An in situ high pressure FT-IR study of CO_2/H_2 interactions with model ZnO/SiO_2, Cu/SiO_2 and $Cu/ZnO/SiO_2$ methanol synthesis catalysts

Graeme J. Millar, C.H. Rochester *
Department of Chemistry, The University, Dundee DD1 4HN, UK

and

Kenneth C. Waugh
Katalco R & T, ICI Chemicals and Polymers Ltd., PO Box 1, Billingham, Cleveland TS23 1LB, UK

Received 31 January 1992; accepted 5 May 1992

In situ FT-IR spectroscopy allows the methanol synthesis reaction to be investigated under actual industrial conditions of 503 K and 10 MPa. On Cu/SiO_2 catalyst formate species were initially formed which were subsequently hydrogenated to methanol. During the reaction a steady state concentration of formate species persisted on the copper. Additionally, a small quantity of gaseous methane was produced. In contrast, the reaction of CO_2 and H_2 on ZnO/SiO_2 catalyst only resulted in the formation of zinc formate species: no methanol was detected. The interaction of CO_2 and H_2 with $Cu/ZnO/SiO_2$ catalyst gave formate species on both copper and zinc oxide. Methanol was again formed by the hydrogenation of copper formate species. Steady-state concentrations of copper formate existed under actual industrial reaction conditions, and copper formate is the pivotal intermediate for methanol synthesis. Collation of these results with previous data on copper-based methanol synthesis catalysts allowed the formulation of a reaction mechanism.

Keywords: Surface FT-IR; methanol synthesis; copper catalysts

1. Introduction

The mechanism of methanol synthesis from a $CO/CO_2/H_2$ feedstock over copper-based catalysts has been the subject of much controversy for several years [1,2]. It is generally agreed that a linear relationship exists between copper metal surface area and methanol synthesis activity, for CO_2 containing mixtures [3-5]. In apparent contrast to the results of Chinchen et al. [3], Burch and co-workers [6-8] argued that the nature of the support oxide present could have a significant effect on the catalytic activity. Isotopic labelling experiments [9,10] produced evidence that methanol was made almost exclusively from the carbon dioxide component of the feedstock. Furthermore Bowker et al. [11] demonstrated that the coadsorption of hydrogen and carbon dioxide on copper resulted in the formation of formate species, which were concluded to be the pivotal intermediate for methanol synthesis. However, recently Burch et al. [12] have suggested that under typical methanol synthesis conditions (503 K, 5–10 MPa) formate species may not actually be involved in the synthesis mechanism.

To try and resolve this dichotomy the interaction of CO_2/H_2 mixtures with Cu/SiO_2, ZnO/SiO_2 and $Cu/ZnO/SiO_2$ catalysts at 503 K and 10 MPa was studied using in situ FT-IR spectroscopy.

2. Experimental

The preparation of $Cu/ZnO/SiO_2$ catalysts has been described elsewhere [13]. Briefly, silica (Cab-O-Sil M5, 200 m^2 g^{-1}) was co-impregnated with an aqueous solution containing copper(II) acetate monohydrate (BDH AnalaR grade) and zinc(II) acetate (BDH AnalaR grade). Following drying in air at 383 K for 5 h the catalyst was pressed into a self-supporting disc. Subsequently the catalyst was calcined in oxygen (50 cm^3 min^{-1}) at 623 K for 1 h, and then reduced in hydrogen at 623 K for 18 h. The reduced catalyst which contained 5 wt% Cu and a quantity of ZnO equivalent to 29 mol% of the copper loading, was then evacuated at 623 K for 30 min. Cu/SiO_2 and ZnO/SiO_2 catalysts were prepared in an analogous manner to the $Cu/ZnO/SiO_2$ catalyst, the only difference being the omission of zinc(II) acetate and copper(II) acetate monohydrate, respectively, from the impregnating solution.

The stainless-steel high-pressure transmission infrared cell used in this investigation has been detailed elsewhere [14]. Spectra were recorded with a Perkin-Elmer 1750 FT-IR spectrometer, operating at 4 cm^{-1} resolution.

