

THE INDIRECT LIQUEFACTION OF COAL AND
COPROCESSING OF COAL WITH HEAVY OILS

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SUMMARY

The report written last year summarized the various approaches to indirect coal liquefaction, pointing out processes already commercial and those that will become commercial in the near and in the more distant future. This report will extend work on indirect liquefaction to four areas of possible importance either not covered or only referred to briefly previously.

The subjects to be discussed are listed below; all extend our knowledge of indirect liquefaction in the synthesis of alcohols:

- (a) the synthesis of methanol via methyl formate
- (b) the role of carbon dioxide in the methanol synthesis
- (c) the synthesis of methanol using noble metal catalysts
- (d) a new, high-yield sulfur-tolerant catalytic synthesis of higher alcohols

With the mandated withdrawal of lead tetraethyl from gasoline, alcohols, with their high octane numbers, will soon become more important as motor fuels.

Two new routes to methanol were briefly mentioned in the earlier report:

(a) the synthesis of the alcohol via methyl formate and (b) the pathway involving the partial oxidation of methane and C_2-C_5 hydrocarbons to methanol. Although there is continuing research and interest in the latter method, it suffers severely from a lack of selectivity and will not be further discussed. The route to methanol via an alkyl formate is promising and will be expanded upon in the discussion that follows.

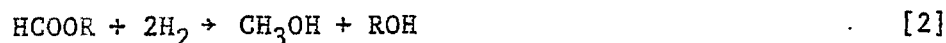
Methanol is an important article of commerce, both as a fuel and as a source of chemicals. Over a billion gallons of methanol were produced in 1984 in the United States (Webber, 1985). World annual production of methanol,

about 12 million tons in 1981, is expected to reach some 20 million tons per year in 1990 and about 40 million tons per year by the end of the century (Keim, 1983).

THE SYNTHESIS OF METHANOL VIA METHYL FORMATE

INTRODUCTION

The route via alkyl formates is a two-step synthesis that avoids the thermodynamic limitations of the presently practiced methanol synthesis. The general equations for these reactions may be written:



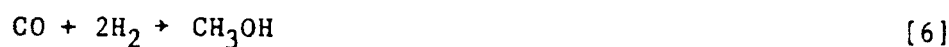
If the starting alcohol is methanol ($\text{R} = \text{CH}_3$), the reaction, starting with one mole of methanol, would yield two moles of that alcohol.

The synthesis of methanol via methyl formate has had a curious history. It was patented first by Christiansen (1919) some 65 years ago and then by BASF (1925). It has also been described in other patents (Couteau and Ramiouille, 1978; Sennewald and Feldmann, 1955; Shell International, 1964; Reichle et al., 1958) as well as in technical papers (Aguilo and Horlonko, 1980; Gjaldbaek, 1948; Kaplan, 1982). The reaction conditions would likely be less energy intensive than present processes for the synthesis of methanol. Economic benefits of the two-stage methanol synthesis over the direct process from synthesis gas were stressed in these patents and publications. Thus, the reaction in Eq. [1] has been reported to proceed in a homogeneous phase at only 350K and 3-4 MPa while the reaction in Eq. [2] occurs on a heterogeneous catalyst at about 430K and 3 MPa (Brendlein, 1954).

Sorum and Onsager (1984) also stressed the advantages brought about by the use of a liquid phase over a gas phase reaction. Among these, they pointed out better conditions for heat removal, higher conversions per reactor

pass and less unconverted reactant to recycle. It would seem that this methanol synthesis would have lower investment costs for equipment and reduced costs of operation.

A pilot plant for the synthesis of methanol was erected in Germany in 1945 (Kirk-Othmer, 1967). A modified version of the synthesis of methanol via methyl formate [Eq. 3-5] was described by Brendlein (1954). The catalyst,



operating temperature and pressure used for the hydrogenation of the methyl formate formed to methanol [Eq. 5] were copper chromite, 373-443K and 2-6 MPa, respectively.

It is fair to ask, at this point, if the present commercial manufacturers of methanol are or have been at all interested in synthesizing methanol via the formate route? The answer is "yes". At least one of the world's major manufacturers of methanol has initiated research on the formate route and considers it a subject well worthy of investigation (Short and Spencer, 1985). Research on the formate route to methanol has been sporadic largely because there is no incentive for a major manufacturer to disturb the present huge infrastructure, built up over many years, for the one-step synthesis of methanol culminating in the presently favored Cu-ZnO-Al₂O₃ catalyzed methanol synthesis pioneered by ICI (1968;1973). The desirability for obtaining a synthesis of methanol in higher conversions with attendant lower costs of gas recycle compression were described in the last report.

In most cases, the synthesis of methanol via methyl formate has been carried out in two separate steps. However, some recent literature points out an even more promising route which consists of the coproduction of methanol and methyl formate in a single pass over two catalysts, one a homogeneous and the other a heterogeneous catalyst. We shall first review the two-stage synthesis, after which we shall summarize the available literature concerning a one-step synthesis of methanol and methyl formate.

THE TWO-STAGE SYNTHESIS OF METHANOL VIA METHYL FORMATE

Carbonylation of Methanol

The carbonylation of methanol to methyl formate is an equilibrium reaction whose dependence on temperature and pressure is shown in Table II.1.

Table II.1: Effect of Temperature and Pressure on Methanol Conversion

Temperature (°K)	Pressure (MPa)	Equilibrium conversion of methanol in % by weight
353	2	20
353	4	40
353	6	62
353	8	85
373	2	10
373	4	20
373	6	35
373	8	52

The reaction conditions selected for industrial production are governed by thermodynamic, kinetic and economic considerations in order to obtain a high reaction rate as well as a high concentration of HCOOCH_3 along with a minimum investment. As mentioned earlier, the carbonylation of methanol is currently carried out in the liquid phase at about 350K and 3-4 MPa in the

presence of a homogeneous catalyst which is an alkaline alkoxide. The process encounters some difficulties for which solutions have been proposed.

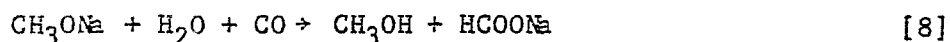
Most drawbacks of this process are of chemical origin. For example, as far as the catalyst is concerned, the earlier studies favored sodium methoxide (BASF, 1925; Christiansen, 1919). However, even though this alkali methoxide has a good solubility in methanol, it is sparingly soluble in methyl formate. This implies that both conversion and addition of methanol should be closely monitored so that the proportion of unconverted methanol is continuously high enough to maintain the catalyst in solution. However, this requires use of an excess of methanol (Schoenbrunn and Durell, 1971).

Some proposals to circumvent, at least partly, this difficulty have been made. According to a British patent (Shell International, 1964), it is by far better to replace the sodium alkoxide catalyst by alkoxides of heavier alkali metals (K, Rb, Cs). These have two major advantages over the sodium compounds. In addition to a much higher activity, the alkoxides, as well as their formates, are much more soluble in the reaction mixture. Examples of catalysts such as the 2-methoxyethylate of potassium and others have been given along with a list of organic promoters (Shell International, 1964). At this point, it is worthwhile to note that the commercially practiced Leonard process has recently claimed a proprietary additive to CH_3ONa that improves the methyl formate yield at lower pressure (Kaplan, 1982).

