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Role of ZnO in methanol synthesis on copper catalysts

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The varied results obtained by different groups concerning synergy between ZnO and Cu metal in methanol synthesis catalysts are shown to be a result of different experimental test conditions. It is suggested that synergy, when it occurs, arises from H spillover from ZnO to Cu metal.

Keywords: copper catalyst, zinc oxide, methanol synthesis, synthesis gas reactions, hydrogen spillover

1. Introduction

After much experimental work over two decades, there is general agreement [1–5] on most aspects of the mechanism of methanol synthesis over industrial catalysts, typically $Cu/ZnO/Al_2O_3$. Copper is present in the catalyst as copper metal, the critical reaction steps (although possibly not all reaction steps) take place on the copper metal surface, with methanol being formed predominantly from CO_2. Important surface intermediates are CO_2^-, CO_3 and HCOO. A comparison [6–8] of results obtained by several groups with different catalysts containing Cu/Zn showed consistent values of TOF for the reaction.

Nevertheless the role of ZnO in the catalyst is still a matter of controversy. There is no doubt of the importance of ZnO in the preparation of Cu/ZnO catalysts, in the prevention of Cu sintering during operation and in the removal of catalyst poisons [9], but conflicting experimental results have led to sharp differences of opinion on the possible role of the ZnO surface in the reaction mechanism. Some workers [10] found one linear correlation between rate of methanol synthesis and copper metal surface area for a variety of supported copper catalysts (i.e. constant TOF), so concluded that the support was irrelevant for the reaction. Various other workers [2,3,11,12] have found reaction synergy with ZnO or other oxide supports. Linear correlations of rate of methanol synthesis with copper metal surface area were frequently obtained but with slopes dependent on Cu support, i.e. with different TOF values. Evidence for hydrogen spillover between Cu and ZnO phases has been found from kinetic results with mixed catalysts [3,13] and from NMR experiments with Cu/ZnO catalysts [14].

In this paper it is suggested that the differences in experimental results arise mainly from the different experimental conditions used by various workers.

2. Experimental conditions

It seems unlikely that the conflicting experimental results obtained by different groups can be attributed to inadequate experimental techniques, especially as consistent values for TOF for Cu/ZnO catalysts have been obtained [6–8] by several research groups working with different catalyst preparations under a wide range of experimental conditions.

The experimental conditions (I) used by the ICI group [10,15] are in several respects different from those used by most other workers. The significant features are:

(a) High total pressure, typically 50 bar.

(b) High $H_2/(CO + CO_2)$ ratio. Typical reactant gas mixture, $80\,H_2/10\,CO/10\,CO_2$.

(c) High space velocity, typically 30,000 h^{-1}. This gives low conversions, well below equilibrium.

The pressure and inlet gas composition were chosen because they were typical of those used industrially [9], with the low conversion giving catalyst test conditions corresponding to the inlet zone of a methanol synthesis reactor.

Under these test conditions good correlations of rate of methanol synthesis with copper metal area were obtained, i.e. constant TOF, for various supports, with and without zinc oxide. No estimate of experimental error was given the earlier paper [10] (the results were obtained in several microreactors in two laboratories) but careful analysis of errors in the later paper [15] indicated a second-order effect of support phases on the near-constant TOF. Similar results have also been obtained by Fujitani et al. [16]. Thus this group of experimental results led to the conclusion that no special synergy (or at most only a small effect) was exerted by the zinc oxide on methanol synthesis occurring on copper metal.

Most other research groups, e.g. [2,3,12,13] have used rather different experimental conditions (II) for testing the activity of methanol synthesis catalysts:

(a) Low-medium total pressure, typically 1–10 bar.

(b) Low $H_2/(CO + CO_2)$ ratio, frequently stoichiometric, i.e. $2H_2/CO$ or $3H_2/CO_2$.

(c) High conversions, sometimes approaching close to equilibrium.

Under these test conditions strong dependence of methanol synthesis activity on support composition is usually seen, with catalysts containing ZnO in the support giving highest TOF values. These results, in conflict with those obtained under conditions (I), indicate strong synergy by ZnO in the reaction.

Thus, the main reason for the discrepant observations on the synergy of ZnO can be attributed to the differences in experimental test conditions used by different workers. Possible reasons for this are examined below.

3. Reaction mechanism under conditions (I)

It is possible that the reaction mechanism for methanol synthesis, or at least the rate-determining step, is not the same under conditions (I) and (II). This could account for the variable effects of ZnO.

