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THE ADSORPTION AND DECOMPOSITION OF CARBON DIOXIDE ON POLYCRYSTALLINE COPPER

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The interaction of carbon dioxide with polycrystalline copper has been studied by radiolabelling techniques using {14-C} carbon dioxide, and by temperature programmed desorption. It is shown *inter alia*, that: carbon dioxide is weakly adsorbed at the clean surface; that this acts as precursor which, on activation, produces adsorbed carbon monoxide and surface oxygen; and that this oxidised copper surface then adsorbs carbon dioxide more strongly yielding a state which can be hydrogenated first to formate, and thereafter to methanol.

Recent results have shown that in the synthesis of methanol from carbon monoxide/carbon dioxide/hydrogen mixtures over copper/zinc oxide/alumina catalysts the immediate precursor to methanol is the carbon dioxide molecule of the reactant mixture [1,2]. It has also been shown [3] that it is the copper component of the catalyst which effects this reaction and that the pivotal intermediate in the synthesis is a formate, produced on the surface of the copper by the interaction of adsorbed hydrogen and carbon dioxide [4]. Copper has also been shown to be active in the forward and reverse shift reactions (reactions (1) and (− 1) respectively).

$$CO + H_2O \underset{-1}{\overset{1}{\rightleftarrows}} CO_2 + H_2 \qquad (1)$$

so that it becomes clear that an understanding of the nature of the chemisorption of carbon dioxide on copper is relevant to two industrially important catalytic reactions.

In spite of this some considerable confusion still exists in the literature as to the exact nature of the interaction of carbon dioxide with copper metal surfaces. Collins and Trapnell [5] found no adsorption of carbon dioxide on evaporated copper films while, more recently, Habraken et al. [6], using a combination of AES, LEED and ellipsometry, could find no interaction of carbon dioxide with a

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Cu(111) single crystal. From UPS and XPS analyses, Norton and Tapping [7] proposed that carbon dioxide was 'almost certainly' physically adsorbed on copper and, subsequently, the existence of a weakly adsorbed state of carbon dioxide on polycrystalline copper (ΔHads = 18 kJmol^{-1}) has been confirmed by gas adsorption chromatography [2].

In stark contrast to the accumulated evidence from these studies, Wachs and Madix [8] determined that 99% of the carbon dioxide adsorbed on a Cu(110) single crystal, at −93° C, dissociated to form carbon monoxide and a surface oxygen species. The formation of carbon monoxide by the interaction of carbon dioxide with copper/zinc oxide catalysts is further evidence that a route exists by which carbon dioxide may dissociate on metallic copper surfaces [9,10,11].

This paper describes the adsorption and reaction of carbon dioxide on unsupported polycrystalline copper powders in order to determine the characteristic features of the decomposition reaction. Further, the role which adsorbed oxygen, produced by carbon dioxide dissociation, plays in modifying the nature and extent of subsequent molecular carbon dioxide adsorption is also detailed.

Two completely different, but complementary, experimental techniques have been used. The adsorption of {14-C} carbon dioxide, on polycrystalline copper, at ambient temperature and low pressures ($<$ 10 torr), was monitored, *in situ*, using previously described experimental methods [12]. A flow microreactor system, as described elsewhere [13], allowed carbon dioxide to contact the copper surface over a wide range of temperatures (−60° C–225° C). This interaction could then be examined by temperature programmed desorption (T.P.D.). Both experimental systems allowed *in situ* determination of copper metal surface areas by nitrous oxide decomposition [13].

The unsupported copper surfaces were prepared by reducing AnalaR cupric oxide (B.D.H.) in a hydrogen/nitrogen or hydrogen/helium flow (6% hydrogen; 1 atm; 25 cm^3 min^{-1}) at a temperature of 240° C. The surfaces prepared in the flow system were further 'scrubbed' of oxygen by treatment in a 6% carbon monoxide/helium flow at 200° C. Any hydrogen, or carbon monoxide, which had become adsorbed on the copper surface during the reduction treatment, was removed by prolonged heating in a stream of helium. The surface area of the reduced powder was ~ 3 m^2 (g Cu)$^{-1}$.