It is important that the starting materials for the synthesis of methyl formate should be as free as possible of carbon dioxide. This gas may react with the catalyst to yield sodium methyl carbonate, thus removing the catalyst from the reaction:



The catalyst also reacts with water to give methanol and unwanted sodium formate:

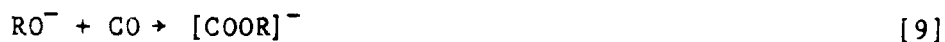


As long as the gaseous feed is free of water and CO_2 , the methyl formate synthesis can be carried out with pure CO or with synthesis gas containing up to 30% of H_2 . In the latter case, it has been reported that, in addition to avoiding a separation of CO and H_2 , the presence of H_2 helps strip out the formate (Kirk-Othmer, 1967).

There are few studies dealing with the carbonylation of $\text{C}_1 - \text{C}_4$ alcohols in the presence of the corresponding sodium alkoxide (Gjaldbaek, 1948; Tonner et al. 1983). In spite of very slight discrepancies between the two studies (Gjaldbaek, 1948; Tonner et al., 1983), the rate of formation of the various formates was found to increase in the order: methanol < ethanol < n-propanol < isopropanol ~ isobutanol ~ tert-butanol < sec-butanol.

In all cases the reaction was found to be almost completely selective, that is, only the expected alkyl formate was obtained beside a small quantity of solid sodium formate which was not great enough to interfere with reaction kinetic studies. It was first suspected that the CO solubility in the feed alcohol is an important factor in determining the relative reactivity of the various alcohols; Tonner et al. (1983), however, disproved this possibility. For the set of alcohols used, they found that the fastest reaction (with sec-butanol) and the slowest one (with methanol) took place in the alcohols that had, respectively, the lowest and the highest CO solubilities.

Based on the fact that all the reactions were found to be first order with respect to CO, and also on the above classification of reaction rates, Tonner et al. (1983), following earlier work, suggested a two-step mechanism for the formate synthesis.



This mechanism is in agreement with the primary role played by the various alkyl radicals in governing the reactivity of the corresponding alcohols. An increase in the electron-donating effect of the alkyl substituents should correspond to alkoxide anions (RO^-) having stronger basicity and consequently higher reactivity. This implies an increase in the overall reaction rate. The exception shown by the behavior of tert-butanol was attributed to steric effects.

Another point relates to the catalytic activity of the alkoxide catalyst as a function of the nature of the alkali metal. Tonner et al. (1983) have shown that catalyst activity in the carbonylation of ethanol to ethyl formate increased in the order: $\text{LiOEt} < \text{NaOEt} < \text{KOEt}$. These findings agree with the postulation that the alkali metal with the lowest ionization potential should form alkoxide ions, RO^- , most easily.

Hydrogenolysis of Alkyl Formates

Thermodynamic calculations show that methanol may be obtained in very high yields by contacting H_2 with any alkyl formate at atmospheric pressure and temperatures below 473K. For kinetic reasons, an appropriate catalyst is needed.

Christiansen (1919) studied the hydrogenolysis of methyl formate as a final step in the two-stage methanol synthesis. He claimed that the reaction proceeds fairly well in the gaseous phase over a more or less reduced copper oxide at about 180°C under ordinary or higher pressure. The hydrogenolysis of methyl formate was also studied in some extent in other patents (Brendlein, 1954; Higdon et al., 1974).

A significant contribution has been published recently by Sorum and Onsager (1984). They studied the thermodynamics and kinetics of methyl formate hydrogenolysis and suggested a reaction mechanism. Based on a set of assumptions, the thermodynamic calculations led to the conclusion that a liquid phase reaction is more efficient than a gas phase reaction as it offers a higher methyl formate conversion. The influences of temperature, pressure, the ratio between the liquid and the gas phase volumes as well as the composition of the liquid phase ($\text{HCOOCH}_3 + \text{CH}_3\text{OH}$) before reaction were studied. The optimum conditions for achieving more than 98% conversion of methyl formate to methanol at equilibrium were found to be:

- total pressure higher than 6 MPa
- $V_{\text{liq}}/V_{\text{gas}}$ higher than 0.2
- temperature about 440K
- initial concentration of methyl formate (in methanol) higher than 5%.

Six commercial copper chromite catalysts have been tested for catalytic performance. The Mn-promoted catalyst (39% Cu, 32% Cr, 2.5% Mn) was found to be the best as it yielded more than 98% of methanol at 413-458K and 7 MPa. Small quantities of CO, CO₂ and CH₄ were also detected.

Evans et al. (1983) found that, in the hydrogenolysis of methyl formate, selectivities to methanol higher than 90% can easily be obtained provided the temperature is kept below 413K. Small amounts of CO (~ 10%) were also

detected in the products. Moreover, the selectivity to methanol was found to depend neither upon conversion nor upon the initial ratio of methyl formate to hydrogen. This suggests that the formation of the two products, methanol and CO, follows two parallel pathways.

COPRODUCTION OF METHANOL AND METHYL FORMATE

Possibly an even more promising route for methanol synthesis would be to carry out the previous two steps (carbonylation and hydrogenation) in the same reactor. Indeed, some evidence for the feasibility of such a process is presently available.

Evans et al. (1983) pointed out the possibility of undertaking both reactions (equations [4] and [5]) simultaneously in pressurized autoclaves containing both alkali metal (a homogeneously catalyzed reaction involving CO) and copper-based catalysts (a heterogeneously catalyzed reaction involving H₂). Imyanitov et al. (1972) have actually shown that both reactions can occur in the same reactor.

According to Petroleum Information (1982), Aker Engineering has carried out a two-component liquid-phase catalytic system which converts synthesis gas to a mixture of methanol and methyl formate in a single step at 383K and pressures as low as 0.5 MPa. The composition of the final mixture can be monitored by varying the reaction conditions. Again the first catalytic action involves a homogeneous catalyst such as an alkaline and/or an alkaline earth alkoxide which catalyzes the liquid-phase carbonylation of methanol. The second catalyst, used for the heterogeneous hydrogenation of the formate, is currently a copper chromite oxide. As in the two-step synthesis, the mixture should be free of H₂O, CO₂ and sulfur compounds, for the reasons already mentioned. Aker Engineering claims, according to their economic study, that the process is cheaper to install and operate than the

conventional methanol synthesis. This is mainly due to the milder reaction conditions.

The Brookhaven group (Sapienza et al., 1985) has also reported a one-step liquid phase synthesis of methanol over a "NiC" catalyst. It is possible that the methanol is formed via the intermediacy of methyl formate in this process.

