# THE ACTIVITY OF $Cu-ZnO-Al_2O_3$ METHANOL SYNTHESIS CATALYSTS

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Methanol is made (1) with greater than 99% selectivity when a high pressure gas mixture of CO, $CO_2$ and $H_2$ is passed over a catalyst containing Cu, ZnO and $Al_2O_3$ at between 220°C and 300°C. Other than that the reaction is exothermic there seem to be few further facts about which complete agreement exists (2, 3). With increasing emphasis being placed worldwide on methanol synthesis processes because of the possible role which methanol may play in the future either as a feedstock or a fuel, there is now a considerable interest in the chemistry of the synthesis reaction. We have sought for many years to gain an understanding of the mechanism of methanol synthesis on $Cu-ZnO-Al_2O_3$ catalysts for the purely pragmatic reason that we hope thereby to discover ways of improving, still further, the already impressive performance characteristics of these catalysts.

Our approach has been to apply a wide range of techniques, particular emphasis being placed, where possible, on the use of practical catalysts under industrial working conditions, with the aim of answering the following questions:

(i) Is methanol synthesised from CO or $CO_2$?

(ii) What is the state of the copper in a working catalyst?

(iii) What roles are played by the ZnO and $Al_2O_3$ components in the commercial catalyst?

(iv) What is the mechanism and which reaction step is rate determining?

(v) What are the active sites for methanol synthesis on a $Cu/ZnO/Al_2O_3$ catalyst?

## MEASUREMENT OF CATALYST ACTIVITY

Activity is determined under standard conditions of 250°C, 50 atms, SV 40,000 $hrs^{-1}$, gas composition 10% CO, 3% $CO_2$, 67% $H_2$, 20% $N_2$ in standardised pseudoisothermal reactors operating from a single large gas battery with a common purification system. Each catalyst sample is reduced under standard conditions (5% $H_2$ in $N_2$ at 1 atm for 15 hrs) and exposed to reaction gas for pre-set periods of time. To a first approximation, activity is proportional to methanol concentration in the outlet gases - an assumption reasonably defensible provided catalyst activity does not vary too widely between samples, and as long as equilibrium is not closely approached. The reproducibility of activity measurements is shown by the exit concentration of methanol (measured to 99% confidence limits) from 23 replicate runs with a standard industrial catalyst. An arbitrary activity of unity was assigned to this catalyst.

## THE ROLE OF CARBON DIOXIDE

In 1975 Kagan et al[4] reported work with labelled carbon oxides which showed that methanol synthesis proceeds through carbon dioxide rather than carbon monoxide eg

$$CO + H_2O \rightarrow CO_2 + H_2 \rightarrow CH_3OH + H_2O \qquad (1)$$

This work has been repeated and confirmed by us. With $^{14}CO_2$ as a component, gas containing equal moles of CO and $CO_2$ has been reacted over the standard $Cu\text{-}ZnO\text{-}Al_2O_3$ catalyst under the standard conditions as described above. Space velocity was varied between 10,000 and 240,000 $hrs^{-1}$ and the exit gases analysed for the separated components and their corresponding radioactivities measured. Results are shown in Figure 1 and reveal clearly that synthesis proceeds via carbon dioxide. 'Scrambling' of radioactivity via the shift reaction:

$$^{14}CO_2 + H_2 \rightleftharpoons {}^{14}CO + H_2O \qquad (2)$$

is negligible at high space velocities and indicates that under methanol synthesis conditions the reverse water gas shift reaction (ie left to right above) is slower than the methanol synthesis reaction. This coupled with the fact that methanol radioactivity is always higher than that of the $CO_2$ suggests there may be no intermediate common to the water gas shift and synthesis reaction.

## THE STATE OF COPPER IN A WORKING CATALYST

Accurate measurement of the copper surface area of reduced $Cu-ZnO-Al_2O_3$ catalysts by the use of the reaction between nitrous oxide and surface copper atoms is now routine and reproducible.

The method has been described by previous authors (5, 6) and in its most convenient form the evolution of nitrogen following a pulse of nitrous oxide is measured. With this technique a number of $Cu-ZnO-Al_2O_3$ catalysts of different synthesis activity and covering a range of copper particle sizes has been examined. The results shown in Figure 2 illustrate a linear dependence of synthesis activity on total copper surface area.