Figure 1 shows an isotherm produced by the adsorption of {14-C} carbon dioxide on polycrystalline copper (0.17 g). The surface count rate is directly proportional to the {14-C} carbon dioxide surface coverage, but does not readily permit an accurate calculation of the total coverage. However, by comparison with the extent of {14-C} carbon monoxide adsorption on a similar copper sample (fig. 1), which is expected to give a monolayer coverage of 1×10^{15} molecules cm^{-2} under the temperature and pressure conditions used, the total {14-C} carbon dioxide coverage is of the order of 5×10^{14} molecules cm^{-2}. This surface coverage cannot be ascribed to 'physical adsorption' but, rather, indicates substantial carbon dioxide *chemisorption* on the polycrystalline surface. Indeed,

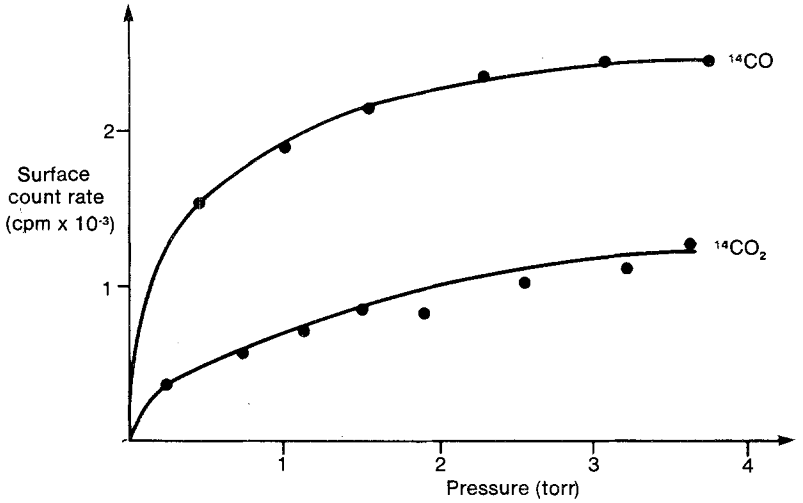

Fig. 1. The adsorption of $^{14}CO_2$ and ^{14}CO on 0.17 g of polycrystalline copper at 20 ° C.

on pumping it was found that only 80% of the adsorbed radiolabel could be removed from the copper surface. The residence time of the 20% (1×10^{14} molecules cm^{-2}) retained on the surface ($>$ 15 mins at 10^{-4} torr) allows a lower limit on the desorption activation energy to be calculated as ca. 90 kJ mol^{-1}, by substitution of this time into the Frenkel equation.

The nature of the strongly adsorbed radiolabel is clarified by reference to fig. 2. This shows the T.P.D. profile obtained subsequent to the interaction of a carbon dioxide/helium stream (10% carbon dioxide; 1 atm; 25 cm^3 min^{-1}) with polycrystalline copper, at 26 ° C, for a five minute period. Carbon monoxide was found to desorb from the copper surface in the temperature range 90 ° C–120 ° C, with an activation energy of desorption of ca. 100 kJ mol^{-1} (assuming a pre-exponential factor of 10^{13} sec^{-1}). The quantity of carbon monoxide evolved

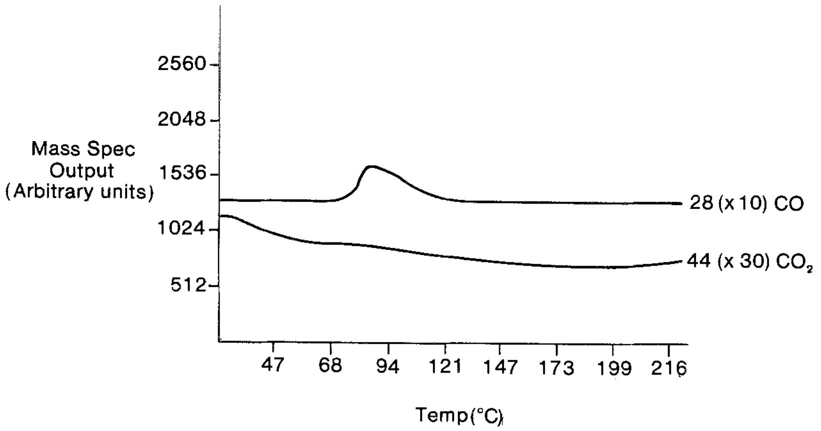

Fig. 2. T.P.D. following CO_2 adsorption on copper at 26 ° C (5 mins).

Table 1
Extent of CO_2 decomposition on polycrystalline copper

Temp (° C)	Time of contact (mins)	% CO monolayer
225	10	18
26	5	9
26	65	25
−60	15	13

from the surface must be considered to represent a lower limit on the total coverage since desorption would be expected to occur, at a finite rate, when the copper sample was swept out with helium for 15 minutes before temperature programming. The true carbon monoxide coverage was therefore obtained by determining the total oxygen coverage on the copper surface (by reaction with carbon monoxide at 200° C) and back-calculating the associated carbon monoxide surface coverage. After five minutes reaction with carbon dioxide at 26° C, the coverage was found to be 9% of a carbon monoxide monolayer (0.9×10^{14} molecules cm^{-2}). After 65 minutes, at the same temperature, 25% of a carbon monoxide monolayer was observed on the copper surface (table 1 and fig. 3).