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**RECENT ADVANCES IN UNDERSTANDING THE MECHANISM
OF THE SYNTHESIS OF METHANOL**

INTRODUCTION

The synthesis of methanol from synthesis gas (CO + H₂), as reported last year in this study, is always carried out commercially in the presence of carbon dioxide. If CO₂ is removed from the feed gases in the commercial synthesis, the activity of the catalyst declines precipitously. The mechanism by which CO₂ enhances the methanol synthesis has remained, until recently, a rather complete mystery. Indeed, the mechanism of the synthesis of methanol, while much studied, is still far from being understood although significant progress has been made in the last few years, Chinchin et al. (1984) have recently come up with the somewhat surprising statement that "other than that the reaction is exothermic there seem to be few further facts about which complete agreement [on the mechanism of the methanol synthesis] exists" (Klier, 1982; Kung, 1980). Understanding the mechanism of the synthesis would aid in finding ways of improving the already impressive performance of catalysts used for the commercial synthesis of methanol.

The synthesis of methanol has been assumed for many years to proceed by the catalytic hydrogenation of CO according to the following equation:



This discussion will be concerned chiefly with the low-pressure methanol synthesis using the Cu-ZnO-Al₂O₃ catalyst, although the findings undoubtedly are applicable to the ZnO-Cr₂O₃ high-pressure catalyst synthesis.

It is relevant to note that data obtained in the synthesis of methanol can be divided into two categories: those obtained when operating at

commercial conditions, and data obtained under conditions that differ from commercial operations, usually in small laboratory units at varying temperatures, pressures, H_2/CO ratios, CO_2 concentrations, etc.

The discussion that follows will attempt to deal with the following pertinent questions with the warning that published results are, in many cases, conflicting. However, certain conclusions do emerge. Emphasis will be placed, where possible, on the use of practical catalysts under industrial working conditions.

Data to answer the following questions are needed:

a - Is the carbon in the methanol derived from CO , from CO_2 , or from both components?

b - What is the function of water in the synthesis of methanol?

c - What is the part played by the water-gas shift (wgs) reaction?

d - What is the nature of the catalyst under commercial operations?

e - What roles are played by ZnO and by the Al_2O_3 support?

f - Can we arrive at a plausible mechanism for the synthesis of methanol?

g - Can we postulate a reaction step that is rate-determining?

The listing of these questions outlines the difficulties in understanding the mechanism of the methanol synthesis and in themselves, tells us what we should know in order to improve the present methanol synthesis process. We shall not attempt to assemble and correlate all the published data because it is too extensive and a number of present conflicts are still unresolved.

IS THE CARBON IN THE METHANOL DERIVED FROM CO , FROM CO_2 , OR FROM BOTH COMPONENTS?

For a long time, the chemistry of CO_2 hydrogenation has been associated with that of CO (Netta, 1955; Saeeden, 1982) considering that the

transformation of CO₂ to CO takes place through the reverse of the water-gas shift (wgs) reaction (Eq. [2]). It is then considered that the CO is further hydrogenated to methanol according to equation [3]. Acceptance of this route to methanol may be a major reason why workers in this area have seemed not to be concerned with the detailed contribution of CO₂.



Fairly recently a series of papers published by Kagan et al. (1975a; b; c; 1976), Rozovskii (1980) and Rozovskii et al. (1975;1976;1977) have reported a surprising conclusion: not only does the conversion of CO₂ to methanol not proceed through a free CO intermediate but the hydrogenation of CO to methanol under commercial conditions likely occurs exclusively via the intermediacy of CO₂. This conclusion was first strongly suggested by the isotopic distribution of ¹⁴C among the reaction products of the conversion of CO₂ to methanol in the presence of a small amount of ¹⁴CO. The reaction was carried out using a commercial catalyst (Cu-ZnO-Al₂O₃), at 0.5 MPa with a gaseous feed mixture of CO₂/CO/H₂/N₂ of 22/1.2/73/4 (Kagan et al., 1975a). It was found that, in the course of the reaction, the concentration of CO₂ decreased while that of CO and that of CH₃OH increased. In addition, the possible formation of CO by decomposition of methanol was ruled out. This means that under the actual experimental conditions, reaction [2] occurred from left to right. However, the comparison between the specific radioactivity of CO and that of CH₃OH enabled the authors to conclude that reaction [3] did not occur. Furthermore, the CO₂ remaining at the end of the experiment exhibited a

certain radioactivity. Since the label transfer from methanol was excluded, it was concluded that CO was converted to CO₂. According to the authors this means not only that the transformation of CO₂ into methanol proceeds without the intermediacy of free CO, but that the synthesis of methanol from CO-H₂ takes place through CO₂ as an intermediate.

Furthermore, Kagan et al. (1975b) reported a radiotracer study performed under more realistic conditions ($H_2/CO = 2$, $^{14}CO_2 = 4\%$, $P = 0.5$ MPa). They confirmed their previous conclusion and extended it to an industrial zinc-chromium oxide catalyst as well. Other proofs for the absence of free CO as an intermediate in the conversion of CO₂ to methanol were provided by studying the reaction at high flow rates so that the wgs was kept far from equilibrium (Kagan et al., 1975c; Rozovskii 1980; Rozovskii et al., 1976).

Chinchin et al. (1984) from ICI repeated the same type of experiments performed by Kagan et al. (1975a; b). The reaction temperature and pressure as well as the catalyst (Cu/ZnO/Al₂O₃) pretreatment were similar to those used industrially. An equimolar mixture of CO and $^{14}CO_2$ was hydrogenated at varying but high flow rates. They fully confirmed that the synthesis proceeds via carbon dioxide.

Kung et al. (1984) and Liu et al. (1984) found that the initial rate of methanol formation increases with increasing CO₂/CO ratio. Kuznetsov et al. (1982) also confirmed the conclusions of Kagan et al. (1975a; b; c; 1976) and Rozovskii et al. (1975; 1976; 1977). However, Klier and coworkers reported a different picture of the mechanism(s) of the methanol synthesis. Using mixtures of $H_2/(CO + CO_2) = 70/30$ at 7.5 MPa over a Cu-ZnO-Al₂O₃ catalyst they observed a sharp maximum in the specific rate of CH₃OH formation at $H_2/CO/CO_2 = 70/28/2$. Based on the assumption that Cu⁺ ions dissolved in the ZnO matrix constitute the active sites (Herman et al., 1979), they (Klier, 1982; Klier et

al., 1982) postulated that CO_2 had a stabilizing effect on monovalent copper. At low concentration of CO_2 (<2%) a rapid deactivation of the catalyst occurs as a consequence of the reduction of Cu^+ to inactive metallic copper in the highly reducing H_2/CO environment. At a high concentration of CO_2 (>2%), a retarding effect takes place due to the strong adsorption of CO_2 which prevents CO from contacting the active sites thus preventing the hydrogenation of CO. This interpretation was corroborated by the authors with other experimental facts (Klier, 1982; 1984a; Klier et al., 1982).

