Catalysis Letters 60 (1999) 45–49

The role of surface oxygen on copper metal in catalysts for the synthesis of methanol

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Received 17 December 1998; accepted 23 April 1999

Discrepancies in experimental measurements of adsorbed oxygen coverage on copper metal surfaces in working $Cu/ZnO/Al_2O_3$ catalysts are interpreted in terms of two types of adsorbed oxygen. The first, O(a), is identical with that observed in studies of single-crystal copper surfaces. The second, $O^*(a)$, not seen in single-crystal studies, is more strongly bonded to the metal surface. It is suggested that the adsorption sites of $O^*(a)$ contain Zn as well as Cu, from surface α-brass (copper/zinc alloy) formation during catalyst reduction. Earlier experimental results on O(a) coverages on various supported copper catalysts are re-assessed. Only catalysts containing Zn (or Ga) gave abnormally high coverages: with other supports, basic or acidic, O(a) coverages are less than $\sim$0.1.

Keywords: surface oxygen, copper metal, zinc oxide, methanol synthesis, synthesis gas reactions, copper/zinc alloy

1. Introduction

A novel interpretation [1] of the mechanism of methanol synthesis over copper catalysts under industrial conditions, subsequently expanded, e.g. [2,3], has found general acceptance. Methanol is formed predominantly from CO_2, not CO. Copper is present in the working catalyst as copper metal. The rate of synthesis is proportional to copper metal area, showing that the critical reaction steps in the synthesis occur on the copper metal surface. An adsorbed formate on the copper metal surface is a key intermediate and hydrogenolysis of this formate is probably the rate-determining step. Other important surface intermediates are CO_2^- and CO_3. A comparison [4–6] of results obtained by several groups with different catalysts containing Cu/Zn showed consistent values of TOF for the reaction. Nevertheless, it is still commonplace for workers in the area to write, e.g., "... the nature of the active sites and the reaction mechanism is still subject to considerable controversy" [7]. Most of this controversy concerns non-industrial catalysts (e.g., Cu/SiO_2 [8], Cu/ZrO_2 [9], alloy-based Cu/CeO_2 [10,11]) and/or non-industrial conditions, e.g. [12].

For methanol synthesis over $Cu/ZnO/Al_2O_3$ catalysts under industrial conditions argument has been largely confined to two aspects. First, the possible role of surface oxygen on copper metal and the oxidation states of surface copper atoms; secondly, the possible effects of zinc oxide in the catalyst. The various roles of zinc oxide in the system are discussed elsewhere [13,14]. A significant coverage of O(a) on copper was found experimentally [1–3,15] and this coverage, measured with a variety of supported copper catalysts, was observed [1] to depend on the oxide support (these data were omitted from a later paper [15]). These results were later confirmed and extended by Fujitani et al. [16]. The species O(a), not necessarily a single species, was seen as important in the mechanism of methanol synthesis both as intermediate and promoter [2]. This view was challenged by Campbell [17,18], who argued that the coverage of O(a) should be negligible during methanol synthesis. Although the validity of this extrapolation from surface chemistry was questioned [19], later experimental results with a $Cu/ZnO/Al_2O_3$ catalyst [7] supported the view that *in situ* O(a) coverage is negligible. It has also been suggested [20] that the O(a) coverage found in *in situ* but post-reaction measurements arose from the decomposition of surface carbonate but, at least for catalysts containing zinc oxide, the observed coverages of O(a) are too high to have been formed from surface carbonate [21,22].

All commercial copper catalysts for methanol synthesis and the water–gas shift reaction contain zinc oxide. This fulfils several functions (formation and maintenance of small Cu metal crystallites, poison absorption, etc.) about most of which there is little controversy [14]. Nevertheless there is still uncertainty about ZnO (or other bases) stabilising Cu^+ sites on the copper metal surface. The observed [16] dependence of specific activity for methanol synthesis on O(a) coverage on copper, for catalysts with different oxide supports including ZnO, also requires explanation. The possible formation of dilute α-brass (copper/zinc alloy) in the surface of copper crystallites has been analysed theoretically [23] and subsequently Nakamura et al. [24–26] have found experimental evidence of ZnO migration and surface brass formation under relevant conditions.