This time-dependency of the amount of decomposition of the carbon dioxide at constant temperature indicates that a significant activation energy is associated with the reaction. However, the results presented in table 1 also reveal that, surprisingly, the decomposition reaction is enhanced under low temperature conditions. It is therefore possible that the decomposition mechanism involves a precursor pathway. It should be noted that, at −60° C, the dosing conditions used (10% carbon dioxide, 1 atm, 25 cm^3 min^{-1}) would produce a surface coverage of 13% of a monolayer of carbon dioxide on the copper of the state whose heat of adsorption has been determined to be 18 kJ mol^{-2} [2].

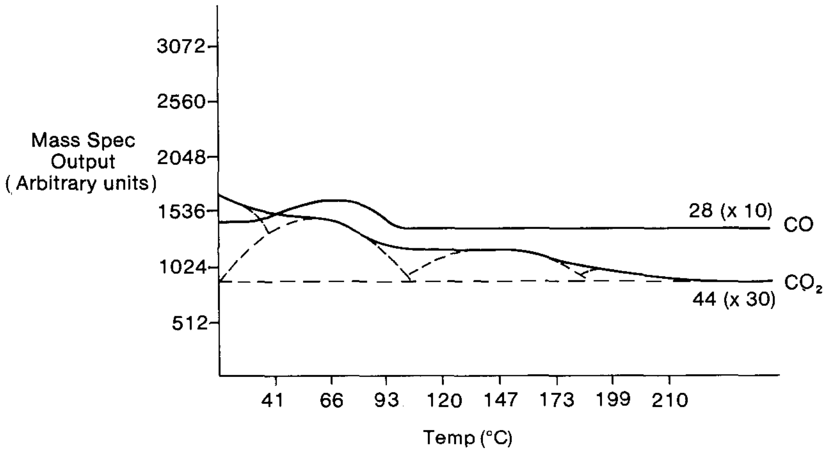

Fig. 3. T.P.D. following CO_2 adsorption on copper at 26° C (65 mins).

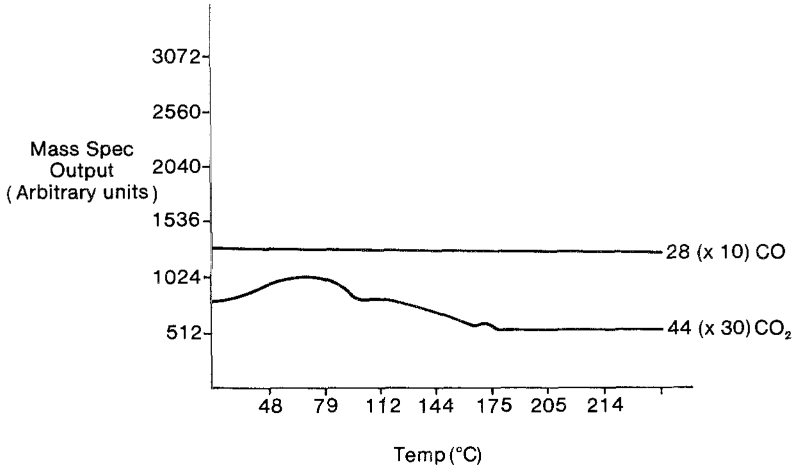

Fig. 4. T.P.D. following CO_2 adsorption on fully oxidised copper.

Comparison of figs. 2 and 3 shows that the extent of molecular carbon dioxide chemisorption is clearly a time dependent process. A broad range of desorption states are evident but, as is shown in fig. 3, this profile is probably the convolution of four distinct adsorbed states (E(des) = 83, 102, 117 and 128 kJ mol^{-1} by solution of the Redhead equation [14] at the peak maximum temperature, assuming a pre-exponential term of 10^{13}s^{-1}). This profile is similar in nature to that produced on contact of carbon dioxide with a fully oxidised copper surface (fig. 4) and it is therefore concluded that the strongly adsorbed, molecular carbon dioxide species are associated with the adsorbed oxygen produced by carbon dioxide dissociation.

While the T.P.D. analyses allow description of the chemical nature of strongly chemisorbed material, radiotracer adsorption studies revealed that this material accounts for only 20% of the "carbon dioxide-generated" adsorbates at ambient temperature. The bulk of the *molecular* carbon dioxide adsorbates, accounting for 80% of the carbon dioxide adsorption process, are unlikely to be associated with metallic copper (cf. refs. [2,5,6] and [7]). They must, therefore, be relatively weakly bound species adsorbed on an oxidised copper surface. Evidence for this is found in fig. 5, which demonstrates the presence of molecularly bound carbon dioxide whose heat of adsorption only allows detection in a sub-ambient T.P.D. analysis. The heat of adsorption derived from this (< 70 kJ mol^{-1}) is consistent with the establishment of substantial carbon dioxide coverages at ambient temperature.