On $\text{Cu-Cr}_2\text{O}_3$, even though Cu^+ species were found to be responsible for CO adsorption and subsequent methanol formation (Apai et al., 1984a;b; Monnier et al., 1984; 1985), CO_2 was found to decrease the rate of methanol synthesis (Monnier et al., 1984). Competitive adsorption of CO and CO_2 on Cu^+ sites was invoked to account for this finding (Monnier et al., 1984).

The foregoing review of the influence of CO_2 on the methanol synthesis shows that the situation is indeed confusing and further research is needed to clarify the picture. However, it does appear that, under commercial conditions, the principal and perhaps the only species being reduced is CO_2 , while CO is primarily transformed to CO_2 via the wgs. Indeed at the present time methanol is being synthesized from feeds containing more CO_2 than CO (Short and Spencer, 1985).

ROLE OF WATER AND OF THE WATER-GAS SHIFT REACTION (wgs)

Considering these interpretations of the role of CO_2 in the methanol synthesis, it becomes necessary to investigate the effect of water as well. Indeed, even when using a water-free synthesis gas, water vapor will be formed in the reactor as a result of both the synthesis reaction from CO_2 [Eq. 1] and the reverse of the wgs reaction. Rozovskii (1980), summarizing the work he reported along with Kagan and others (Kagan et al., 1975a; b; c; Rozovskii et

al., 1975; 1976; 1977) noticed that the reduction of CO_2 to methanol was strongly inhibited by water, while obviously the wgs cannot proceed in the absence of water. The author stressed the fact that precise knowledge of the effect of water is a prerequisite for a correct kinetic model to be proposed, and consequently to a better control and optimization of the process. However, subsequent results of other workers were rather at odds with these findings.

Vedage et al. (1984), using a $\text{Cu/ZnO} = 30/70$ mol% catalyst and a reactant feed of $\text{H}_2/\text{CO} = 70/30$ mol% studied the influence of water at 7.5 MPa. They found that the rate of methanol formation reached a maximum for mixtures containing 2.2 and 0.7 mol% of water, respectively at 225 and 215°C. It was assumed that, at low concentrations, water provides hydroxyl groups to the catalyst surface. These species react with CO, yielding surface formates which are believed to be a reaction intermediate. However, excess of water inhibits methanol synthesis by blocking the sites that activate the hydrogen necessary for the conversion of the surface formate into methanol.

Kung et al. (1984) and Liu et al. (1984) found, however, that addition of water suppresses the methanol synthesis in all cases. Competitive adsorption of water on the active sites was put forward to account for these findings.

Under commercial conditions, the concentration of water at steady state is very small. It is believed that water exerts a promoting effect probably by maintaining a high degree of hydroxylation of the catalyst surface.

The part played by the wgs is also a matter of dispute. In a detailed kinetic study, Kagan et al. (1975b) and Rozovskii et al. (1976) reported that the formation of methanol from CO_2 and the wgs have no common intermediate. Similar conclusions were drawn by Chinchin et al. (1984). However, several other workers (Amenomiya and Tagawa, 1984; Edwards and Schrader, 1984; van

Herwijnen and de Jong, 1980; van Herwijnen et al., 1980; Vedage et al., 1984) believe that the methanol synthesis and the wgs are mechanistically coupled - share a common intermediate, i.e., formate. It is obvious that this aspect of the methanol synthesis needs further investigation.

ACTIVE SITES AND NATURE OF THE COPPER CATALYST

On copper-based catalysts, four different sites have been claimed to be active in the synthesis of methanol:

a - Cu^+ dissolved in ZnO in the case of low pressure synthesis catalysts $\text{Cu-ZnO-M}_2\text{O}_3$ (Bulko et al., 1979; Herman et al., 1979; 1981, Klier, 1982, Parris and Klier, 1984), or as a crystalline copper chromite surface phase in the case of $\text{Cu-Cr}_2\text{O}_3$ (Apai et al., 1984a; b; Monnier et al., 1984; 1985).

b - Cu^0 (Andrew, 1980; Fleisch, 1984, Fleisch and Mieville, 1984; Friederich et al., 1983a; b; Mardsen et al., 1980; Notari, 1981);

c - Cu^0 in contact with an oxidized surface site such as Cu^+ or ZnO (Chinchen et al., 1984);

d - Cu^+ in interaction with an "electronically altered" zerovalent copper Cu^+-Cu^0 (Okamoto et al., 1982; 1983; 1984).

Moreover, according to numerous authors (Bowker et al., 1981; 1982; 1984; Poels and Ponc, 1983; Kung, 1980), the role of the anion vacancies in the support cannot be ignored. Bowker et al. (1984), for example, reported that CO_2 and H_2 interact on polycrystalline ZnO pre-reduced in H_2 to yield methanol, while CO and H_2 give only CO_2 and a highly defective ZnO. It was also shown that the initial rate of methanol formation from CO_2 and H_2 on this highly defective ZnO is almost 20 times higher than that obtained on the H_2 pre-reduced sample. Moreover the excess of methanol thus formed is approximately equal to the number of anion vacancies produced by CO/ H_2 mixture. The authors (Bowker et al., 1984) concluded that during the

hydrogenation of a mixture of carbon oxides, the role of CO is confined to the creation of defects which are very efficient for CO₂ adsorption and its selective transformation into methanol.

Under typical conditions of methanol synthesis some 20-25% of the copper surface does not adsorb N₂O (Chinchen et al., 1984); it is believed to be in an oxidized state. Moreover, Chinchen and Waugh (1985) reported that the oxidized fraction of copper depends upon the pressure and the composition of synthesis gas, particularly the CO₂/CO ratio. Accordingly, Fleisch (1984) and Fleisch and Mieville (1984), using a feed gas of 73% H₂, 25% CO and 2% CO₂, found that surface copper was entirely metallic. In light of the results reported by Klier (1982) and others (Karwacki et al., 1984) it may be concluded that the fraction of Cu unavailable for N₂O adsorption consists of monovalent Cu⁺.

Chinchen et al. (1984) demonstrated that under standard commercial conditions, the Cu was partly oxidized, and the same linear relationship between the metallic Cu surface area and catalytic activity was found to apply for Cu supported on a variety of oxides (ZnO, Al₂O₃, MgO, MnO, ZnO-Al₂O₃). This led the authors to emphasize the role of Cu⁰ surface atoms in contact with an oxide surface site (Cu⁺ or support) as the active sites for methanol formation. However, because of the linear correlation found between the methanol activity and the metallic surface area as determined under reaction conditions, Chinchen et al. (1984) feel that the rate-determining step should occur on metallic copper.

It is worth noting that such active sites are very similar to those proposed previously by Okamoto et al. (1982; 1983; 1984). In light of the results reported above it is believed that under synthesis conditions the catalyst surface is in a dynamic state (Chinchen et al., 1984; Short and

Spencer, 1985) where the number of active sites depends on the CO/CO₂ ratio (Chinchen and Waugh, 1985) and very likely upon the H₂/H₂O ratio as well. Accordingly, any significant change in H₂O and/or CO₂ contents of the reaction medium is expected to alter the catalyst surface and hence the reaction pathways (Short and Spencer, 1985).