In this paper an attempt is made to reconcile the apparently conflicting evidence on the role of O(a) in methanol synthesis.

2. Experimental measurement of O(a) coverage

Here it is assumed that, in the absence of evidence to the contrary, the experimental methods used by different groups of workers are valid and that the apparent discrepancies arise from interpretation rather than practical incompetence. The techniques used and results obtained fall into two groups.

(i) The post-reaction examination of working catalysts by reaction with N_2O has been used by the ICI group [1–3,15,27,28] and others, e.g. [16]. The method determines the *free* copper metal surface area after the removal of all adsorbed intermediates except O(a). The reasons for ascribing the loss of area solely to O(a) have been given before [2]. Further, this has been confirmed [28] by the quantitative, post-reaction conversion of O(a) to CO_2 in reduction with CO. It has also been shown [2], contrary to later suggestions [7], that the observed decrease in copper metal surface area is due to adsorbed species and not a result of sintering: subsequent re-reductions of the catalysts, followed by another treatment with N_2O, showed negligible loss of copper metal surface. Some results from experiments at 50 bar are shown in table 1. When the differences in catalyst preparation and methanol synthesis conditions are taken into account, the agreement between the two sets of results is encouraging. Catalysts containing zinc or gallium oxides gave O(a) coverages in the range 0.1–0.4. Similar values have been found [2] with a commercial $Cu/ZnO/Al_2O_3$ catalyst. In contrast, copper supported on a range of other oxides of different properties all gave values for O(a) coverage of $\sim$0.1 or less.

Post-reaction analyses of catalysts always have the disadvantage that changes to the catalyst may occur between reaction and analysis. Thus Bailey et al. [20] have suggested that the main part of the O(a) observed post-reaction derives from CO_3(a) decomposition. Recent surface chemistry by Carley et al. [29] has shown unambiguously that any CO_3(a) present during synthesis (i.e., in the presence of CO_2) is converted to O(a) on purging (i.e., on the removal of CO_2). However, the results of the reaction of pure CO_2 with a commercial $Cu/ZnO/Al_2O_3$ catalyst [21,22] demonstrates that the copper metal surface in zinc-containing catalysts would need to be completely covered with CO_3(a) to give the O(a) coverages of table 1. The main advantage of post-reaction analysis, i.e., an *in situ* but not *in tempore* analysis, is that it is free from the time scale of the catalytic reaction. Thus the N_2O reaction technique gives a maximum value of O(a) coverage.

Table 1
Experimental determination of O(a) coverage in working catalysts by post-reaction measurement of Cu metal surface area with N_2O.

Catalyst	Fractional O(a) coverage	
	[1]	[16]
Cu/ZnO	–	0.23
$Cu/ZnO/Al_2O_3$	0.36	0.22, 0.10
$Cu/ZnO/ZrO_2$	–	0.23
$Cu/ZnO/Cr_2O_3$	–	0.14, 0.11
$Cu/ZnO/Ga_2O_3$	–	0.18
Cu/Ga_2O_3	–	0.16
Cu/SiO_2	–	0.07
Cu/Al_2O_3	0.09, 0.15	0.09
Cu/Cr_2O_3	–	0.11
Cu/ZrO_2	–	0.10
Cu/MgO	0.01, 0.09, 0.15	–
Cu/MnO	0.01, 0.05, 0.11	–

(ii) The Topsøe group used [7] a technique which is both *in situ* and *in tempore*, i.e., the imposition of transient changes in CO or CO_2 during methanol synthesis. By following the changes in concentration of gas-phase species leaving the catalyst, O(a) coverages on the catalyst can be deduced. This type of technique has the advantage of avoiding the ambiguities from post-reaction treatment. However, it does have two disadvantages. All analyses have to be on the time scale and conditions (temperature, gas mixture, etc.) of the catalytic reaction and the surface state of the catalyst is deduced solely from the products of the catalytic reaction. The experiments of Muhler et al. [7] were at atmospheric pressure, so differing from industrial practice in this respect but it seems unlikely that the discrepancies in results can be explained solely in terms of this pressure difference.