These results show that the interaction of carbon dioxide with copper is extremely complicated. The initial interaction is via a weakly held state ($\Delta H = 18$ kJ mole^{-1}) which acts as a precursor to dissociation. The catalytic importance of this dissociation is that it demonstrates unequivocally that the reverse shift reaction is a sequential process, the initial step of which is decomposition of the

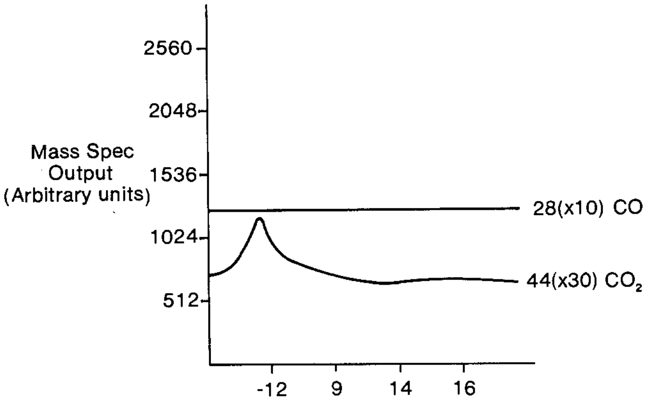

Fig. 5. T.P.D. following CO_2 adsorption on copper at −60 °C (15 mins).

carbon dioxide on the copper surface to give adsorbed carbon monoxide and a surface oxygen species, the latter then being scavenged by the hydrogen in the gas phase. It does not therefore proceed via the formate intermediate as has been suggested [15,16,17].

The equilibria which are involved in the forward and reverse shift reactions are shown in reversible reactions (2) and (3), of which the decomposition of water on copper, although surprising, has already been reported [2], the even more surprising result of the decomposition of carbon dioxide on copper (reaction (2)) now having been shown.

$$CO + O_{(s)} \rightleftarrows CO_2 + Cu \tag{2}$$

$$H_2O + Cu \rightleftarrows H_2 + O_{(s)}. \tag{3}$$

The partially oxidised copper surface produced by the decomposition of the carbon dioxide adsorbs carbon dioxide stronger ($\Delta H \sim 80$ to 128 kJ mol^{-1}) giving rise to a long lived molecular state which is probably the precursor to methanol by its being hydrogenated to formate and thence to methanol.

References

[1] G.C. Chinchen, P.J. Denny, D.G. Parker, G.D. Short, M.S. Spencer, K.C. Waugh and D.A. Whan, Am. Chem. Soc. Div. Fuel Chem. 29 (1984) 178.

[2] G.C. Chinchen, M.S. Spencer, K.C. Waugh and D.A. Whan, J. Chem. Soc. Farad. Trans. (1) 83 (1987) 2193.

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

[4] M. Bowker, R.A. Hadden, H. Houghton, J.N.K. Hyland and K.C. Waugh, J. Catal. 109 (1988) in press.

[5] A.C. Collins and B.M.W. Trapnell, Trans. Farad. Soc. 53 (1957) 1476.

[6] F.H.P.M. Habraken, E. Kieffer and G.A. Bootsma, Surface Sci. 83 (1979) 45.
[7] P.R. Norton and R.L. Tapping, Chem. Phys. Lett. 38 (1976) 207.
[8] I.E. Wachs and R.J. Madix, J. Catal. 53 (1978) 208.
[9] K. Kleir, Adv. in Catal. 31 (1982) 243.
[10] G.C. Chinchen, C. Plant, M.S. Spencer and D.A. Whan, Surface Sci. 184 (1987) 370.
[11] G.C. Chinchen, S. Kinnaird and G. Webb, J. Chem. Soc. Farad. Trans. (1), in press.
[12] D. Cormack, S.J. Thomson and G. Webb, J. Catal. 5 (1966) 224.
[13] G.C. Chinchen, C.M. Hay, H.D. Vandervell and K.C. Waugh, J. Catal. 103 (1987) 79.
[14] P.A. Redhead, Trans. Farad. Soc. 57 (1961) 641.
[15] T. Tagawa, G. Pleizer and Y. Amenomiya, Appl. Catal. 18 (1985) 285.
[16] Y. Amenomiya and T. Tagawa, 8th Int. Congr. Catal., Vol. II (1984) p. 557.
[17] T. van Herwijnen and W.A. de Jong, J. Catal. 63 (1980) 83.