In this work we have adhered to the standard reduction procedure because the resulting surface is representative of the initial state of the real catalyst surface in industrial use. Reduction, however with either CO or pure $H_2$ results in a 25% increase in copper surface area showing that some copper still remains oxidised after standard reduction treatment.

The available metal surface area associated with a working catalyst surface can be measured in a variation of the technique by sweeping the working system clean with inert gas and then switching in a pulse of nitrous oxide. The efficacy of this treatment can be measured by fully re-reducing the oxidised surface and redetermining the total surface area to ensure that no irreversible surface changes have occurred. Results shown in Table 1 reveal that about 30% of the initial copper surface of a typical industrial catalyst is unavailable for reaction with nitrous oxide under working conditions, ie is probably oxidised. The proportion of oxidised sites on the working surface will almost certainly be a function of the ratios of carbon dioxide to carbon monoxide and of steam to hydrogen as well as temperature. The catalyst surface is therefore in a dynamic state and it may be anticipated that the nature of the surface will vary in a fixed bed reactor from top to bottom, being a function of the ambient gas composition. This emphasises the uncertainties inherent in extrapolating from experimental results obtained under conditions differing significantly from those used practically.

The oxidised surface of the copper crystallites probably consist partly of $O_{(ads)}$ and $OH_{(ads)}$. The interchange of these species via hydrogen and water is well established (7-9) and likely to occur under methanol synthesis conditions.

## THE ROLE OF SUPPORT OXIDES

The establishment of a correlation between copper surface area and methanol synthesis activity does not rule out a role for the supporting oxides in the detailed mechanism of synthesis. For example, some essential, but not rate-determining, steps in the reaction mechanism may occur on the support. Alternatively, if the surface/adsorbate complex involved in the rate determining step were a copper species, the presence of which was determined by juxtaposition with zinc oxide (zinc-copper contiguity) then the copper surface area correlation given above would still be obtained.

However, certain possible roles can be ruled out, for example, rate determining adsorption of any species onto a zinc or aluminium site.

One way in which evidence can be brought to bear on the role of zinc or aluminium oxides is to prepare high area catalysts in which one or the other oxide is omitted and to measure the activity/unit copper area compared with a standard copper-zinc-alumina catalyst. This has been done for a series of binary compositions containing copper allied respectively with the oxides of aluminium, manganese and magnesium. Results are shown in Figure 3 and compared with the standard $Cu-ZnO-Al_2O_3$ correlation. To a first approximation they reveal, surprisingly, no unique role for either zinc oxide or alumina in determining methanol synthesis activity. The copper surface areas of these catalysts under synthesis conditions are given in Table 1. As with the $Cu-ZnO-Al_2O_3$ catalysts, re-reduction gave an increase in copper area in all but one sample, but the proportion of copper surface covered by oxide was always much smaller. The high level of surface oxidation in copper/zinc catalysts may be a consequence of surface brass formation.

The area measurements therefore strongly suggest that only copper metal/copper oxide and probably only the copper metal surface is implicated in the rate determining step of synthesis and any oxide with appropriate basicity is substantially equally effective in promoting copper surface area and corresponding synthesis activity. Considerations of catalyst stability are, of course, not pertinent at this point.

## MECHANISM OF METHANOL SYNTHESIS

The combination of temperature programmed desorption (TPD) and temperature programmed reaction spectroscopy (TPRS) has been used to examine the mechanism via adsorption, desorption and decomposition of reaction intermediates. These techniques have shown that on $Cu/ZnO/Al_2O_3$ catalysts, the observed intermediate on the surface of the Cu and ZnO components of the catalyst is the formate species. Methanol adsorption (Figure 4) at room temperature on to a catalyst in which the surface copper is about 25% oxidised (see above) was characterised by two main peaks in the desorption spectrum: (i) by the coincident desorption of $H_2$ and $CO_2$ at a peak maximum temperature of 440K - a fingerprint of the existence of a formate species adsorbed on the copper component (10) and (ii) by the coincident desorption of $H_2$ and CO at 580K - characteristic of a formate species adsorbed on zinc oxide (11, 12).

The same two formate species are observed after the adsorption of formaldehyde on this partially oxidised catalyst, in addition to which methanol itself is desorbed at 360 K. This latter is characteristic of desorption of methanol from copper 110 (13), suggesting that it has in fact been formed on the copper component of the catalyst in preference to the zinc oxide component.

