Adsorption and reaction induced morphological changes of the copper surface of a methanol synthesis catalyst

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The morphology (surface structure) of the copper component of an industrial $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst has been studied by carbon monoxide temperature programmed desorption (CO TPD). The initial state morphology produced by hydrogen reduction at 513 K showed evidence of the existence of Cu(111), Cu(110) and Cu(211) surfaces. Surface oxidation of the copper by CO_2 decomposition at 213 K followed by CO reduction at 473 K did not reproduce the initial state morphology, most of the Cu(110) surface being lost; at the same time there was a six-fold increase in the surface population of the (211) face. This new surface produced by CO_2 decomposition at 213 K and CO reduction at 473 K was considerably less active in its ability to decompose CO_2 at 213 K. Treatment of it with hydrogen at 513 K for 16 h caused the surface to reconstruct almost completely to its original state, with the Cu(110) face reappearing and the Cu(211) face being reduced in population to roughly its original value. The ability of the copper to decompose CO_2 was proportionately restored. It is evident that in the synthesis of methanol using $CO/CO_2/H_2$ mixtures over $Cu/ZnO/Al_2O_3$ catalysts, the morphology of the surface of the copper will be in a continuous state of restructuring, which, depending on the conditions, has the potential to result in chaotic behaviour.

Keywords: morphology, copper, methanol synthesis

1. Introduction

Photo-emission electron microscopy (PEEM) has shown the surface of a platinum single crystal (e.g. Pt(110)) to be in a state of continuous fluxional reconstruction during the oxidation of carbon monoxide [1]. This fluxional reconstruction has been termed "self-organised" since large areas of the surface ($\sim 10^5$ Å^2) are either in the form produced by CO adsorption or are oxygen covered. These vast areas of the surface have been shown to interchange at second intervals, these interchanges being accompanied by oscillations in the rate of production of CO_2 [1]. Should it be general, the implications of this observation for our understanding of the mechanisms of catalytic reactions are far-reaching and considerable. Static chequer board models of surfaces with ball and stick models of intermediates and adsorbates will have to be re-defined, while cherished concepts, such as structure sensitivity, will have to be re-examined.

Indeed the phenomenon of adsorbate and reaction induced reconstruction has been shown to be prevalent and, importantly, reactively significant. Scanning tunnelling microscopy has shown that Cu(110) is reconstructed by oxygen at room temperature forming a (2×1) OCu(110) overlayer [2,3]. We have also shown that the oxygen deposited on the surface of the Cu component of $Cu/ZnO/Al_2O_3$ (60 : 30 : 10) methanol synthesis catalyst by CO_2 decomposition causes an activated reconstruction of the Cu(110) surface to the Cu(211) surface and a concomitant loss of CO_2 decompositional activity. Reduction of the copper by CO at 473 K does not reproduce the original state [4].

The purpose of this paper is to define the morphology of the Cu surface of the $Cu/ZnO/Al_2O_3$ catalyst, after well defined pre-treatments, namely:

(i) at the outset, i.e. after H_2 reduction,

(ii) after CO_2 decomposition at 213 K and re-reduction by CO at 473 K, and

(iii) after CO_2 decomposition and H_2 re-reduction.

The intention also is to investigate the nature of the driving force of the morphological change and to determine whether the morphological change produced by reaction can be reversed. The technique to be used for determining the morphology of the Cu component of the catalyst, before and after reaction, is CO temperature programmed desorption (TPD), having first adsorbed the CO from a CO/He stream (10% CO, 1 bar, 25 cm^3 min^{-1}) at 77 K. Chemisorption of CO on a $Cu/ZnO/Al_2O_3$ catalyst has been shown to be specific to the Cu component [5]. Its bond strength to the copper is known to be structure sensitive [6] and so the CO TPD spectrum will, therefore, be a fingerprint of the morphology of the Cu as a result of well defined pre-treatments.

Identification of the crystal faces extant of the surface of the copper component of the polycrystalline catalyst will be made by comparison of the CO desorption peak maximum temperatures obtained by TPD from the polycrystalline catalyst with those obtained by TPD of CO from well defined single crystal copper surfaces.