A conclusion may be made that, to make methanol synthesis possible, it is necessary to have a dual site (A-B), one of which (A) adsorbs H₂ dissociatively and the other one (B) adsorbs and activates CO (or CO₂). It is reasonable to suggest that under commercial conditions the A sites are metallic copper while several candidates, acting separately or jointly play the role of B sites, such as:

(i) Cu⁺ as suggested by Klier and coworkers (Herman et al., 1979; Klier, 1982);

(ii) hydroxyl sites located on the support which may form reactive intermediates such as formate when contacting CO₂ (Chinchen et al., 1984; Amenomiya and Tagawa, 1984);

(iii) anion vacancies in the support, the role of which has been stressed by several authors (Bowker et al., 1981; 1982; 1984; Poels and Ponc, 1983; Kung, 1980) as reported earlier.

ROLE OF THE SUPPORT

It has been shown that hydrogen can adsorb dissociatively on pure ZnO (Griffin and Yates, 1982a; b; Kung, 1980), making hydrogenation reactions possible over this oxide. This idea was extended to Cu/ZnO methanol synthesis catalysts without convincing proof (Herman et al., 1979). Actually, recent results showed that when supported by ZnO, copper adsorbs hydrogen more readily than does ZnO (Roberts and Griffin, 1984a; b). Earlier results showed that copper can chemisorb hydrogen dissociatively (Prichard et al., 1975)

especially at high temperatures (Kwan, 1954) and high pressures (Alexander and Prichard, 1972). Balooch et al. (1974) also demonstrated that copper catalyzes the H_2/D_2 exchange reaction. There is sufficient evidence that during methanol synthesis, hydrogen is activated on copper or on copper interacting with an oxidized site such as $Cu^{\delta+}-O^{\delta-}$ (Henrici-Olive and Olive, 1982; Klier, 1984b; Roberts and Griffin, 1984a; b).

Apart from catalyst stability, Chinchin et al. (1984) demonstrated that no unique role can be assigned to either ZnO or Al_2O_3 . Several catalysts supported on MgO, Al_2O_3 , and MnO have been shown to fit the same activity- Cu^0 surface area correlation. They concluded that all these supports are equally effective.

The role of ZnO and Al_2O_3 on the reducibility of copper is not clear. Ruggeri et al. (1982) reported that ZnO slows down the reducibility of Cu^+ to Cu^0 , while Fleisch and Mieville (1984) found that CuO/ZnO is much more reducible than unsupported CuO ; however, when Al_2O_3 is added the reduction of copper is retarded.

Klier et al. (1982) and Himelfarb et al. (1984) concluded that oxides such as Al_2O_3 or Cr_2O_3 , when added to Cu/ZnO , do not play a significant role. Andrew (1980) confined the role of ZnO to the adsorption of poisons present in the synthesis gas.

Despite these discrepancies, it may be justified to suggest that the role of the support is to disperse the active phase, and eventually to provide basic sites on which CO_2 (or CO) may adsorb. The advantage of the present ZnO- Al_2O_3 combination would be its ability to maintain that dispersion under actual synthesis conditions.

RATE-DETERMINING STEP AND REACTION MECHANISM

Without going into too much detail, the mechanisms proposed for methanol synthesis may be represented schematically as shown in Figure 1. At present, surface formate (Amenomiya and Tagawa, 1984; Deluzarche et al., 1977; 1982; Edwards and Schrader, 1984; Kung, 1980; Ueno et al., 1970), formyl (Edwards and Schrader, 1984; Lavalley et al., 1982; Saussey et al., 1982) and methoxide (Deluzarche et al., 1977; Edwards and Schrader, 1984; Ueno et al., 1970) have been convincingly shown to occur during methanol formation. Some proposed mechanisms ignore the passage via a formate species and some others claim that the hydrogenation of a formyl surface intermediate leads to a hydroxymethyl species rather than to methoxide. A central question is how and on which site the surface formate is formed. Several pathways are possible and several sites have been proposed. The major differences between all "first" steps suggested rest on three aspects:

- Is the active copper species reduced (Cu^0) or oxidized (Cu^+)?
- Is the hydrogen containing species a hydride or a hydroxide?
- Is the carbon containing species CO or CO_2 ?

It has already been reported that the answers to these questions depend essentially on the experimental conditions (temperature, pressure, CO/CO_2 and $\text{H}_2/\text{H}_2\text{O}$ ratios). However, the details of the proposed pathways are not well known as they certainly depend on the nature of the B sites. Under commercial conditions, the following seems to be true (Chinchen et al., 1984):

- The primary act is a reaction between adsorbed CO_2 (on B) and a hydrogen species adsorbed on metallic Cu leading to a formate species.
- The rate-determining step occurs on metallic copper after the formation of the surface formate species.

At least three hydrogenolysis steps are needed in order to transform formate species into methanol. Unraveling the problem of which one of these steps is rate-limiting is still a challenging field of investigation.

