rate of 0.88×10^{-4} mol m^{-2} h^{-1} (based on copper area) which was around 12% of the activity measured under the same conditions for the catalyst prepared from the Cu–Zn–Al alloy. As a result of that study Bridgewater et al. [51] concluded that the same active species are involved in methanol synthesis in both types of catalyst and that these species involve copper metal.

Since commercial methanol synthesis is conducted in fixed-bed converters that may be either multiple adiabatic beds with interbed cooling or water-cooled shell and tube reactors [53], much of the recent work at UNSW has used Raney Cu–Zn catalysts in pellet form [45,47–49]. These catalysts have been prepared by leaching pellets of similar size to those used in industry [54]. The pellets of Cu–Al and Cu–Zn–Al alloys are produced by pouring the melts into molds of the desired diameter (5.4 mm) and cutting the resulting rods of alloy to the desired length of 3.8 mm [54]. The research using pellets has mainly been conducted using catalysts prepared with sodium zincate enriched sodium hydroxide solutions since they have been shown to be highly active and selective [47–49].

Curry-Hyde et al. [47,49] have made detailed comparisons of pelleted zinc oxide-promoted Raney copper catalysts and two different pelleted commercial co-precipitated catalysts at 493 K, 4.5 MPa, 91% H_2, 5% CO and 4% CO_2. It was found [47] that, under these conditions, the yields of Raney copper–zinc catalysts produced by leaching a Cu–Al–Zn alloy in a 6.1 M NaOH/0.62 M Na-zincate solution at 303 K were 1.1 kg l^{-1} h^{-1} and 0.6 kg l^{-1} h^{-1}, respectively. The yield for the better of the two commercial catalysts under the same conditions was 0.6 kg l^{-1} h^{-1}. It was demonstrated that the superior yield of the best Raney copper–zinc catalyst could be achieved over a wide range of GHSVs from 11 000 to 80 000 h^{-1} [49].

Considerations other than yield are important when comparing catalysts. Curry-Hyde et al. compared the amounts of water produced during methanol synthesis using pellets of Raney copper–zinc with those for the best commercial catalyst tested [49]. It was found that for the GHSV range from 11 000 to 80 000 h^{-1} the Raney catalyst produced significantly more water in the methanol product. This is a disadvantage industrially since it introduces greater energy costs in the separation stage of the process. It also gives an indication that the Raney catalysts convert more CO_2 by reaction (5) than the conventional catalyst for the synthesis gas composition employed. This phenomenon has been the subject of a recent fundamental study of the mechanism of methanol synthesis over copper and zinc-promoted copper surfaces using Raney copper catalysts [50]. Product purity is also important in methanol synthesis and the methanol produced over the Raney copper–zinc catalyst contained lower concentrations of ethanol, propanol and butanol than the two commercial co-precipitated catalysts tested [49].

The potential to use Raney copper–zinc catalysts for methanol synthesis has led to the award of a number of international patents [the most recent being ref. [55]]. There has recently been increased interest in slurry phase methanol synthesis using zinc-promoted copper catalysts [56]. Since the original Raney nickel and Raney copper catalysts were developed for use in powdered form for liquid phase hydrogenation reactions it is obvious that Raney copper–zinc methanol synthesis catalysts have great potential for use in slurry phase reactors. The liquid phase process originally proposed by Chem Systems [57] has been developed by Air Products [58] and a commercial process will shortly be brought on-line to produce methanol for peak shaving in electric power production from coal using the Coal Gasification Combined Cycle process.

6. Mechanism of methanol synthesis

Chinchen et al. [59] have presented an excellent paper which reviews recent studies by researchers at ICI that have contributed greatly to an understanding of the methanol synthesis reaction. In the paper they have considered the following issues:

- Methanol from carbon monoxide or carbon dioxide?
- Where on the catalyst?
- Why zinc oxide?
- What is the mechanism?

Studies of methanol synthesis using Raney copper and zinc-promoted Raney copper have contributed to an understanding of these questions.