3. Results and discussion

A gaseous mixture of CO_2 (1 MPa) and H_2 (9 MPa) was exposed to a reduced Cu/SiO_2 catalyst at 503 K (figs. 1 and 2) in the sealed, high pressure infrared cell. The spectrum obtained after a contact time of 20 min (fig. 1a) clearly showed the growth of bands at 2935, 2856, 1551 and 1351 cm^{-1}, which are characteristic of an adsorbed copper formate species [15,16]. The remaining maximum at 1625 cm^{-1} was indicative of the presence of molecular water [17]. After a reaction time of 24 h (fig. 1b) peaks were discerned at 3016, 2959, 2933(sh), 2857, 1620, 1560 and 1351 cm^{-1}. The maxima at 2959, 2857 and 1460 cm^{-1} are very similar to bands detected as a consequence of methanol adsorp-

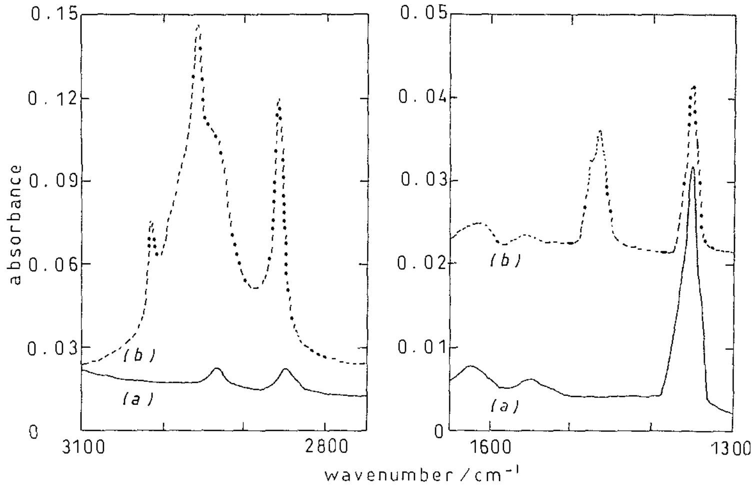


Fig. 1. The interaction of a CO_2 (1 MPa) : H_2 (9 MPa) mixture with a reduced Cu/SiO_2 catalyst at 503 K for (a) 12 min and (b) 24 h.

tion on silica [18]. As before bands at 2933(sh), 1560 and 1351 cm^{-1} are assigned to bridging formate on copper [15]. The remaining peak at 3016 cm^{-1} can be ascribed to the presence of a small quantity of gaseous methane [19]. The identification of methane as a minor reaction product was in agreement with the results of Bartley and Burch [6]. Upon extending the reaction time from 24 to 72 h (fig. 2) all bands due to methanol and methane increased in intensity. The absorbance of the maximum at 1351 cm^{-1} typical of bridging copper formate

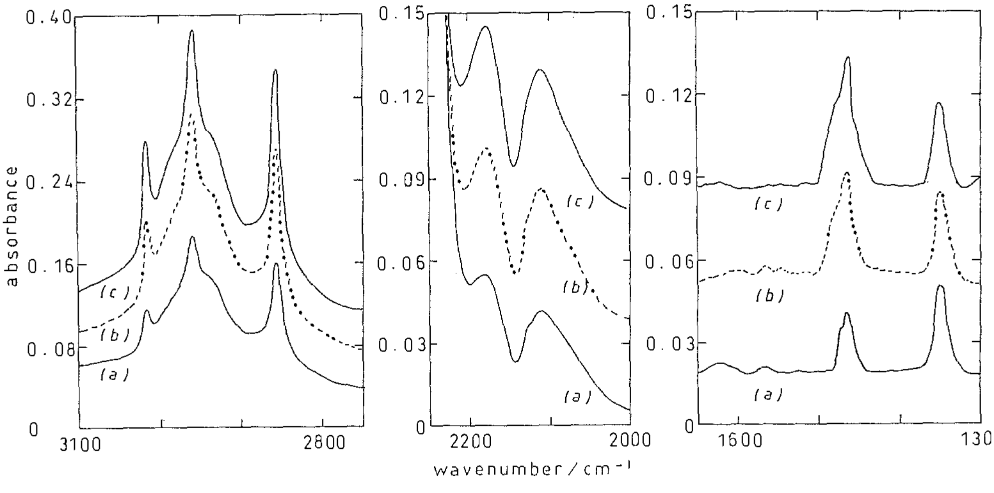


Fig. 2. The interaction of a CO_2 (1 MPa) : H_2 (9 MPa) mixture with a reduced Cu/SiO_2 catalyst at 503 K for (a) 24 h, (b) 48 h and (c) 72 h.