As almost complete independence of synthesis rate on Cu support composition is found under conditions (I), all the critical reaction steps occur on the copper metal surface. There is much evidence [1] that the rate-determining step is hydrogenolysis of adsorbed formate $2H(a) + HCOO(a) \rightarrow CH_3O(a) + O(a)$. For this to be the case, there has to be a quasi-equilibrium supply of H(a) and HCOO(a), i.e. the chemisorption of H_2 and CO_2 on the copper surface has to be facile. These requirements do not raise any fundamental problems [1,5,17], and at low conversions the coverage of adsorbed species on the copper metal surface remains comparatively low.

The second-order effects on TOF could be related to effects proposed in the next section, or indeed could arise from weak promotion, traces of alkali, copper metal morphology, etc. They will not be discussed further.

4. Reaction mechanism under conditions (II)

Although large support effects are found under conditions (II), the constancy of TOF for supported copper catalysts of the same composition indicates that the reaction steps are the same under conditions (I) and (II), with the rate-determining step (rds) being associated with the copper metal surface. As above, the rds is probably formate hydrogenolysis provided that the supply of chemisorbed H_2 and CO_2 is sufficient. There seems no doubt [5] that CO_2 chemisorption, via CO_2^- and carbonate, will be sufficiently fast under conditions (II). In contrast, the supply of H(a) from hydrogen chemisorption on the copper surface under conditions (II) must be lower than under conditions (I) due to lower partial pressure of hydrogen, increased coverage of adsorbed species from CO and CO_2 (due to different reactant stoichiometry) and increased coverage of adsorbed species from H_2O and CH_3OH (due to higher conversions). If the rate of chemisorption of H_2 is insufficient to maintain a quasi-equilibrium concentration of H(a), then the rds can swing from formate hydrogenolysis to hydrogen chemisorption, with a decrease in overall rate.

For a catalyst consisting of copper on an inert support (e.g. Cu/SiO_2) this change of rds from conditions (I) to (II) provides an explanation for the low activity of these catalysts under conditions (II). As the rds under both conditions takes place on the copper metal surface, linear relations between rate of synthesis and copper metal area are found under all conditions. The alternative explanation, that the rds remains as formate hydrogenolysis under conditions (II) but is somehow slowed down by conditions (II), looks implausible.

For copper catalysts containing ZnO as one of the support components, methanol synthesis activities under conditions (II) are higher than, eg., Cu/SiO_2 and the TOF values found are within the same range as those under conditions (I) [6–8]. Thus the rds for these catalysts is the same under both sets of conditions, probably hydrogenolysis of HCOO(a). If hydrogen chemisorption on the copper surface is inadequate under conditions (II), then there must be an additional source of H(a) with these catalysts and hydrogen dissociation on ZnO is an obvious source, with spillover from ZnO to Cu surfaces. Hydrogen spillover in these catalysts has been discussed by Burch et al. [3] and recently Stone [18] suggested that hydrogen dissociation on ZnO could be important in methanol synthesis. Confirmation of hydrogen spillover comes from the observation that a catalyst bed made of separate Cu/SiO_2 and ZnO/SiO_2 particles is as effective as a bed of $Cu/ZnO/SiO_2$ particles [3,13]. Possible bifunctional mechanisms involving methyl formate or other molecular intermediates were ruled out by experiments with consecutive mixed beds [3]. Zinc migration and its effect on methanol synthesis under some experimental conditions has been demonstrated with physical mixtures of Cu/SiO_2 and ZnO/SiO_2 catalysts [19,20] and with model catalysts of zinc-deposited polycrystalline copper [21] and zinc-deposited Cu(111) [20]. However, zinc migration cannot provide a complete explanation of the synergy observed, e.g., with mixed Cu/SiO_2–ZnO/SiO_2 catalyst beds. With different experimental conditions to those used by Nakamura et al. [19,20], Burch et al. [3] separated the catalyst components after methanol synthesis over a mixed Cu/SiO_2–ZnO/SiO_2 catalyst bed and then re-tested the Cu/SiO_2 component alone. No enhanced activity was observed. Burch et al. [3] concluded that any Zn which might have been transferred to the Cu was not responsible for the observed synergy. They concluded that hydrogen spillover was the only plausible mechanism for the effect of ZnO under their experimental conditions.