In a typical experiment pulses of CO were dosed repeatedly into a 5% CO_2/H_2 stream already producing methanol over $Cu/ZnO/Al_2O_3$ catalysts. Any adsorbed oxygen on copper was expected to give CO_2, but the amount of extra CO_2 formed during the CO pulses was negligibly small. Similar results were obtained in other experiments, in which a 6% CO_2/H_2 stream was changed in one step to a 5% CO/5% CO_2/H_2 stream. Muhler et al. [7] concluded from this work that there was little or no oxygen adsorbed on the copper metal surface of the catalyst during methanol synthesis. It should be noted that the transient technique gives a minimum value of O(a) coverage.

Other experimental work [30] with clean polycrystalline copper agrees with the Topsøe group's results. Post-reaction analysis of the copper surface found almost a monolayer of adsorbed formate and negligible coverage of adsorbed oxygen. In these experiments the copper surface was cooled under reaction gas, thus allowing the persistence of adsorbed formate. In contrast, a He purge at reaction temperature, customary in the N_2O measurement of copper metal surface area [2,15,27], removes all adsorbed species other than O(a).

3. The paradox of values of O(a) coverage

The discrepancy of high experimental values for O(a) coverage from N_2O chemisorption measurements and low values from transient experiments arises only with Cu/ZnO catalysts (and possibly Cu/Ga_2O_3-containing catalysts). Values of high coverages are observed only with these catalysts (table 1) and the Topsøe group have used their transient techniques only with a standard $Cu/ZnO/Al_2O_3$ catalyst [31].

If it is assumed that both experimental techniques give results valid for the working methanol synthesis catalysts, then the paradox can be resolved only if the major part of the O(a) coverage on the copper surface reacts too slowly with CO for the production of CO_2 to be significant in the transient experiments. This form of O(a) – denoted $O^*(a)$ – cannot be identified as any species of adsorbed oxygen observed in single-Cu-crystal experiments. As Campbell and co-workers have rightly observed [17,18], O(a) on Cu surfaces reacts rapidly with CO, so very low coverages of O(a) are to be expected. Thus $O^*(a)$, as a less readily reduced species, is probably more strongly bonded to the copper surface. In view of the wide variety of stable and transient oxygen species now known to be formed on metal surfaces [29,32], it is not surprising that two adsorbed oxygen species co-exist on the copper surface of a working catalyst. The features requiring explanation are (i) why $O^*(a)$ has not been observed in single-Cu-crystal experiments, and (ii) why high coverages of $O^*(a)$ are observed almost solely in Cu/ZnO catalysts. The answer may well lie in surface copper/zinc alloy (α-brass) formation.

Theoretical aspects of α-brass (copper/zinc alloy) formation in Cu/ZnO-containing catalysts have already been examined in some detail [23]. Although bulk α-brass formation would not be expected (and has not been found experimentally) in working methanol synthesis catalysts, the formation during catalyst reduction of α-brass in the surface layers of the copper crystallites is certainly possible. Further there is experimental evidence [24–26] of zinc migration and surface brass formation under reducing conditions in several Cu/ZnO systems. The somewhat less-reducing gas mixtures (higher CO_2 and H_2O levels) present under synthesis conditions should cause some surface oxidation [23]. This could take the form of either an adsorbed oxygen atom bonded to a zinc atom (or zinc and copper atoms) in the surface α-brass or of a ZnO decoration of the copper metal surface. Chadwick et al. [33] found that Cu/ZnO catalysts in which bulk α-brass formation had been induced by high-temperature reduction gave the same specific methanol synthesis activity as catalysts which had been reduced by standard methods. Thus α-brass formation is not detrimental to methanol synthesis. Adsorbed formate is a key intermediate in methanol synthesis [1–3,9,15,19,20,24–26,28]. In FTIR studies Rochester et al. [34–36] observed a bridging formate across a mixed Cu–Zn site and they concluded that species of this type could play a significant role in the methanol synthesis mechanism. Clausen et al. [37] found changes in the morphology of metallic copper crystallites on ZnO (but not on SiO_2), dependent on the oxidation potential of the synthesis gas mixture. These changes were attributed to a wetting/non-wetting phenomenon at the Cu/ZnO interface, i.e., further evidence of Cu/ZnO alloy interaction in these systems.