As noted earlier in this paper, when using a synthesis gas of composition 91% H_2, 5% CO and 4% CO_2, a zinc-promoted Raney copper catalyst produced a higher water-to-methanol ratio in the product than that observed for a commercial co-precipitated catalyst [49]. In a recent study [50] methanol synthesis was studied at 523 K and 4.5 MPa over unpromoted Raney copper, zinc oxide, promoted Raney copper produced by leaching a $CuAl_2$ in sodium zincate enriched sodium hydroxide solution and a commercial co-precipitated catalyst. Four different synthesis gas feed compositions with CO_2/CO ratios of 0.25, 0.50, 1.14 and 2.0 while keeping the $H_2/(CO_2+CO)$ ratio at 85/15 were used over a wide range of space velocities. All catalysts produced similar patterns of conversion with increasing space times (decreasing space velocities). CO conversions were initially low for synthesis gas containing CO_2/CO ratios less than one and did not achieve maximum values until the conversion of CO_2 had reached a constant level. For synthesis gas containing CO_2/CO ratios greater than one, CO conversion was suppressed by CO_2.

Significant methanol synthesis was observed over unpromoted copper with the yield being largely independent of synthesis gas composition. However, when zinc oxide was present on the surface of Raney copper, the methanol yield passed through a maximum for a synthesis gas containing a CO_2:CO ratio of 0.5. The presence of 7.3 wt.-% ZnO on the surface of Raney copper increased the yield of methanol by a factor of 1.3 to 2.5 depending on the synthesis gas composition. However, the Raney catalyst leached in sodium hydroxide containing sodium zincate had twice the surface area. Thus the specific yields (on a unit surface area basis) were almost identical. This strongly supports the view of Chinchen et al. [59] that no unique role can be ascribed to ZnO (or Al_2O_3). Chinchen et al. measured similar turnover numbers for methanol synthesis for copper supported on oxides such as MnO, MgO and SiO_2 as well as ZnO and Al_2O_3. The use of Raney copper of high surface area ($28\ m^2\ g^{-1}$) has enabled methanol synthesis to be studied over unpromoted copper under commercial operating conditions and has confirmed that copper is the active species in methanol synthesis [50].

In an extensive study using electron microprobe analysis [48] it has been found that the specific activity of zinc oxide-promoted Raney copper catalysts increases with the mass of zinc oxide present on the surface of the copper. It has been suggested [48] that the dispersion of ZnO on the copper surface increases with the ZnO loading and that this results in a highly promoted copper surface for methanol synthesis from CO_2 and CO. A more detailed discussion of the role of ZnO in Raney copper in light of recent literature for other systems can be found in references [48] and [50].

There has been much controversy in the literature regarding the activities of CO_2 and CO in methanol synthesis. However, the recent literature using isotopic labelling [11] suggests that direct conversion of CO_2 to methanol via reaction [5] is the major route and that methanol synthesis and the water-gas shift reactions occur to a lesser extent. Bowker et al. [12] have proposed that only the formate species on the copper surface participate in the methanol synthesis although formate can adsorb on ZnO. This was supported by Neophytides et al. [60] who found that the formate species adsorbed on ZnO is less active than that formed on copper. They found that copper formate hydrogenation on a methanol catalyst is easier than its decomposition, which has a higher activation energy. They attributed this behaviour to alterations in the catalytic activity of copper, due to interfacial interactions with ZnO, thereby leading to the enhanced methanol synthesis activity.

In a recent study [50] using Raney copper–zinc oxide-promoted Raney copper and a commercial co-precipitated catalyst, the conversions of CO_2 and CO were measured for different CO_2/CO ratios from 0.25 to 2.0 over a wide range of space times (reciprocal space velocities). Using the low conversion data obtained at low space times it was possible to estimate the rates of conversion of CO_2 and CO. Table 1 shows the rate of CO_2 conversion to the rate of CO_2+CO conversion for the three quite different catalysts. It was shown that all catalysts perform similarly in conversion of CO_2 and CO. The results are consistent with those of the isotopic labelling study of Chinchen et al. [11]. In both studies it has been demonstrated that CO_2 is the major reactant under industrial conditions.

