Catalysis Letters 5 (1990) 55–60

THE ROLE OF HYDROGEN IN METHANOL SYNTHESIS OVER COPPER CATALYSTS

R. BURCH and S.E. GOLUNSKI

Catalysis Research Group, Chemistry Department, University of Reading, Whiteknights, P.O. Box 224, Reading, RG6 2AD, U.K.

M.S. SPENCER

School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, P.O. Box 912, Cardiff, CF1 3TB, U.K.

Received 29 November 1989; accepted 6 March 1990

The experimental observation that the activity of a series of zinc oxide supported copper catalysts is related to the surface area of the copper is examined in the light of recent evidence that hydrogen spillover from copper to zinc oxide is facile. A model is proposed which explains the effect of zinc oxide on copper in terms of a reversible transfer of hydrogen between copper and zinc oxide. It is suggested that the *rate determining step* normally occurs on the surface of the copper but that the *rate of reaction* can be dependent on the availability of spillover hydrogen from the zinc oxide.

1. Background

An interesting paradox exists concerning the activity of methanol synthesis catalysts based on copper. On the one hand, it is well established that the specific activity (rate of methanol production per unit area of copper) depends on the choice of support [1–8]. On the other, it is known that for specific supports there is quite a reasonable correlation between the activity and the copper surface area [9–16]. The paradox is as follows: how can the activity of copper be promoted by zinc oxide while at the same time the specific activity of copper in Cu/ZnO catalysts is essentially constant and independent of the ZnO content? This question is addressed in this letter.

2. Correlation between activity and copper surface area

In recent years a number of research groups have investigated both the activity and the copper surface area of methanol synthesis catalysts containing both copper and zinc oxide. The results were obtained under widely varying experi-

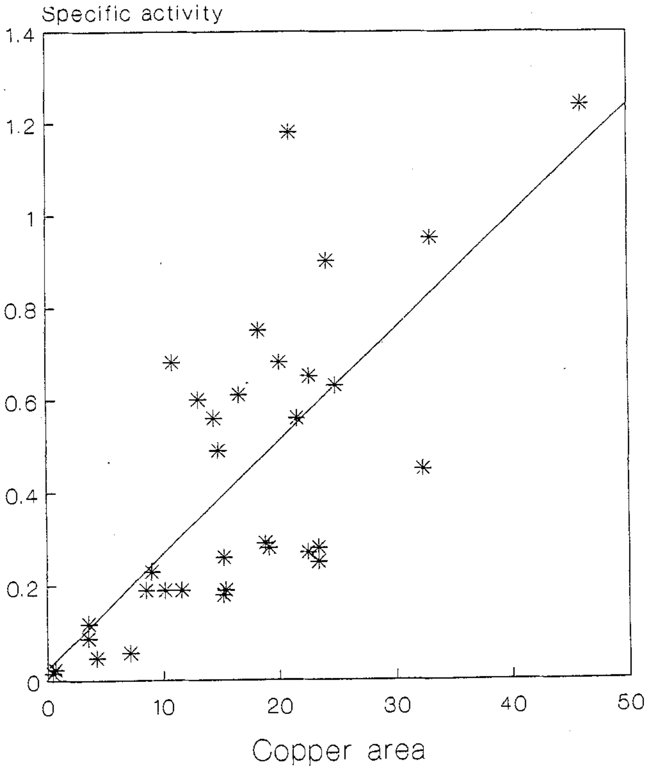


Fig. 1. Correlation between the standardised specific activity and the copper surface area for the synthesis of methanol over copper-containing catalysts, see text for details. (Units are: activity, $10^5 \times$ mol g_{cat}^{-1} s^{-1}; surface area, m^2 g_{cat}^{-1}.)

mental conditions using many different catalysts. However, by applying a simple kinetic analysis it is possible to derive a self-consistent set of data. To do this we have chosen as "standard" conditions a temperature of 240 ° C and a pressure of 50 bar. By using an activation energy of 60 kJ mol^{-1} and by assuming a linear correlation between activity and total gas pressure we have derived the data shown in fig. 1. The detailed numerical data and the references from which they were derived will be published elsewhere [17]. All the results were obtained with Cu/ZnO or Cu/ZnO/Al_2O_3 catalysts in CO/CO_2/H_2 gas mixtures.

Figure 1 shows a good correlation between activity and copper surface area, particularly when account is taken of the range of experimental conditions used by the original authors and the simple standardisation procedure. The experimental results come from work in eight laboratories, with catalysts prepared by three techniques (co-precipitation, impregnation and Raney) and used at 493–543 K, 1.0–70 bar in different CO/CO_2H_2 mixtures. We would argue, therefore, that, within experimental error, the activity of Cu/ZnO catalysts for the synthesis of methanol is proportional to the copper surface area. No such correlation exists between activity and the ZnO content. This is emphasized by the fact that for the catalysts shown in fig. 1 the ZnO content varies from 1% to 93%.