It follows that at least three stable surface oxygen species could be present on copper crystallites surfaces during methanol synthesis, subsequent to surface α-brass formation during catalyst reduction:

(i) Oxygen bonded solely to surface copper atoms, i.e., O(a). The coverage of this species on the working catalyst is low, certainly <0.1.

(ii) Oxygen bonded to both copper and zinc atoms (the zinc atoms include those in surface α-brass and in the edge of a ZnO decoration of copper). This can be identified with $O^*(a)$.

(iii) Oxygen bonded solely to zinc atoms. This species is unaffected under synthesis conditions [14]. Although α-brass can be formed from Cu/ZnO, zinc oxide alone cannot be reduced to zinc metal [23].

Another experimental observation can be explained in terms of surface brass formation. Muhler et al. [7] found, in their transient experiments, that the gas composition (CO, CO_2 concentrations) settled to steady values in about 1 min after a change of feed gas but the rate of methanol formation took about 30 min to reach a new steady state. Fujitani et al. [16] have shown that the specific rate of methanol synthesis is a function of O(a) coverage. Thus a slow change in O(a) coverage from surface alloy formation, as proposed here, would give the corresponding slow change in the rate of methanol synthesis. Changes in copper crystallite morphology [37], associated with changes in oxidation potential of the gas phase, may also be significant. This would be in accord with Muhler et al. [7]: "... a dependence of the amount of active sites on the CO/CO_2 ratio in the feed is also possible".

A similar catalyst model can be put forward for the catalysts containing gallium oxide (table 1). Like zinc oxide, gallium oxide is readily reducible (in contrast to the other oxide supports in table 1) and surface alloy formation is plausible.

It should be emphasised that the more complex model of catalyst surface proposed here does not necessitate any major change in the synthesis reaction mechanism put forward earlier [1–3] in which adsorbed oxygen functions as both intermediate and promoter. Changes in the synthesis mechanism have been expansions of composite reactions, e.g., the recognition of the importance of $CO_2^-(a)$ and $CO_3(a)$ in the conversion of CO_2 to adsorbed formate [20–22,29,34–36].

4. Other support effects

Of the catalysts not containing zinc oxide, silica-supported copper has been studied most widely, e.g. [1,3, 8,9,12,15,16,19,34–36,38]. Many of these experimental results appeared to be conflicting but this can now be seen to be largely the consequence of different experimental conditions [13,14]. For example, the lack of methanol synthesis activity found with a copper/purified silica catalyst [12,38] disagreed with the observation of activity in other copper/silica catalysts [1,8,15,16] and even unsupported copper [1,15,30]. However, these contrasting results can now be understood, at least qualitatively, from the results of surface chemistry studies which have shown the necessity for

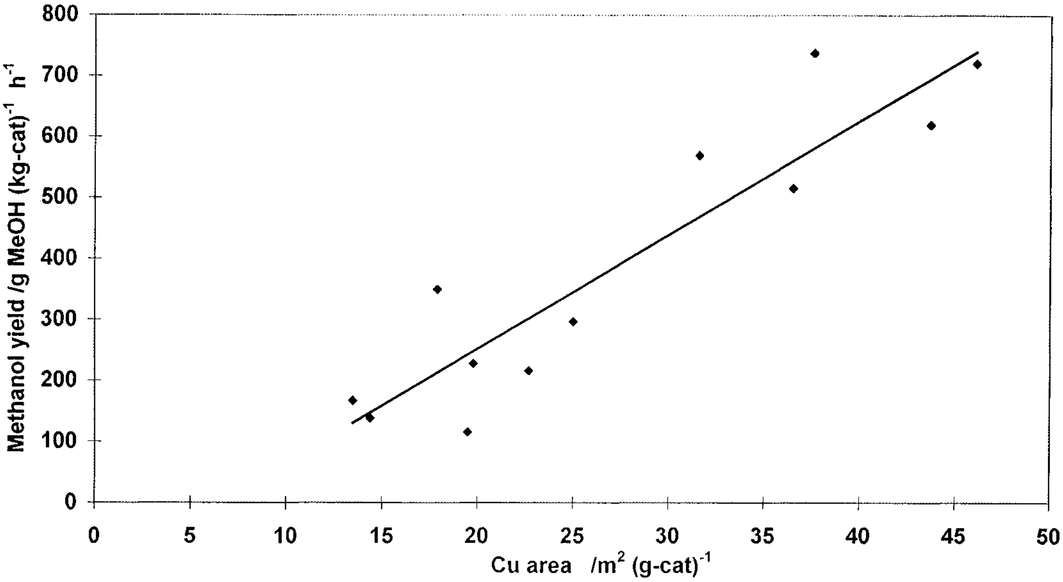

Figure 1. Catalyst activity plotted against copper metal surface area for catalysts consisting of copper supported on several different oxides. Data from table 2 of Fujitani et al. [16], re-plotted for comparison with earlier results of Chinchen et al. [1,3,6,15].