The results of Sizgek et al. [50] using unpromoted Raney copper and zinc oxide-promoted catalysts provide support for the following reaction mechanism for methanol synthesis proposed by Bowker et al. [12] based on CO_2 being the predominant reactant.

Table 1
Ratios of rates of conversion of CO_2 to the sum of the rates of conversion of CO_2 and CO over three copper-based catalysts at 523 K and 4.5 MPa

Syngas	Ratio $\frac{r_{CO_2}}{r_{CO_2}+r_{CO}}$			
CO_2/CO	RC[a]	RCD[b]	Cat. X[c]	Average
0.25	0.59	0.56	0.65	0.60±0.05
0.50	0.71	0.67	0.65	0.68±0.03
1.14	0.92	0.87	0.87	0.89±0.03
2.00	0.87	0.86	0.95	0.89±0.06

[a] $CuAl_2$ leached in 6.1 M NaOH at 274 K for 50 hours ($S_{BET}=28.0$ $m^2 g^{-1}$).
[b] $CuAl_2$ leached in 6.1 M NaOH/0.62 M Na-zincate at 274 K for 140 hours ($S_{BET}=58.1$ $m^2 g^{-1}$).
[c] Co-precipitated commercial catalyst ($S_{BET}=79.0$ $m^2 g^{-1}$).

$$CO_2 \rightleftharpoons CO_{2ads} \tag{11}$$

$$H_2 \rightleftharpoons 2H_{ads} \tag{12}$$

$$CO_{2ads} + H_{ads} \rightleftharpoons HCOO_{ads} \tag{13}$$

$$HCOO_{ads} + 3H_{ads} \rightleftharpoons CH_3OH + O_{ads} \tag{14}$$

$$CO + O_{ads} \rightleftharpoons CO_2 \tag{15}$$

$$H_2 + O_{ads} \rightleftharpoons H_2O \tag{16}$$

Bowker et al. [12] found that methanol was formed almost entirely from CO_2 at higher CO_2/CO ratios and concluded that there cannot be a common carbon containing surface intermediate common to both the shift reaction and methanol synthesis.

7. Water-gas shift reaction

Methods of preparation of suitable Raney catalysts have been discussed earlier. The work of Mellor [16] is particularly interesting in that WGS activity — expressed as conversion of carbon monoxide — has been related to preparation and, in particular, to the copper surface area. The results are summarised in Fig. 2, which shows a correlation between copper surface area and catalytic activity. Analysis revealed that ca. 70% of the results could be explained in terms of a linear relation between activity and metal surface area.

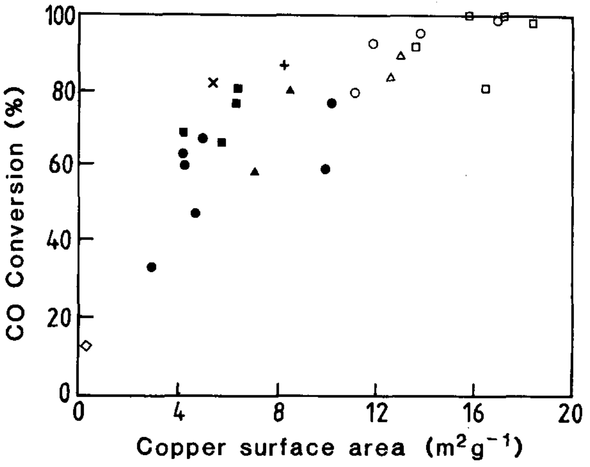


Fig. 2. The dependence of Raney copper WGS activity on copper surface area (ref. [16]). (△) = Cat. A: Cu (61.5), Zn (15.1), Al (19.1). □ = Cat. B: Cu (72.4), Zn (13.3), Al (12.9). ○ = Cat. C: Cu (69.3), Zn (6.9), Al (19.5). × = Co-precipitated Cu–Zn–Al (initial activity). + = Industrial ICI 53-1 (initial activity). ◇ = Copper powder. Open symbols = initial catalyst activity. Closed symbols = final catalyst activity. Temperature = 473 K; total GHSV = 1000 h^{-1}; dry gas composition = 10% CO/90% N_2; CO:H_2O = 1:22.5; pressure = 0.825 kPa; catalyst volume = 2±0.1 ml.