did not change, indicating that a steady state concentration of copper formate was present. The detection of broad bands at 2180 and 2113 cm^{-1} attributed to gas-phase carbon monoxide demonstrated that the reverse water–gas shift reaction had occurred. The shoulder at 2126 cm^{-1} can be assigned to linear CO adsorption on oxidised copper sites [20]. In addition, upon opening the infrared cell following the reaction, the pungent aroma of formaldehyde was noted. The involvement of formaldehyde in the synthesis mechanism has already been deduced from methanol and formaldehyde adsorption studies on Cu/SiO_2 catalysts [18,21].

From this investigation we can conclude the following:

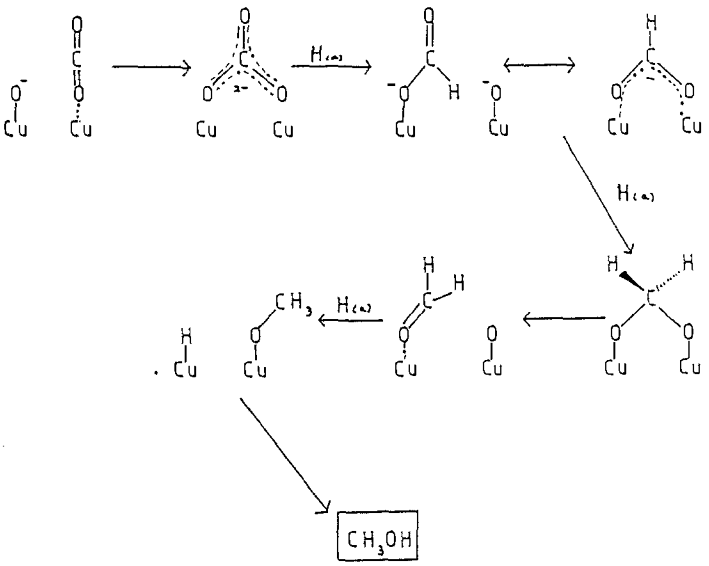
(1) Bridging copper formate was formed initially before methanol production occurred, suggesting that copper formate species were the precursor to methanol.

(2) Under typical industrial operating conditions, a significant steady state concentration of copper formate was present.

(3) Methoxy species were not detected on the copper component suggesting that copper formate was indeed the pivotal intermediate for methanol synthesis. Moreover it would appear that the rate determining step for methanol synthesis was the hydrogenation of copper formate.

(4) Under reaction conditions the copper is covered to an unspecified extent with oxygen atoms.

Collation of these results obtained under high pressure and temperature conditions with previous studies of CO_2 hydrogenation [22] and formaldehyde and methanol oxidation on Cu/SiO_2 catalysts allowed the following reaction mechanism for methanol synthesis on copper to be formulated:



The main features of this mechanism are:

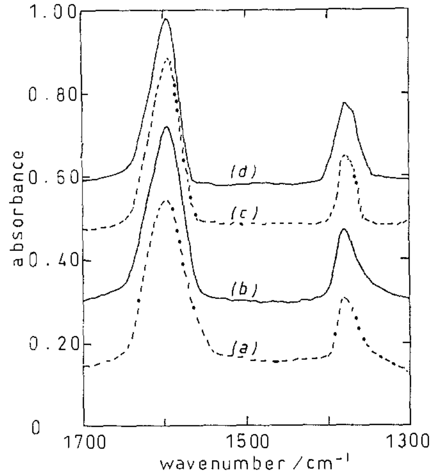


Fig. 3. The interaction of a CO_2 (1 MPa) : H_2 (9 MPa) mixture with a ZnO/SiO_2 catalyst at 503 K for (a) 1 h, (b) 24 h, (c) 48 h and (d) 72 h.

(1) Adsorbed oxygen acted as a promoter for CO_2 adsorption to form symmetrical carbonate ions. A critical aspect of CO_2 adsorption was the requirement for an active site composed of Cu^+ and Cu^0 species.