3. The role of hydrogen

The fact that ZnO promotes the activity of Cu while at the same time the activity is directly proportional to the Cu surface area cannot be explained by existing models. These, broadly, fall into three categories: those models in which all the activity and where the complete reaction is believed to occur on the copper; those models where the activity is believed to reside exclusively on the (modified) oxide; and those models where both the copper and the oxide act in concert through a classical bifunctional mechanism involving the transfer of reaction intermediate through the gas phase.

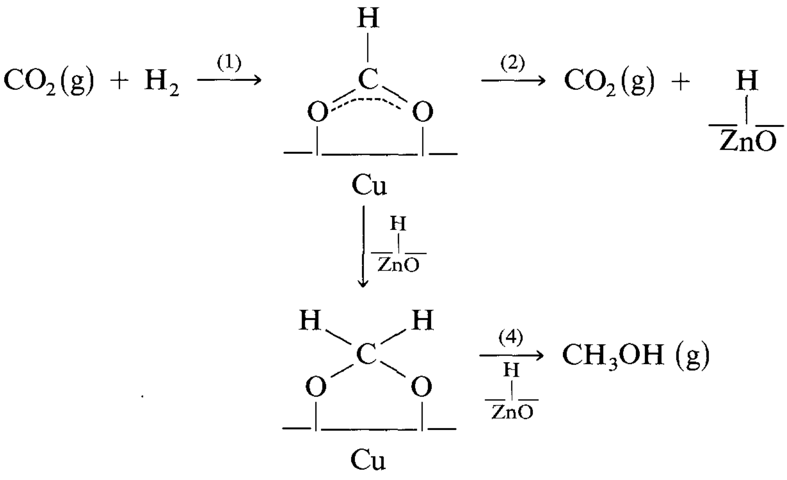
We believe that this paradox in methanol synthesis over Cu catalysts can be explained by considering the role of hydrogen. Recently, Dennison et al. [18] have demonstrated using ^{1}H NMR that after exposure to hydrogen there is a peak in the NMR spectrum which can be designated to atomic hydrogen chemisorbed on ZnO. The intensity of this peak is substantially enhanced in the presence of copper. Furthermore, Burch et al. [8,19] have used temperature-programming techniques to demonstrate that during the decomposition of formate on copper, hydrogen spillover occurs from Cu to ZnO. Since formate is known to be generated on copper from CO_2 and H_2 very easily under typical methanol synthesis conditions, it is probable that under these conditions hydrogen will spillover from Cu to ZnO where the NMR evidence shows that it can be stored in an atomic form.

Hydrogen spillover has been discussed for a number of years and there appears to be good evidence that it is a real phenomenon [20,21]. Moreover, the surface diffusion rate can be very large, and, given the close proximity of the Cu and ZnO in a Cu/ZnO catalyst it is reasonable to believe that large quantities of hydrogen could be transferred reversibly between the two components under reaction conditions. In addition to the NMR and temperature-programmed techniques referred to above independent evidence has been presented that ZnO has a large capacity for storing hydrogen [22].

The stepwise mechanism which we propose for the synthesis of methanol can be described in scheme 1.

In step (1) co-adsorption of CO_2 and H_2 generates the Cu formate. This is a very unstable species and will have a typical half-life under reaction conditions of about 0.3 s [22]. Decomposition of Cu formate back to CO_2 and hydrogen (step (2)) will release CO_2 into the gas phase, but atomic hydrogen may spillover onto the ZnO where it is trapped in a loosely held form.

In step (3), hydrogen atoms from the ZnO diffuse back to the Cu where they interact with another Cu formate molecule to convert this into a more fully



Scheme 1.

hydrogenated intermediate (HCO_2 into H_2CO_2, for example). We see this as a critical step because of the instability of Cu formate. Since the turnover number for methanol synthesis is only 10^{-2} molecules/Cu atom/s [14] and the half-life of Cu formate is only about 0.3 s [22] the probability of a Cu formate being converted into methanol is obviously very low. Clearly, anything which can enhance the hydrogenation of Cu formate will lead to an overall increase in methanol synthesis activity. We believe the critical rate determining step in methanol synthesis involves the addition of the first hydrogen atom to the Cu formate (step (3)) to stabilise it against decomposition back to CO_2 and H_2.

This model is capable of explaining the results shown in fig. 1. Since the half-life of Cu formate is so short, and the turnover number for methanol synthesis is so small, only a tiny amount of atomic hydrogen would be needed to maintain a flux of hydrogen onto the Cu at a sufficient rate to significantly increase the rate of hydrogenation. It is worth pointing out that although ZnO promotes the activity of Cu, the magnitude of the effect is numerically quite small, i.e., less than one order of magnitude. Thus, the effect of ZnO is to increase the turnover number from about 10^{-3} to 10^{-2} molecules/Cu/s. Put another way, the *average* time taken to produce a methanol molecule on a Cu site when ZnO is added only decreases from 1000 to 100 s. Thus, methanol synthesis even in a very good industrial catalyst is still a slow process, certainly when compared with the rates of diffusion of hydrogen over oxide surfaces [20,21].

