Catalysis Letters 1 (1988) 439–444

SYNERGY AT A DISTANCE IN THE SYNTHESIS OF METHANOL OVER COPPER CATALYSTS

R. BURCH *, R.J. CHAPPELL and S.E. GOLUNSKI

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

Received 28 September 1988; accepted 25 October 1988

Physical mixtures of Cu/SiO_2 and ZnO/SiO_2 catalysts have been studied for the synthesis of methanol from $CO/CO_2/H_2$ at 250 °C and 10 bar pressure. It is found that the activities are very much higher for the physical mixtures than would be expected from the activities of either of these two catalysts in isolation. The results suggest that the high activity of conventional $Cu/ZnO/Al_2O_3$ catalysts may arise from a synergy between the Cu and ZnO phases.

1. Introduction

The synthesis of methanol from $CO/CO_2/H_2$ mixtures using $Cu/ZnO/Al_2O_3$ catalysts is an important industrial process. Although this reaction has been studied extensively, the nature of the active centres is still a matter of debate [1–3]. Most recently it has been suggested [4–11] that the reaction occurs exclusively on the Cu and that the activity is directly proportional to the Cu surface area so that the ZnO is believed to have no special role in the synthesis of methanol.

This model cannot be of general applicability since we have found that the area specific activities of Cu/ZnO catalysts (i.e., the activity per unit area of Cu) are much higher than those of Cu/SiO_2 or Cu/ZrO_2 catalysts [2,3]. A similar support effect has been reported recently by several other groups of workers [12–15].

This support effect has been attributed to a direct interaction at the interface between the Cu and the ZnO [16]. However, such an interfacial interaction, although possibly important, is not essential. In the present work we demonstrate that an enhanced activity for the synthesis of methanol can be obtained by using physical mixtures of Cu/SiO_2 and ZnO/SiO_2 catalysts.

---

* [redacted].

2. Experimental

(a) MATERIALS

The Cu/SiO_2 catalyst was prepared by wet impregnation of an acid-washed silica (Davison 57, nominal surface area 300 $m^2 g^{-1}$) which had been crushed and sieved to retain the 250–425 micron portion. The impregnating solution was prepared by dissolving Cu acetate in 2M ammonia solution (pH = 9). The silica was added to an appropriate amount of this solution and the excess water evaporated off slowly in an oven. The sample was dried at 110 ° C overnight and then calcined in flowing O_2 (33 cm^3 $min^{-1} g_{cat}^{-1}$) by heating at 1 ° C min^{-1} to 400 ° C and holding at this temperature for 10 h. The nominal Cu content, by weight, was 5%.

The ZnO/SiO_2 catalyst was prepared by wet impregnation of the silica with a solution of Zn nitrate and dried and calcined as before. The nominal ZnO content, by weight, was 20%.

(b) CATALYST TESTING

The sample (100 mg), comprising either the pure catalyst or a 25%/75%, 50%/50% or 75%/25% mixture, was placed in a glass-lined stainless steel reactor (i.d. = 4.0 mm) and held in position by glass wool plugs and aluminium rods. Prior to catalyst testing the catalysts were reduced in flowing H_2 by heating at 1 ° C min^{-1} to 350 ° C and holding at this temperature for 10 h. The temperature was then lowered to the reaction temperature (250 ° C) and the reactor was pressurised with the reaction mixture. The reactant gas ($10\%CO/10\%CO_2/80\%H_2$, British Oxygen Company mixed gas) was passed through the catalyst bed, the flow (10 cm^3 min^{-1}) being controlled by a Krohne massflow controller. The pressure (10 bar) was controlled by a back pressure regulator (GO valve) which was heated, together with all the tubing downstream of the reactor to about 130 ° C. The reaction products were sampled with a heated gas sampling valve, separated on a Poropak Q column and analysed with a Perkin Elmer 8500 FID gas chromatograph linked to a COMUS data system. Samples for analysis were taken at intervals of 0.5 h and the mass specific activity was calculated as the percentage conversion of CO_2 to methanol, the units being mol $g_{cat}^{-1} min^{-1}$. The mass specific activities were converted to area specific activities (mol CO_2 converted $m_{Cu}^{-2} min^{-1}$) by dividing by the surface area of the Cu as determined separately [3] by N_2O frontal chromatography.

Remeasurement of the Cu area of the Cu/SiO_2 after use as a catalyst using the conditions outlined above demonstrated that there was no significant change in the Cu area during the methanol synthesis reaction.