either high pressure of CO_2 [22,29,32] or the presence of a base [38–40] for the formation of the CO_2^-(a) intermediate. Yoshihara et al. [30] confirmed this in studies with clean polycrystalline copper. A total pressure of at least 5 bar, with excess hydrogen, is needed to obtain the same specific rates as those measured with commercial Cu/ZnO catalysts.

Comparative results, including measurements of O(a) coverage, for a range of supports were obtained by Chinchen et al. [1] and Fujitani et al. [16]. In the more recent work [16] Fujitani et al. showed that the specific activity for methanol synthesis is a function of O(a) coverage, with a maximum at about 17% coverage. However, when their results are plotted as activity (g-cat.)$^{-1}$ against specific copper surface area (figure 1), the resulting graph is similar to those obtained earlier [1,15] for copper on a range of supports and even for a group of $Cu/ZnO/Al_2O_3$ catalysts [3]. This linear relationship was implicitly assumed by Fujitani et al. in the use of specific activity in their figure 1 [16]. Chinchen and Spencer [3] stated: "In methanol synthesis, catalyst activity is proportional to the copper metal surface area of the working catalyst, although the scatter of the experimental points is more than would be expected from the experimental errors. There may therefore be a small second-order effect of catalyst composition, etc., on the specific synthesis activity". Fujitani et al. [16] have now identified one cause of this second-order effect as the result of variations in O(a) coverage. As the proposed mechanism for methanol synthesis involves both the bare and O(a)-covered surfaces [2], it is not surprising that the plot of specific activity against O(a) coverage is a "volcano" curve.

A question remains on the nature of the O(a) species present on the copper surfaces of these varied, non-zinc-containing catalysts. As noted above (table 1), the coverages are all smaller than those on zinc- (or gallium-)containing catalysts but even so, by extrapolation of the experimental results of Muhler et al. [7] and by Campbell's arguments [17,18], it seems unlikely that it can all be accounted for as simple O(a) on copper metal. Alloy formation, as proposed above for Cu/ZnO catalysts, is scarcely credible for, e.g., a Cu/SiO_2 under typical methanol synthesis conditions. Oxygen atoms at copper metal/support interfaces, could well appear as surface oxygen, if reducible. However, it is likely [41] that peripheral sites of this type are of negligible importance in conventional precipitated copper catalysts. This would not be the case for copper crystallites "decorated" with particles of support: the proportion of peripheral sites could then be much greater. Also, O(a) remaining after CO_3(a) decomposition [20], although insufficient to explain O(a) coverages on Cu/ZnO catalysts, could make a significant contribution to these lower coverages. Thus it is likely that the coverages of O(a) observed (table 1) in post-reaction analyses of these catalysts were built up with O(a) from several sources.

5. Conclusions

(1) The contrary results for *in situ* O(a) coverages on $Cu/ZnO/Al_2O_3$ catalysts, obtained by different experimental methods, can be resolved in terms of two stable adsorbed oxygen species: one, the "normal" O(a) on Cu, and the second, a more strongly adsorbed species.

(2) Both experimental and theoretical evidence point to surface copper–zinc alloy (α-brass) formation as the origin of the second O(a) species.

(3) Types of O(a) from several sources may contribute to the low total O(a) coverages of non-zinc-containing catalysts.

(4) Experimental surface science results have been essential in the resolution of catalytic problems in methanol synthesis. Nevertheless, the complexity of the methanol synthesis system confirms our earlier statement: “Caution is needed in using results from a [111] plane of copper obtained under ‘surface science’ conditions to interpret the behaviour of a methanol synthesis catalyst operating with a mixed gas feed at elevated pressure” [19].

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