Mellor [16] suggests that second order effects may influence the results and this is born out by observations of similar relationships for methanol synthesis, where catalytic activity is believed to originate, at least in part, from Cu–ZnO interfaces [6]. Leaching a Cu/Zn/Al alloy in a zincate rich solution gave a more even distribution of ZnO across the catalyst particle, and the specific methanol synthesis activity increased with the mass of zinc per unit total surface area [6]. Similar experiments were carried out by Mellor using zincate leached alloys for WGS [16]. It was found that the stability of the catalyst improved significantly on adding zinc oxide, but that the total activity was lower because precipitated ZnO blocked part of the surface area. Insufficient data are given to relate specific activities to zinc concentrations on the copper surface.

In view of the identification of second order effects by Mellor and the observed catalysis across a Cu/ZnO interface, it seems highly likely that at least some promotion of WGS occurs at such interfaces. Any consideration of the reaction mechanisms must, then, include both components of the catalyst.

One of the earliest mechanisms proposed for WGS involved the transfer of an oxygen from water to carbon monoxide via the catalytic surface [61]. This redox mechanism can thus be written as two reactions

$$H_2O + M = MO + H_2 \qquad (17)$$

$$CO + MO = CO_2 + M \qquad (18)$$

This reaction mechanism appears to explain the operation of high-temperature catalysts such as Fe_3O_4 [62] and, as recently as 1992, has been suggested to explain results over Cu/ZnO catalysts [63]. Study of the reverse WGS reaction using FT-IR showed evidence of the formation of two types of formate species, but the authors concluded that these species were not necessarily intermediates in the reaction. Rates of formation of CO_2 in the absence and presence of hydrogen were very similar, and the redox mechanism was suggested to be paramount [63,64].

Some support for this suggestion comes from study of the kinetics of reaction. A kinetic model based upon a statistical mechanical treatment of the redox mechanism was found to give an excellent description of the kinetics, provided it was assumed that the active surface consisted of Cu only [65]. The reactions considered included:

$$H_2O + * = H_2O* \qquad (19)$$

$$H_2O* + * = OH* + H* \qquad (20)$$

$$2OH* = H_2O* + O* \qquad (21)$$

$$OH* + * = O* + H* \qquad (22)$$

$$2H* = H_2 + 2* \qquad (23)$$

$$CO + * = CO* \qquad (24)$$

$$CO* + O* = CO_2* + * \qquad (25)$$

$$CO_2* = CO_2 + * \qquad (26)$$

Reactions (20), (22) and (25) were considered to be possibly rate determining and, as a result, the number of parameters in the model was large. Nonetheless, excellent agreement could be obtained with results obtained over single crystals of copper [66] and over industrial catalysts [67].

Disagreement with these proposals is evident for low-temperature catalysis. Van Herwijenen et al. [5] rejected the redox mechanism on the grounds that neither CuO nor Cu_2O could be formed under reaction conditions. However, Chinchen et al. [59,68] demonstrated that both reactions (17) and (18) could occur on copper, the apparent discrepancy being due to the fact that oxygen coverage is limited to half a monolayer or less [69].

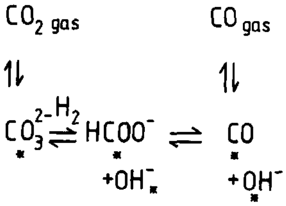
One other possibility has received considerable support, based on the intermediate formation of formates. A typical mechanism that was suggested by Andreev et al. [38] is as follows:

Grenoble et al. [70] originally suggested that formic acid itself could be an intermediate, with the acid migrating from the support to the metal before decomposition.