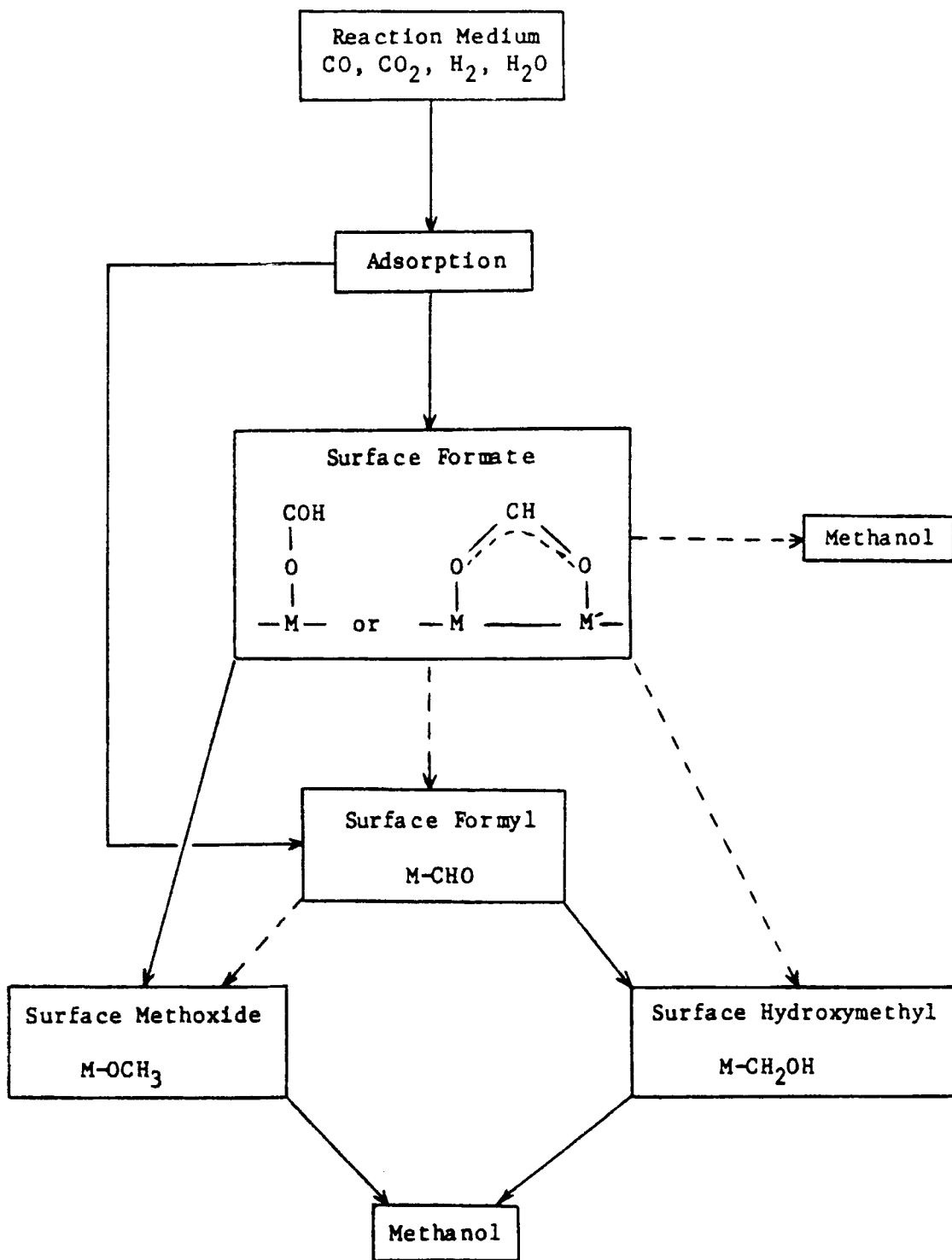


Figure 1: Possible Pathways for Methanol Synthesis

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METHANOL SYNTHESIS OVER TRANSITION METALS

INTRODUCTION

The formation of oxygenated compounds from syngas has been shown to occur on a variety of metals (Poels and Ponec, 1983) and oxides (He et al., 1985). Provided some requirements concerning catalyst preparation and reaction conditions are fulfilled, the following metals were found to exhibit significant activity and selectivity toward alcohols synthesis:

Fe (Anderson, 1980; Pijolat and Perrichon, 1985; Razzaghi et al., 1984),

Co (Courty et al., 1982; Gall et al., 1952; Grandvallet et al., 1984),

Ru (Kellner et Bell, 1981),

Ir (Ichikawa, 1978b),

Pt (Meriaudeau et al., 1984; Naccache et al., 1985; She et al., 1985),

Rh (Bhasin et al., 1978; Gastner et al., 1980; Ellgen et al., 1979;

Ichikawa, 1978a; b; c; Ichikawa and Fukushima, 1985a; b; Ichikawa et al., 1984; Ichikawa and Shikakura, 1981; Kawai et al., 1985; Katzer et al., 1981; Kuznetsov et al., 1984; Takeuchi and Katzer, 1981; 1982; Watson and Somorjai, 1981; 1982),

Pd (Driessen et al., 1983; Fajula et al., 1982; Fleisch et al., 1984;

Hicks and Bell, 1984; 1985; Hicks et al., 1984; Ichikawa et al., 1985;

Kikuzono et al., 1981; Poels et al., 1981; 1982; 1984; Ponec, 1982; Poutsma et al., 1978; Ryndin et al., 1981).

As far as the selective synthesis of methanol is concerned, it is easy to conclude from the literature that the experimental procedures, including catalyst preparation, the nature of metal precursors, and the nature and origin of the support as well as the reaction conditions, play very important roles in directing CO hydrogenation toward the desired product. Numerous catalytic systems containing Pd have been reported to hydrogenate CO

exclusively to methanol; however, more work is needed to improve their activity and stability with time on stream.

Several ideas are now under discussion in order to rationalize the relationship between the ability of transition metals (Pd, Rh, Pt) in making oxygenates from (syngas) and the experimental procedure as defined above. However, the problem is being approached in five different ways. As it is not possible for the time being to conciliate these points of view, we shall just summarize them hoping that a more comprehensive picture will soon emerge.

ACID-BASE PROPERTIES OF THE SUPPORT

The role of the basicity of the support in generating an effective catalyst for methanol synthesis was stressed by several authors (Ichikawa, 1978b; c; Ichikawa and Shikakura, 1981; Katzer et al., 1981). Ichikawa (1978b; c) found that when CO hydrogenation is carried out on Rh supported acidic metal oxides such as SiO_2 or Al_2O_3 , the products obtained are mainly hydrocarbons. In contrast, when basic supports are used, more than 95% selectivity to methanol can be achieved. Similarly, Pd containing catalysts become efficient in methanol synthesis when basic oxides such as alkali and alkaline earth oxides are used as additives (Kikuzono et al., 1981).

As has been mentioned for Cu-ZnO- Al_2O_3 catalysts, surface formate species are most likely to be reaction intermediates in the methanol synthesis over supported group VIII metals. Accordingly, the role of the basicity of the support is believed to be related to an enhancement of the rate of formation as well as the stability of such an intermediate (Kagami, et al., 1983).

ELECTRONIC STATE OF THE CATALYST

There is growing evidence that for both Rh and Pd, cationic centers (Rh^{n+} , Pd^{n+}) are required for oxygenate formation. This issue has been lately

reviewed by Poels and Ponec (1983); we shall therefore confine the discussion to the main results with particular emphasis on most recent findings.

Castner et al. (1980) and Watson and Somorjai (1981; 1982) were among the earliest workers who pointed out that the presence of oxygen in interaction with Rh (preoxidation, use of Rh oxide or LaRhO_3) is necessary for the hydrogenation of CO to oxygenates. Related observations have also been reported by Iwasawa et al. (1982) and Poels et al. (1984). Recently, Ichikawa and Fukushima (1985a), using X-ray Photoelectron Spectroscopy (XPS) measurements claimed that Rh on SiO_2 , which is active in hydrocarbons formation, exhibits an electronic state similar to that of Rh metal, while an Rh^+ state is present in Rh/ ZnO , a methanol synthesis catalyst. For catalysts active in C_2 oxygenate formation such as Rh supported on ZrO_2 or TiO_2 -doped silica, an electronic state between Rh^0 and Rh^+ was found. They concluded that Rh^0 is active for CO dissociation, Rh^+ is active for CO insertion and the rhodium in the intermediate electronic state is active for both processes.

In a series of papers, Ponec and coworkers also stressed the role of ionic species of Pd (Poels and Ponec, 1983; Poels et al., 1982; 1984; Driessen et al., 1983), Rh (She et al., 1985) and Pt (Poels and Ponec, 1983; Poels et al., 1984) in oxygenates synthesis catalysts. They were able, for example, to correlate the methanol synthesis activity over promoted Pd/ SiO_2 with the amount of ionic palladium as determined by extraction with acetylacetone. The idea that Pd^{n+} ions may facilitate the addition of $\text{H}^{\delta-}$ to CO to yield formyl species was suggested, among other possible roles of Pd^{n+} in catalyzing the methanol formation (Poels and Ponec, 1983). Recent support for this proposal was provided by Hindermann et al. (1984) who found a correlation between activity for methanol formation and the concentration of formyl species as determined by chemical trapping.