(2) Carbonate ions were hydrogenated to copper formate species which were the longest lived intermediates for methanol synthesis.

(3) Hydrogenation of copper formate to methanol via dioxymethylene and formaldehyde resulted in the production of an additional surface oxygen species, as consistent with the overall stoichiometry of the methanol synthesis reaction,

$$CO_2 + 2\,H_2 \rightleftharpoons CH_3OH + O.$$

Consequently the role of CO in a $CO/CO_2/H_2$ feedstock is envisaged to be to keep the catalyst surface in the partially reduced state required for carbonate formation.

3.1. INTERACTION OF CO_2/H_2 WITH ZnO/SiO_2 AT 503 K AND 10 MPa

A gaseous mixture of CO_2 (1 MPa) and H_2 (9 MPa) was exposed to a ZnO/SiO_2 catalyst, which had undergone the same calcination and reduction procedure as the Cu/SiO_2 catalyst, at 503 K (fig. 3). The only maxima detected during the reaction period were at 1597, 1381 and 1371 cm^{-1} which are ascribed to zinc formate species [23,24]. No methanol was produced on ZnO/SiO_2 under the conditions employed in this study.

3.2. INTERACTION OF CO_2/H_2 WITH $Cu/ZnO/SiO_2$ AT 503 K AND 10 MPa

A gaseous mixture of CO_2 (1 MPa) and H_2 (9 MPa) was exposed to a reduced $Cu/ZnO/SiO_2$ catalyst at 503 K (fig. 4). Initially (fig. 4a) bands due to zinc

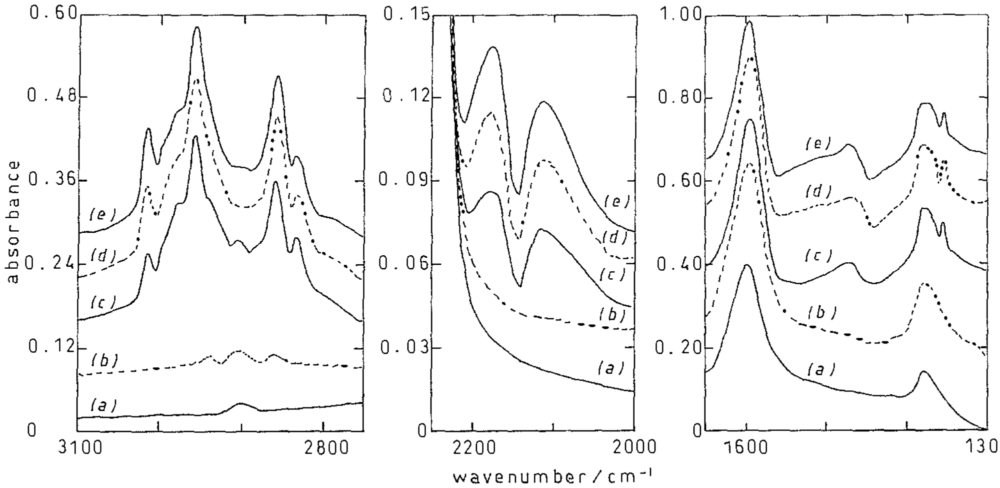


Fig. 4. The interaction of a CO_2 (1 MPa):H_2 (9 MPa) mixture with a reduced $Cu/ZnO/SiO_2$ catalyst at 503 K for (a) 1 h, (b) 3 h, (c) 24 h, (d) 48 h and (e) 72 h.

formate appeared at 2900, 1595 and 1383 cm^{-1}. As time elapsed (fig. 4b) maxima developed at 2935 and 2856 cm^{-1} which were characteristic of copper formate. After 24 h (fig. 4c) bands were detected at 2958, 2858 and 1468 cm^{-1} indicative of methanol adsorbed on silica [18]. Peaks at 2937(sh) and 1355 cm^{-1} due to copper formate were also present in addition to maxima at 1595 and 1383 cm^{-1} ascribed to formate species associated with zinc oxide. A peak at 3015 cm^{-1} was due to gaseous methane. Broad bands at 2175 and 2117 cm^{-1} were typical of gas-phase carbon monoxide. Finally a band at 2834 cm^{-1} can be assigned to methoxy groups on zinc oxide [25]. This was probably produced as a consequence of readsorption of methanol on to zinc oxide. Extending the reaction time caused an increase in all of the bands associated with methanol, carbon monoxide and methane. However, maxima assigned to formate species on copper and zinc oxide did not change appreciably.