(c) CHEMICAL ANALYSIS OF USED CATALYSTS

The catalyst particles after use were separated by hand into black and white components, corresponding to the Cu/SiO_2 and ZnO/SiO_2, respectively. These separated samples were dissolved in concentrated HNO_3 and analysed by atomic absorption. The results showed that there was no detectable contamination of the ZnO/SiO_2 by Cu (detection limit < 0.02 wt.%). The amount of Zn in the Cu/SiO_2 sample was < 0.1 wt.%. This represents an upper limit on the level of Zn contamination since it was practically impossible to exclude all the ZnO/SiO_2 particles from the CuO/SiO_2 sample.

3. Results

In all experiments the catalysts were stable after a short time on stream, so the results refer to an essentially steady state situation. Figure 1 shows very clearly that the activity of all the physical mixtures is higher than expected. Indeed, for the 25%/75% ($Cu/SiO_2//ZnO/SiO_2$) mixture the activity per unit area of Cu is

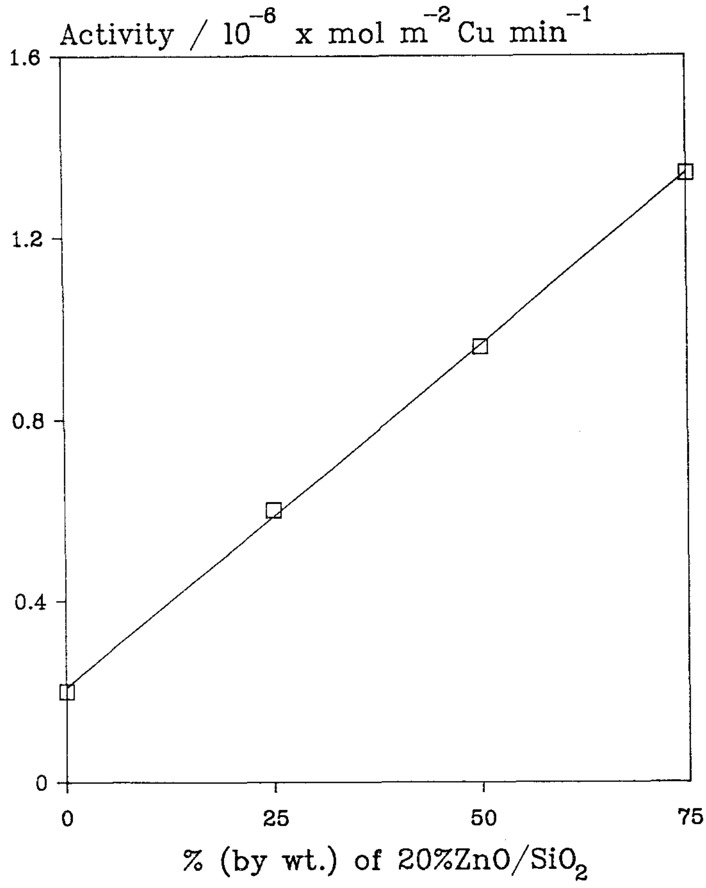

Fig. 1. Area specific activities of physical mixtures of Cu/SiO_2 and ZnO/SiO_2 catalysts, for the synthesis of methanol from $CO/CO_2/H_2$, as a function of the ZnO/SiO_2 content of the mixture.

comparable (within a factor of two) to that of a conventional co-precipitated Cu/ZnO catalyst tested under the same conditions of temperature (250 ° C) and pressure (10 bar) [3].

These results clearly demonstrate that the activity of a $Cu/SiO_2 + ZnO/SiO_2$ physical mixture for the synthesis of methanol from a $CO/CO_2/H_2$ mixture is much larger than the activity of the component parts of the physical mixture. (The activity of ZnO/SiO_2 is very small.)

A few experiments have been performed using a CO/H_2 reaction mixture (25%/75%). However, the synergy between Cu and ZnO is not observed when there is no CO_2 in the reaction mixture.

4. Discussion

It is clear from our results that there is a strong synergistic interaction between Cu and ZnO in the methanol synthesis reaction from $CO/CO_2/H_2$. However, this occurs even when the two components are present only in a physical mxiture. Our analytical results (see section 2, experimental) exclude the possibility that the synergistic effect we have observed is caused by contamination either of the Cu by ZnO or of the ZnO by Cu as a result of mass transport of one or other of these components during the calcination or reduction pre-treatments.