There is now ample evidence that formates may be formed on surfaces. Shito et al. [71,72] used FTIR to identify formate intermediates in the WGS reaction. Over MgO, they observed that CO reacted with hydroxyl groups to form unidentate, bidentate and bridge type formate intermediates [71]. Only the latter two forms were found on ZnO [72]. The formation and decomposition of bridge and bidentate formates occurred between ca. 398 and 548 K and, when they were formed, the reaction between unidentate formates and water to form bidentate species was favoured [71]. Water was also found to accelerate the decomposition of formates to hydrogen and carbon monoxide [72].

Adsorbed formates have also been observed on Os, Ir [73], CeO_2 [74] and on copper complexes [75]. Formate species have also been observed on Cu/SiO_2 catalysts [76–78], even though Colbourne et al. [79] have suggested that CO and H_2O do not readily react on copper to give formates.

Baiker et al. [80] have suggested that formate is an essential intermediate in the reaction:



The carbonate species on the surface suggested by Baiker et al. has been observed directly by Edwards and Schrader [81], Andreev et al. [38] and by Millar et al. [69]. Subsequent hydrogenation and loss of OH^- groups would then lead to absorbed carbon monoxide which could desorb. Formate decomposition reactions are known to be rapid on copper [82] and to produce CO and H_2.

One interesting finding of Baiker et al. [79] was that combinations of Group IB metals with zirconia were active for methanol synthesis and WGS, but that the activity decreased as the zirconia was converted from amorphous to crystalline. This suggests strongly that ZrO_2 is involved in the reaction sequence, and reemphasises the possibility that the active site is the Cu/ZrO_2 interface [6,83]. Millar et al. [78] have observed formate formation both on copper and on zinc oxide at high pressures, and have also suggested a route to methanol from the formate. However, they found [84,85] that formate formed at the Cu/ZnO interface is relatively unimportant at the high pressures of the industrial reaction. Instead they argued in favour of the creation of an oxygen anion vacancy on the surface of ZnO adsorption led to the formation of carboxylate structures at these defect sites. Hydrogen, spilt over from Cu, also migrated to the same sites.

Although this would infer that Cu/ZnO interactions affect catalyst activity, it is not necessary to have ZnO in WGS catalysts. Thus, for example, Campbell and co-workers [64,66,86] have studied WGS over copper single crystals. As was the case for Ovesen et al. [65], the kinetics of reaction were explained in terms of the redox model [86] and the rates of reaction were of the same order as those observed over commercial catalysts.

Thus it would appear that any effect of ZnO on reaction kinetics is fairly small, even though the concentration of carboxylate and formate species on the surface may be increased. In these terms, then, it is necessary to revisit the question of the mechanism of reaction.

On balance and under reaction conditions, the most probable mechanism of reaction would seem to involve formates or carbonates, despite evidence to the contrary [87]. The reason for this comes from results obtained by Dumpelmann using a stirred tank reactor at high pressures [88]. He was able to separate the rates of reaction to produce methanol from those involved in WGS. The apparent orders of reaction were found to be 0.7 with respect to steam and 1.0 with respect to CO, a result which is very difficult to explain in terms of the redox mechanism.

However, the complexity of the kinetics is such that several mechanisms can be advanced which predict results in agreement with experimental results [65,87,88]. It may well be that further classification of the reaction mechanism for WGS will emerge in the future.

8. Conclusions

Raney copper–zinc catalysts have been shown to have significant potential for use as alternatives to co-precipitated copper–zinc oxide–alumina catalysts used commercially for methanol synthesis and water-gas shift reactions. The Raney method of catalyst preparation by alloying of metals and selective dissolution of the leachable components has been used to provide evidence in support of recently proposed reaction mechanisms for both methanol synthesis and water-gas shift reaction.

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