A pointer to the rate determining step on the copper component of the catalyst and an indication of the role of the support in the mechanism is to be found in microreactor experiments (1 at) on a $Cu/Al_2O_3$ catalyst. Following $CH_3OH$ synthesis, TPRS showed that the formate species existed on the surface of the copper under steady state methanol synthesis conditions ($CO_2/H_2$ feed, 220°C); the same formate species was observed after dosing the catalyst continuously with the same feed ($CO_2/H_2$), but at 100°C, when no detectable reaction occurred, ie neither methanol synthesis nor reverse shift. The rate determining step in the conversion of $CO_2$ and $H_2$ to methanol on the copper component of the catalyst occurs therefore after formation of the surface formate species - probably the hydrogenolysis of the adsorbed formate. TPD experiments on the $Cu/Al_2O_3$ catalyst and on $Al_2O_3$ alone showed the $CO_2$ to be adsorbed on the alumina itself, suggesting that a role of the basic support (both $Al_2O_3$ and ZnO) is the adsorption of the $CO_2$. This could then react at the support/copper interface with hydrogen atoms adsorbed on the copper, forming a formate species on the copper surface, the rate determining step probably being the hydrogenolysis of this adsorbed formate.

Alternatively, at working pressures (50-100 at), $CO_2$ may adsorb on the partially-oxidised copper surface and then react in the same way. Such adsorption of $CO_2$ has been reported by Stone and Tilley (14) for a copper surface, partially oxidised by molecular oxygen. It is clear from these results and those described above, that the adsorption of $CO_2$ is not rate determining.

The nature of the adsorbed $CO_2$ has been suggested in ab initio, self consistent field molecular orbital calculations (15) which showed that unlike other possible molecular interactions no energy barrier existed for the reaction of hydrogen atoms with $CO_2^-$.

The overall methanol synthesis mechanism from $CO_2$ and hydrogen can therefore be written as:

$$CO_2^-{}_{(a)} + H_{(a)} \rightarrow HCO_2^-{}_{(a)} \qquad (3)$$

$$HCO_2^-{}_{(a)} + 3H_{(a)} \rightarrow CH_3OH_{(g)} + O^-_{(a)} \qquad (4)$$

where the subscript a and g relate to adsorbed and gas phase species respectively. The negative charge on the adsorbed $CO_2$ and formate species may be less than unity.

The mechanism does not specify which of the three hydrogenation steps represented by reaction 4 is rate determining, but it seems likely that it is the step which involves carbon-oxygen bond breakage, ie hydrogenolysis.

However, as reaction 4 shows, each copper site at which methanol is synthesised will become oxidised as a consequence of the synthesis reaction. These oxidised sites constitute in the steady state some 30% of the total surface available initially following reduction (see Table 1), the steady state being maintained by the reactions of CO (16) and $H_2$ (8) with $O_{(ads)}$.

Oxidation of CO on partially oxidised copper constitutes part of the shift reaction, while TPRS shows that CO is not a product of Cu(I) formate decomposition. The shift reaction, therefore, under methanol synthesis conditions on Cu-ZnO-$Al_2O_3$ catalysts does not involve the formate intermediate contrary to previous suggestions (18).

Thus:

$$CO_2 + H_2 \rightleftharpoons X \rightleftharpoons CH_3OH \qquad (5)$$

$$X \not\rightleftharpoons CO + H_2O$$

The mechanism proposed resembles that found (11, 12, 19) earlier for the synthesis of methanol from $CO_2$ and $H_2$ over zinc oxide. This reaction is several orders of magnitude slower than copper-catalysed synthesis and it plays no part in the reaction over Cu/ZnO/$Al_2O_3$ catalysts.

## THE ACTIVE SITE

The experimental results indicate that the active site for methanol synthesis consists of a copper(0) surface atom in close proximity to an oxide surface site. These sites are formed in the first instance by reduction with $H_2$, the number of such sites being determined by the $H_2$:$H_2O$ and CO:$CO_2$ ratios. This view is very similar to that proposed by Okamoto et al (17), following their study of reduced CuO-ZnO surfaces by XPS. From work by Habraken et al (16), and Mesters et al (8), CO reacts faster than $H_2$ with $O_{(a)}$, but with a significant activation energy, so it is possible that the CO:$CO_2$ ratio is the more important.