The behaviour of CO_2 hydrogenation on $Cu/ZnO/SiO_2$ appeared to be qualitatively similar to the additive effects of Cu/SiO_2 and ZnO/SiO_2 catalysts. Again methanol was not formed until copper formate species had been produced. Furthermore a steady state concentration of copper formate was detected under typical industrial reaction conditions.

In conclusion the present results are consistent with the proposal that copper formate species are the pivotal intermediate for methanol synthesis and that the rate determining step will be the hydrogenation of these formate structures.

References

[1] K. Klier, Adv. Catal. 31 (1982) 243.
[2] J.C.J. Bart and R.P.A. Sneeden, Catal. Today 2 (1987) 1.

[3] G.C. Chinchen, K.C. Waugh and D.A. Whan, Appl. Catal. 25 (1986) 101.
[4] W.X. Pan, R. Cao, D.L. Roberts and G.L. Griffin, J. Catal. 114 (1988) 440.
[5] R. Burch, S.E. Golunski and M.S. Spencer, Catal. Lett. 5 (1990) 55.
[6] G.J.J. Bartley and R. Burch, Appl. Catal. 43 (1988) 141.
[7] R. Burch, R.J. Chappell and S.E. Golunski, J. Chem. Soc. Faraday Trans. I 85 (1989) 3569.
[8] R. Burch, S.E. Golunski and M.S. Spencer, J. Chem. Soc. Faraday Trans. 86 (1990) 2683.
[9] G.C. Chinchen, P.J. Denny, D.G. Parker, G.D. Short, M.S. Spencer, K.C. Waugh and D.A. Whan, Prepr. Am. Chem. Soc. Div. Fuel Chem. 29 (1984) 178.
[10] G.C. Chinchen, P.J. Denny, D.G. Parker and M.S. Spencer, Appl. Catal. 30 (1987) 333.
[11] M. Bowker, R.A. Hadden, H. Houghton, J.N.K. Hyland and K.C. Waugh, J. Catal. 109 (1988) 263.
[12] R. Burch, S. Chalker and J. Pritchard, J. Chem. Soc. Faraday Trans. 87 (1991) 1791.
[13] G.J. Millar, C.H. Rochester and K.C. Waugh, J. Chem. Soc. Faraday Trans., in press.
[14] J.A. Anderson, M.W. McQuire, C.H. Rochester and T. Sweeney, Catal. Today 9 (1991) 23.
[15] G.J. Millar, C.H. Rochester and K.C. Waugh, J. Chem. Soc. Faraday Trans. 87 (1991) 1491.
[16] B.E. Hayden, K. Prince, D.P. Woodruff and A.M. Bradshaw, Surf. Sci. 133 (1983) 589.
[17] R.K. Iler, *The Chemistry of Silica* (Wiley, New York, 1979).
[18] G.J. Millar, C.H. Rochester and K.C. Waugh, J. Chem. Soc. Faraday Trans. 87 (1991) 2795.
[19] M.W. McQuire, C.H. Rochester and J.A. Anderson, J. Chem. Soc. Faraday Trans. 87 (1991) 1921.
[20] G.J. Millar, C.H. Rochester and K.C. Waugh, J. Chem. Soc. Faraday Trans. 87 (1991) 1467.
[21] G.J. Millar, C.H. Rochester and K.C. Waugh, J. Chem. Soc. Faraday Trans. 87 (1991) 2785.
[22] G.J. Millar, C.H. Rochester, C. Howe and K.C. Waugh, J. Mol. Phys., in press.
[23] D.L. Roberts and G.L. Griffin, J. Catal. 95 (1985) 617.
[24] C. Chauvin, J. Saussey, J.C. Lavalley, H. Idriss, J.P. Hindermann, A. Kiennemann, P. Chaumette and P. Courty, J. Catal. 121 (1990) 56.
[25] A. Ueno, T. Onishi and K. Tamaru, Trans. Faraday Soc. 67 (1971) 3585.