However, other workers do not agree that there is significant involvement of Rh^{n+} or Pd^{n+} in the synthesis of methanol. Katzer et al. (1981) did not find any indication of ionic Rh in a series of supported catalysts and concluded that selective methanol synthesis has to be related to a metal-support interaction. Kikuzono et al. (1981) and Kagami et al. (1983) found that promoted Pd catalysts are more active when they are reduced at higher temperature. They emphasized the role of promoters and supports as they stabilize and enhance the formation of surface formates, considered as a major intermediate in methanol formation. Similar observations were also reported by Deligianni et al. (1984). Bell and coworkers (Fleisch et al., 1984; Hicks and Bell, 1984; 1985; Hicks et al., 1984) found that Pd/La_2O_3 is more active than Pd/SiO_2 even though XPS studies show that Pd in the former catalyst is electronegative rather than cationic.

PARTICLE SIZE EFFECT

Ichikawa et al. (1985), studying CO dissociation and hydrogenation over a series of Pd/SiO_2 catalysts with varying dispersions, pointed out the primary role played by the particle size as a controlling factor for CO dissociation and thus for selectivity for methane versus methanol. They found that small particles are the most active ones in CO dissociation as well as in methane formation. However, as far as the selectivity of CH_4 versus CH_3OH is concerned, Tatsumi et al. (1983) had previously reported the reverse trend.

STRONG METAL-SUPPORT INTERACTIONS (SMSI) AND MORPHOLOGY OF THE METALLIC PARTICLES

In a series of papers, Bell and coworkers (Fleisch et al., 1984; Hicks and Bell, 1984; 1985; Hicks et al., 1984; Ryndin et al., 1981) reported a thorough characterization of several Pd/SiO_2 and Pd/La_2O_3 catalysts along with their catalytic properties in CO hydrogenation. Their principal conclusions

are (a) XPS measurements show that the binding energy (BE) of Pd $3d_{5/2}$ in Pd/SiO₂ is the same as that of metallic Pd, while that of Pd in Pd/La₂O₃ lies at 0.7 eV below the corresponding value for unsupported palladium, indicating that some electron donation from the support to the metal occurs during reduction; (b) the adsorption of CO is much weaker on Pd/La₂O₃ than on Pd/SiO₂; (c) in all silica-supported catalysts 90% of the exposed metallic surface is comprised of Pd(100) while the morphology of the metal in Pd/La₂O₃ samples changes from mainly Pd(100) planes to Pd(111) planes as the metal loading increases; (d) Pd(100) planes are threefold more active in methanol synthesis than Pd(111) and (e) for a fixed morphology, Pd/La₂O₃ is 7.5 times more active than Pd/SiO₂.

It was concluded that the higher performance of Pd/La₂O₃ in methanol synthesis is primarily due to small differences in the relative strength of CO and H₂ adsorption as a result of a combined effect of the support and the morphology of metallic particles.

BIFUNCTIONAL AND DUAL-SITE MECHANISMS

Meriaudeau et al. (1984) and Naccache et al. (1985) studied CO hydrogenation over a series of differently supported Pt catalysts. They found that the mechanical mixture of Pt/ThO₂ and also of Pt/CeO₂ with their separate supports brings about a significant increase in methanol activity. Moreover, Electron Spin Resonance (ESR) experiments showed that hydrogen spillover occurs on these catalysts. The authors concluded that methanol formation over Pt/ThO₂ and Pt/CeO₂ proceeds via a bifunctional mechanism, that is, upon adsorption CO is activated on the support, and the complex (probably formate) thus formed is hydrogenated by spilled over hydrogen.

Conversely, in case of Pt/La₂O₃ and Pt/MgO, no increase in methanol formation was observed when the catalysts were mechanically mixed with their

own supports. ESR measurements also gave no indication of hydrogen migration. The high activity and selectivity of these catalysts was interpreted by assuming a dual-site mechanism which is basically the same as the bifunctional mechanism except that only the CO activated (on the support) in the vicinity of the metal is actually hydrogenated.

Mechanical mixtures of Pt/TiO₂ and also of Pt/Al₂O₃ with their supports did not cause any enhancement in methanol formation while dilution with CeO₂ did. Hydrogen migration was also recognized by ESR. It was concluded that either the formate on TiO₂ or Al₂O₃ is inactive while the formate on CeO₂ is active or the reaction is actually limited by a too slow migration of hydrogen from Pt to Al₂O₃ or TiO₂.

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SOME RECENT WORK ON THE CATALYTIC PRODUCTION OF
HIGHER ALCOHOLS FROM SYNTHESIS GAS

INTRODUCTION

Last year's report discussed the need for and value of predominantly straight chain ($C_1 - C_6$) mixed alcohols made from synthesis gas. The principle uses of such alcohol mixtures are as high octane gasoline extenders, a possible substitute for gasoline or as diesel fuels.

In August, 1985, EPA announced that it would cut the use of tetraethyllead in gasoline by 91% by January 1, 1986 and totally ban its use by 1995. This schedule more or less defines the time limits for introducing large amounts of new octane boosters for gasoline. Mixed straight-chain alcohols with their high octane numbers can help refineries meet the upcoming need for the octane boosters that will be produced in refineries.

Another important use of these higher alcohols may well be as a way of converting remote natural gas currently being flared because the gas has no value locally or because there are no means of transporting it to a suitable site. Conversion of synthesis gas to high energy, high octane mixed higher alcohols would help save energy and increase our supply of high octane motor fuels.

STATE OF THE ART

The Dow Chemical Co. (Haggin, 1984) has announced a new synthesis of $C_1 - C_5$ alcohols that consist mostly of straight-chain compounds. The methanol concentration in these alcohols can be varied from zero to 90%. The octane numbers of the mixed alcohols can reach 120.

The Dow process is based on two key developments. The first is the development of rugged, selective and sulfur resistant catalysts. These consist of agglomerated molybdenum sulfides made by thermal decomposition of

thiomolybdates. The extreme resistance of these catalysts to sulfur poisoning is a great advance since the major problem in a number of other processes is poisoning by even very low levels of sulfur. Synthesis gas made from coal would be especially suitable for this process, since it would not require the extensive sulfur clean-up normally required in processes such as the Fischer-Tropsch process and the methanol synthesis.

Also, unlike the latter processes, the Dow catalysts have a reduced tendency to form coke. This permits the use of synthesis gas with H₂ to CO ratios as low as 0.7 to 1. This resembles the type of gas produced by several second generation coal gasification processes such as the Texaco, Shell and similar processes.

Both fluid bed and fixed bed reactors have been found satisfactory in pilot plant reactors capable of processing up to a ton of synthesis gas per day. Fixed bed reactors are simpler to operate and will probably be used since the catalyst is so rugged.