Thus, in our physical mixtures there is no *direct* contact between the Cu and the ZnO. Therefore, what we have observed is an example of synergy at a distance for the methanol synthesis reaction. This long-distance action has not been reported before for this reaction as far as we are aware although it has been observed in selective oxidation reactions [17].

Since there is no direct physical contact between the Cu and ZnO in our catalysts, the synergy observed must be due to an indirect chemical interaction between the Cu and ZnO. This could occur either through the gas phase or as a result of spillover across the SiO_2 surface. Intuitively, diffusion of a species through the gas phase appears more likely since the diffusion rates will be large. However, spillover cannot be ruled out completely since in favourable circumstances this can occur very rapidly [18]. For example, the diffusion coefficient of hydrogen on SiO_2 has been measured at 100 ° C to be 1.3×10^{-7} cm^2 s^{-1} [19]. This corresponds to a diffusion distance of about 3×10^3 nm s^{-1}.

Finally, the results in fig. 1 show that the extent to which the activity of a Cu/SiO_2 catalyst is increased by the presence of ZnO/SiO_2 depends on the amount of ZnO. It is possible that a promoted Cu surface is the centre of catalytic activity and that the promoter species is created by the ZnO. If the flux of promoter species to the Cu from the ZnO exceeds some critical value then the Cu will attain its maximum possible activity. On the other hand, if the flux of promoter species to the Cu is less than the rate of elimination of the promoter species from the Cu then the activity of the Cu will be lower than the maximum possible.

In conclusion, our results indicate that the activity of a Cu catalyst in the synthesis of methanol from $CO/CO_2/H_2$ is enhanced by the presence of ZnO in a physical mixture. This synergy does not require a direct physical contact between the Cu and the ZnO. Our results appear to exclude the possibility that the active centre comprises Cu^+ ions in the ZnO. Equally, however, the activity does not have a simple dependence on the Cu surface area.

Acknowledgements

We are grateful to the University of Reading, who provided a research studentship for RJC, and to the SERC who provided funds to construct the microreactor and to support SEG.

References

[1] see, e.g., J.C.J. Bart and R.P.A. Sneeden, Catalysis Today 2 (1987) 1.
[2] G.J.J. Bartley and R. Burch, Applied Catalysis, in press.
[3] R. Burch and R.J. Chappell, Applied Catalysis, submitted.
[4] S.P.S. Andrew, Plenary Lecture (paper 12) Post Congress Symposium, 7th Intern. Congress on Catalysis, Osaka, July 1980.
[5] T. Takahama, H. Oshima, A. Ueno and Y. Kotera, Applied Catalysis 5 (1983) 59.
[6] W.L. Marsden, M.S. Wainwright and J.B. Friedrich, I. & E.C. Prod. Res. Dev. 19 (1980) 551.
[7] A.J. Bridgewater, M.S. Wainwright, D.J. Young and J.P. Orchard, Applied Catalysis 7 (1983) 369.
[8] 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.
[9] G.C. Chinchen, K.C. Waugh and D.A. Whan, Applied Catalysis 25 (1986) 101.
[10] T.H. Fleisch and R.L. Mieville, J. Catal. 90 (19984) 165.
[11] J.B. Friedrich, M.S. Wainwright and D.J. Young, J. Catal. 80 (1983) 1.
[12] J. Barbier, Th. Fortin, Ph. Courty and P. Chaumette, Bull. Soc. Chim. France (1987) 925.
[13] B. Pommier and S.J. Teichner, 9th Int. Congress on Catalysis, Calgary, 1988, 2 (1988) 610.
[14] P. Chaumette, Ph. Courty, J. Barbier, T. Fortin, J.C. Lavelley, C. Chauvin, A. Kiennemann, H. Idriss, R.P.A. Sneeden and B. Denise, 9th Int. Congress on Catalysis, Calgary, 1988, 2 (1988) 585.
[15] M.S.W. Vong, M.A. Yates, P. Reyes, A. Perryman and P.A. Sermon, 9th Int. Congress on Catalysis, Calgary, 1988, 2 (1988) 545.
[16] H. Chen, S. Wang, Y. Liao, J. Tsai, H. Zhang and K. Tsai, 9th Int. Congress on Catalysis, Calgary, 1988, 2 (1988) 537.
[17] P. Ruiz and B. Delmon, Catalysis Today 3 (1988) 199.
[18] W.C. Conner, G.M. Pajonk and S.J. Teichner, Advances in Catalysis 34 (1986) 1.
[19] N.E. Lobashina, N.N. Savviv and I.A. Mynasnikov, Kinet. Katal. 24 (1983) 747.