## CONCLUSIONS

Methanol synthesis over $Cu-ZnO-Al_2O_3$ catalysts occurs via carbon dioxide hydrogenation on the partially oxidised copper surface. Oxide species may play a direct part in the synthesis by promoting absorption of $CO_2$ at the copper-oxide interface, reacted $CO_2$ being replenished via the shift reaction which occurs at different sites and by a different mechanism from methanol synthesis. Overall, CO can react at any oxidic or hydroxidic copper(I) site; methanol synthesis probably occurs at copper(O)/copper(I) sites.

Table 1

Total copper area, during use and copper area following use of a standard $Cu/Zn/Al_2O_3$ catalyst and various binary copper/metal oxide catalysts [$m^2$ per g catalyst charged]. Standard methanol synthesis conditions.

| CATALYST | | Cu AREA AFTER REDUCTION | RELATIVE INITIAL ACTIVITY PER g CATALYST | Cu AREA AFTER ACTIVITY TEST | Cu AREA AFTER RE-REDUCTION |
|---|---|---|---|---|---|
| $Cu-Zn-Al_2O_3$ | 60:30:10 | 32.2 | 1.0 | 19.6 | 29.2 |
| Cu-MgO | 60:40 | 9.0 | 0.15 | 7.5 | 8.6 |
| Cu-MgO | 20:80 | 22.6 | 0.21 | 23.4 | - |
| Cu-MgO | 40:60 | 5.9 | 0.13 | 6.1 | 6.4 |
| Cu-MgO | 60:40 | 14.9 | 0.27 | 13.0 | 13.7 |
| $Cu-Al_2O_3$ | 20:80 | 11.7 | 0.45 | 10.6 | - |
| $Cu-Al_2O_3$ | 40:60 | 19.9 | 0.5 | 17.2 | 20.5 |
| $Cu-Al_2O_3$ | 60:40 | 12.7 | 0.40 | 12.2 | 11.6 |
| Cu-MnO | 20:80 | 15.6 | 0.30 | 14.1 | 16.0 |
| Cu-MnO | 40:60 | 15.7 | 0.28 | 15.4 | 16.8 |
| Cu-MnO | 60:40 | 23.9 | 0.38 | 24.7 | 26.2 |

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Figure 1. $C^{14}$ activity of outlet gas components as a function of reactant space velocity

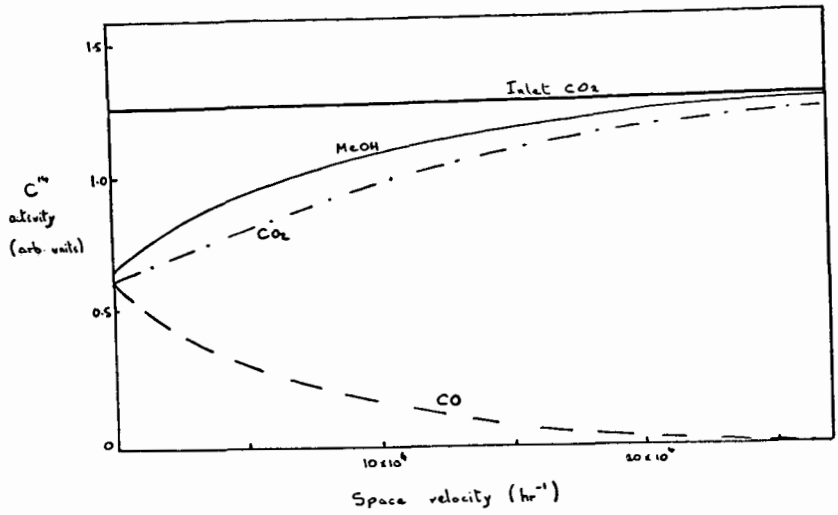



Figure 2. Linear correlation between activity and copper surface area (95% confidence limits) for $Cu-ZnO-Al_2O_3$