A second key development by Dow in this synthesis of higher alcohols from synthesis gas is the development of a low energy method of drying the mixed alcohols, which usually contain about 8% of water. Dow uses a system of zeolite units to remove water; the final product contains as little as 0.2% of water, thus avoiding the costly energy intensive drying by distillation.

In recent years, several other catalysts for higher alcohols synthesis have been investigated. Using a 10 wt% Mo/SiO₂ catalyst promoted with various alkali metal salts, very promising laboratory results have been obtained by Tatsumi et al. (1984, 1985) under mild conditions (523-573 K, 0.15 MPa). Depending on the nature of the promoter, CO hydrogenation (CO/H₂ = 1) yielded a total selectivity in C₁-C₅ alcohols (exclusive of CO₂) as high as 72%. Comparing the influence of a series of alkali salts, it was found that the

enhancement of alcohol formation is strongly sensitive to the nature of both the anions and the cations. The effect of potassium salts decreased in the order $F > Cl > Br > I > CO_3$, and that of a series of chlorides decreased in the order $K > Rb > Na > Li$. In addition, two important features have been underlined (Tatsumi et al., 1984). First, it is possible to use synthesis gases having low hydrogen content, directly without a pre-shift step. Second, the subsequent separation and purification of alcohols is expected to be easy as they are exclusively accompanied by the formation of CO_2 instead of water.

The same catalysts were also tested for the CO_2/H_2 reaction under similar conditions (523 K, 0.15 MPa). Interestingly enough, it was found that CO_2 is more reactive than CO and gives a higher selectivity in alcohols. For example, using Mo-KF/ SiO_2 , some 90% C_1-C_5 alcohols (exclusive of CO) were obtained (Tatsumi et al., 1985). It is believed that to some extent, CO_2 helps maintain an intermediate oxidation state of Mo indicating that some CO_2/CO mixtures may be even more efficient than pure CO_2 .

Alkali promoted Ru-Mo catalysts were found to be effective for the formation of straight-chain primary alcohols via CO hydrogenation. Inoue et al. (1983) tested a series of Ru-Mo- Na_2O_3/Al_2O_3 catalysts under the following experimental conditions: $P = 8.6$ MPa, $T = 528$ K, $H_2/CO = 2/1$. The liquid fraction of the products as condensed in an acetone-solid CO_2 trap contained more than 99% of straight-chain primary alcohols (water excluded). However, inspection of the results reported by Inoue et al. (1983) shows that the overall selectivity towards alcohols as calculated on the basis of CO consumed did not exceed 19%, the remainder being CO_2 and hydrocarbons. At variance with Dow catalysts, where the methanol fraction can be voluntarily changed over a wide range, the alcoholic products obtained by Inoue et al. (1983) followed a Schulz-Flory distribution. This means that a relatively high

methanol content cannot be avoided. Very similar results have been recently reported on a Ru-K/MoO₂ catalyst (Chen, 1985).

Alkali promotion of commercial Cu/ZnO methanol synthesis catalysts was found to increase the formation of higher alcohols, especially ethanol, propanol and 2-methylpropanol. Smith and Anderson (1983) claimed that under their experimental conditions (13 MPa, 558 K, H₂/CO = 1/2), the optimum potassium concentration is about 0.5 wt%. Additionally, they found that the formation of 2-methylpropanol is favored by a low H₂ content in the reactant mixture.

Modified iron catalysts for CO conversion to higher alcohols at relatively low pressure were recently investigated by two groups of researchers. Razzaghi et al. (1984) studied the influence of a variety of additives on the catalytic performances of Fe/SiO₂ and Fe-Cu/SiO₂ catalysts, at a total pressure of 10 MPa. Two major findings were emphasized, (i) the addition of rare earth oxides increases the overall conversion as well as the selectivity toward alcohols, in particular, ethanol, (ii) metals of group Vb and Vlb exert a promoting effect on alcohol selectivity. However, in most cases the overall selectivity in alcohols remains rather low, typically 10-20%.

Pijolat et al. (1985) reported an alcohol synthesis from CO and H₂ on a Fe/Al₂O₃ catalyst at 0.8-3 MPa. Alcohols containing up to 11 carbon atoms were detected along with the corresponding olefins and paraffins. At low temperature and pressure, about 473 K, 0.8 MPa, a total selectivity as high as 65% alcohols (CO₂ excluded) was obtained.

The conversion of CO to C₁-C₇ alcohols over Co-Mo-K/SiO₂ catalysts was studied by Fujimoto and Oba (1985) in the temperature and pressure range of 473-573 K and 1-7 MPa, respectively. The main results drawn from this work

are, (i) reduced cobalt is an essential ingredient for the chain growth of alcohols and hydrocarbons, (ii) molybdenum enhances the catalytic activity, (iii) potassium carbonate exhibit a promoting effect for alcohol synthesis with a parallel suppression of hydrocarbon formation, (iv) the oxygenates obtained are essentially normal alcohols and (v) both alcohol and hydrocarbon distributions fit a Schulz-Flory equation.

The Institut Francais de Petrole (IFP) have developed a Co-Cu based catalyst for the conversion of synthesis gas to C_1-C_6 alcohols under relatively mild conditions (543-593 K, 6-10 MPa). In addition to patented literature (Sugier and Freund, 1978; 1980), information concerning the preparation and activation of these catalysts as well as on the economics and the optimization of the process have been published in the open literature (Courty et al., 1982; 1984; Grandvallet et al., 1984; Sugier et al., 1980).

The IFP catalyst is a homogeneous mixed oxide basically containing copper and cobalt and either aluminum or chromium oxide as well as at least one element from among the alkali and alkaline earth metals. In most of the literature dealing with these catalysts, strong emphasis has been placed on the preparation and activation procedures as they dramatically affect the final catalytic properties. It is claimed that such flexibility in the catalyst composition makes it possible to monitor the distribution of alcohols from 20 to 50% $C_{2+}OH$.

Using a feed mixture ($H_2/CO = 2-2.5$) containing up to 10% CO_2 , 12-18% CO conversion may be achieved in a single pass at 533-593 K and 6-10 MPa. At 90% total conversion of CO , the selectivity toward alcohols can be as high as 70-75%. The typical distribution of these alcohols is: 50-70% methanol, 16-23% ethanol, 8-14% propanol, 4-7% butanol, 2-3% pentanol and 1.5-3% $C_{6+}OH$ (Courty et al., 1984). Depending on the operating conditions and the composition of

the feed mixture, the alcohol fraction may contain as much as 35% water. A separation process based on extractive distillation has been described by Courty et al. (1984).

The main advantages of the IFP process appear to be (i) high mechanical strength of the catalyst allowing even severe operating conditions, (ii) high flexibility in the catalyst composition as a controlling parameter for the alcohol distribution, (iii) the yield in higher alcohols is hardly affected by the presence of CO_2 in the feed mixture and (iv) economic studies show that the process is likely to be competitive with the methanol synthesis for blending with gasoline.

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