The reason why there is such a good correlation between methanol synthesis activity and Cu surface area for Cu/ZnO catalysts as shown in fig. 1 is, we believe, a consequence of the low activity of Cu catalysts in this reaction. Thus, we propose that even a very small amount of ZnO is sufficient to provide all the hydrogen which can be used by the Cu to convert Cu formate into methanol. Increasing the proportion of ZnO in the catalyst above this (small) critical level has no effect on the activity per unit area of Cu because the excess ZnO cannot further enhance the activity of the Cu. Under some conditions, e.g., high hydrogen partial pressure and low conversions [14], it appears that the supply of atomic hydrogen on the copper surface alone can be sufficient and then the support effects are minimised.

It needs to be emphasised that the correlation of catalytic activity with copper area applies only to synthesis in gas mixtures containing CO_2. Methanol synthesis from CO/H_2 (CO_2-free) gas mixtures appears to occur by a different mechanism as discussed elsewhere [17,23]. When a $CO/CO_2/H_2$ reaction mixture is used, the role of the CO is to remove the extra oxygen deposited on the surface of the Cu when a CO_2 molecule is converted into CH_3OH, and thus maintain the active catalyst in the optimum state of reduction for methanol synthesis. Consequently, both CO and CO_2 are removed from the gas phase under typical industrial reaction conditions. However, CH_3OH is formed almost exclusively from the CO_2 in the reaction mixture.

In conclusion, we propose that the *rate determining step* in methanol synthesis over Cu catalysts occurs on the Cu surface and that this explains the correlation between activity and Cu surface area shown in fig. 1. The *rate of the reaction*, however, can be enhanced if a support is used which is capable of storing hydrogen in a readily available atomic form. ZnO appears to be a support *par excellence* for this purpose.

References

[1] G.J.J. Bartley and R. Burch, Appl. Catal. 43 (1988) 141.

[2] R. Burch and R.J. Chappell, Appl. Catal. 45 (1988) 131.

[3] J. Barbier, Th. Fortin, Ph. Courty and P. Chaumette, Bull. Soc. Chim. France (1987) 925.

[4] B. Pommier and S.J. Teichner, *Proc. 9th Int. Congress on Catalysis*, Calgary, 1988, 2 (1988) 585.

[5] P. Chaumette, Ph. Courty, J. Barbier, T. Fortin, J.C. Lavelley, C. Chauvin, A. Kiennemann, H. Idriss, R.P.A. Sneeden and B. Denise, *Proc. 9th Int. Congress on Catalysis*, Calgary, 1988, 2 (1988) 545.

[6] M.S.W. Vong, M.A. Yates, P. Reyes, A. Perryman and P.A. Sermon, *Proc. 9th Int. Congress on Catalysis*, Calgary, 1988, 2 (1988) 545.

[7] R. Burch, R.J. Chappell and S.E. Golunski, Cat. Lett. 1 (1988) 439.

[8] R. Burch, R.J. Chappell and S.E. Golunski, J. Chem. Soc. Farad. Trans. I. 85 (1989) 3569.

[9] S.P.s. Andrew, Plenary Lecture (paper 12) Post Congress Symposium, 7th Int. Congress on Catalysis, Osaka, July 1980.

[10] T. Takahama, H. Oshima, A. Ueno and Y. Kotera, Appl. Catal. 5 (1983) 59.

[11] W.L. Marsden, M.S. Wainwright and J.B. Friedrich, I. and E.C. Prod. res. Dev. 19 (1980) 551.

[12] A.J. Bridgewater, M.S. Wainwright, D.J. Young and J.P. Orchard, Appl. Catal. 7 (1983) 369.

[13] G.C. Chinchen, P.J. Denny, D.G. Parker, G.D. Short, M.S. Spencer, K.C. Waugh and D.A. Whan, A.C.S. Symposium on Methanol Synthesis, Philadelphia, 1984.

[14] G.C. Chinchen, K.C. Waugh and D.A. Whan, Appl. Catal. 25 (1986) 101.

[15] T.H. Fleisch and R.L. Mieville, J. Catal. 80 (1983) 1.

[16] J.B. Friedrich, M.S. Wainwright and D.J. Young, J. Catal. 80 (1983) 1.
[17] G.C. Chinchen, P.J. Denny, M.S. Spencer, K.C. Waugh and D.A. Whan, in preparation.
[18] P.R. Dennison, K.J. Packer and M.S. Spencer, J. Chem. Soc. Farad. Trans. I. 85 (1989) 3537.
[19] R. Burch, S.E. Golunski and M.S. Spencer, J. Chem. Soc. Farad. Trans. I. submitted.
[20] W.C. Conner Jr., G.M. Pajonk and S.C. Teichner, Adv. in Catal. 34 (1986) 1.
[21] W.C. Conner Jr., in: *Hydrogen Effects in Catalysis*, eds. Z. Paal and P.G. Menon (Marcel Dekker, New York and Basel, 1988) Ch. 12.
[22] M. Bowker, R.A. Hadden, H. Houghton, J.N.K. Hyland and K.C. Waugh, J. Catal. 109 (1988) 263.
[23] M.E. Fakley, J.R. Jennings and M.S. Spencer, J. Catal. 118 (1989) 483.