Zirconia is also an efficient promoter of Cu/SiO_2 catalysts for methanol synthesis [12,22], giving values of TOF far exceeding those of Cu/SiO_2 catalysts. Fisher et al. [12] have proposed that in this system methanol is formed by the hydrogenation of species, formed by the chemisorption of either CO or CO_2, on zirconia. This type of mechanism is unlikely to occur on Cu/ZnO catalysts because TOF values are independent of the amount of ZnO present [6,8].

5. Rates of supply of H(a)

A key part of the interpretation above is that the chemisorption of molecular hydrogen on copper metal is fast enough under industrial synthesis conditions to maintain a quasi-equilibrium concentration of H(a). In contrast, under other conditions, the supply of H(a) from H_2 dissociation on copper metal is proposed to be rate-limiting. This can be checked by comparison with the known rates of hydrogen chemisorption on copper surfaces. Chinchen et al. [1] calculated rates of H_2 chemisorption on clean Cu surfaces under industrial methanol synthesis conditions, demonstrating that these rates were several orders of magnitude faster than methanol synthesis. More recently, and with better data, Campbell and Campbell [23] also showed that hydrogen adsorption/desorption on Cu(110) is very fast compared to methanol synthesis rates. Hence, they were able to calculate hydrogen coverages, giving a value of θ_H of 40% of saturation already at 10 bar. This appears to be amply sufficient even under experimental conditions (II). Further, Fisher et al. [12], working under conditions (II), proposed H(a) spillover from Cu to ZrO_2, as part of the ZrO_2 promotion effect, so there does not seem to have been any limit from hydrogen chemisorption in their system.

These calculations appear to rule out any possibility of the supply of H(a) being rate-limiting. However, this is too simple a conclusion. The surface of a working copper catalyst is a salmagundi of adsorbed species, significantly different from a clean crystal surface under UHV, so rates of hydrogen dissociation on the working copper catalyst surface are not readily calculable. The activation energy for hydrogen chemisorption on clean copper is about 60 kJ mol^{-1} [23]. Any increase in this value due to other adsorbed species would obviously give lower rates, but this effect alone may be insufficiently large to account for the limited supply of H(a) for the synthesis reaction under conditions (II). Both adsorbed O and Cs, for example, give little change in the activation energy for hydrogen chemisorption [23,24].

Campbell and Campbell [23] have pointed out an anomaly in these results in relation to methanol synthesis kinetics. They calculate that, on increasing the pressure in methanol synthesis from 10 bar to 100 bar, the increase in θ_H is small ($< 40\%$), because coverage is already high at low pressures of H_2. In contrast, the methanol synthesis rate is approximately first order in H_2 over this range. In further work on the reverse water–gas shift reaction,

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

over Cu(110), Ernst et al. [25] observed reaction orders in H_2 and CO_2 to vary markedly with gas composition and temperature. At moderate and high CO_2/H_2 pressure ratios, the reaction rate depended strongly on hydrogen partial pressure. Explanations for these anomalies in terms of a special high coverage state of H(a) [23] and H-induced surface reconstruction [25] have been put forward but there is no direct experimental evidence for these phenomena.

A DRIFTS study of H_2/CO_2 reactions by Bailey et al. [26] is also relevant. Although this work has been criticised [27], it is likely that the results for the 900–1100 cm^{-1} region are still safe. Peaks derived from methanol, and hence surface hydrogen atom populations, were found to be strongly dependent on the H_2/CO_2 ratio. This indicates, as in other systems described above, that the supply of H(a) available for reaction was more restricted than indicated by simple calculations. Bailey et al. [26] attributed the loss of hydrogen atoms either to migration to the bulk of the copper crystallites or to spillover from the copper to the zinc oxide, followed by absorption into the bulk.

In summary, several groups have found experimental evidence that there are some unexpected limits to the availability of H(a) on Cu for reaction with CO_2 (or an adsorbed derivative of CO_2, e.g. CO_2^- or CO_3). Thus, the high calculated rates of H_2 chemisorption on Cu do not necessarily invalidate the hypothesis that hydrogen supply by spillover from ZnO to Cu can be important in methanol synthesis over Cu/ZnO catalysts.

There are similar difficulties in attempting to calculate rates of H_2 dissociation on ZnO surfaces. Moreover, with ZnO in contact with Cu, the surface population of protons is known from NMR studies [14] to be increased by H-spillover from Cu.

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