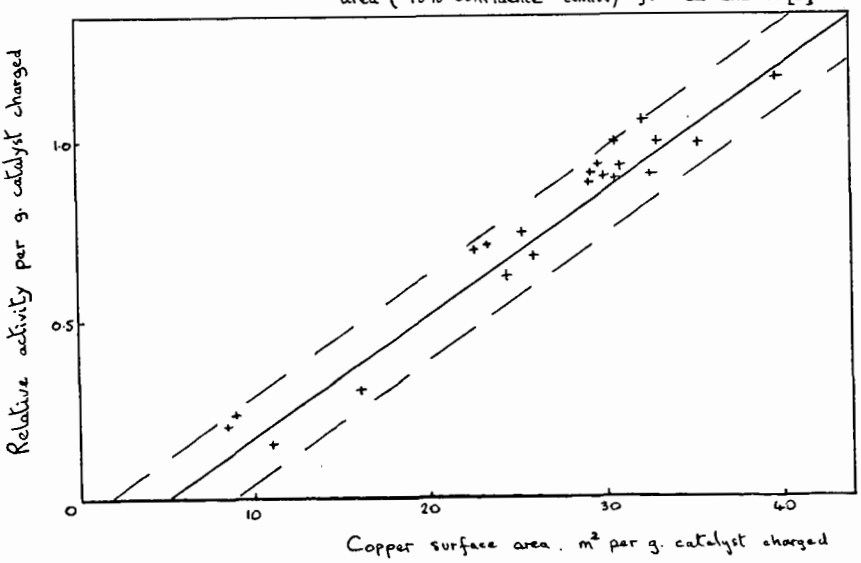


Figure 3 Initial activity of $Cu/Zn/Al_2O_3$ catalysts as a function of metallic copper surface area (solid line) compared with binary copper - metal oxide catalysts

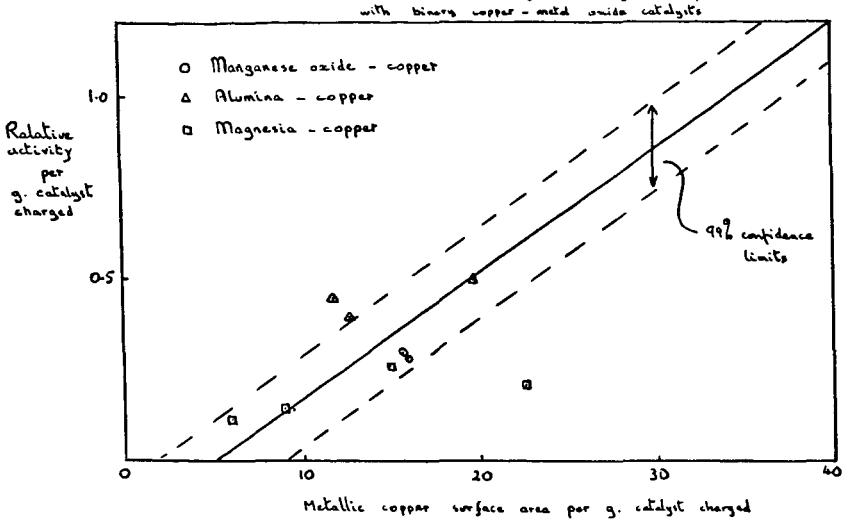
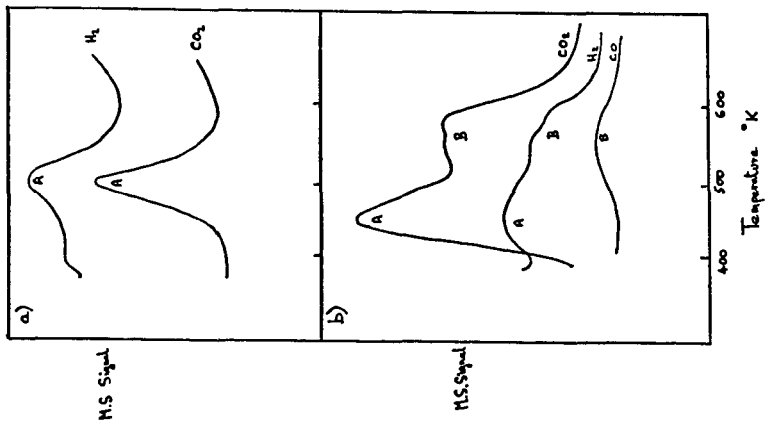



Figure 4




Methanol decomposition on a) unreduced and b) partially reduced $Cu-ZnO-Al_2O_3$ catalyst. Peaks A are associated with Cu(I) formate. Peaks B are associated with Zn formate.