Justification of the validity of the method will be given in section 3.

2. Experimental

The apparatus. The multipurpose tubular microreactor used in these experiments has been described in detail previously [7]. It is a single tube reactor (20 cm long, 0.4 cm wide) connected via a heated capillary to a mass spectrometer (Hiden, Warrington, England) which is capable of following 16 masses with temperature or time.

The gases. The gases CO/He (10% CO), CO_2/He (10% CO_2) and H_2/He (5%) were all 99.995% pure and were used direct from the cylinder.

The catalyst. The catalyst was a typical commercial $Cu/ZnO/Al_2O_3$ (60 : 30 : 10) methanol synthesis catalyst which was supplied by ICI Katalco. Its surface area was found to be 68 $m^2\ g^{-1}$ by N_2 adsorption at 77 K and its copper metal area was determined to be 29.8 $m^2\ g^{-1}$ by nitrous oxide reactive frontal chromatography [7].

3. Results and discussion

This section must be prefaced with the observation that carbon monoxide has been shown to chemisorb on the copper component only of copper/zinc oxide/alumina catalysts [5]. Single crystal studies have shown the strength of bonding of carbon monoxide to copper to be structure sensitive and so a carbon monoxide desorption spectrum from polycrystalline copper should be a fingerprint of the type and of the surface population of the crystal faces extant on the surface of the copper component of the catalyst as a result of specified pre-treatments.

This is a valid basis of identification of the morphology of the surface of the polycrystalline copper even though the lower heating rates required for powdered catalysts (5 K min^{-1} for powdered catalysts compared with 5 K s^{-1} for single crystals) and the possibility of re-adsorption within the catalyst plug or within the catalyst pore might suggest that, in a temperature programmed desorption experiment, there would be a significant difference in the peak maximum temperatures of CO desorbing from the (111) face, say, of single crystal copper and from the same face of copper in a powdered catalyst.

The difference in the values of the peak maxima deriving from the different heating rates can be obtained by solution of the Redhead equation (eq. (1)) for values of the heating rate, β, of 0.08 K s^{-1} and 5 K s^{-1} [8],

$$\frac{E_d}{RT_m^2} = \frac{A}{\beta} e^{-E_d/RT_m},$$

where E_d is the desorption activation energy (kcal mol^{-1}), T_m is the peak maximum temperature (K), R is the gas constant (cal $K^{-1}\ mol^{-1}$), A is the desorption pre-exponential term (s^{-1}) (a value of $10^{13}\ s^{-1}$ is assumed for this term).

For a peak maximum temperature of 180 K for the single crystal experiment ($\beta = 5$ K s^{-1}, CO from Cu(110) [9]), the peak maximum temperature for the desorption of CO from the same crystal face of copper in powdered ($\beta = 5$ K min^{-1}) catalysts would be 8 K lower.

Re-adsorption within the catalyst itself or within the catalyst plug will contribute only minimally to a raising of the peak maximum temperature. That this is the case is evident by solution of the Redhead equation at a given value of β, which produces a linear relationship between the desorption activation energy, E_d, and the peak maximum temperature, T_m. The term E_d/RT_m is therefore constant and so too, then is the desorption half-life. Its value is 18 s. This is the maximum residence time that an adsorbate will spend on the surface at temperatures equal to, or above, the desorption peak maximum. Re-adsorption, therefore, will contribute negligibly to a delay in the adsorbate reaching the detector.

The peak maximum temperature of an adsorbate desorbing from the same crystal face of copper, be it in the form of a single crystal or a catalyst, should be roughly (± 5 K) the same. The temperatures of the desorption peak maxima obtained from single crystal experiments can therefore be used as a valid means of identifying which crystal faces are exposed on the surface of a polycrystalline sample of the same material. Indeed, Ertl and co-workers used their observation of the identity of the desorption peak maxima of nitrogen from potassium doped Fe(111) and from an industrial ammonia synthesis catalyst ($Fe/K/Al_2O_3$) to interpret the role of potassium as a promoter in the catalyst [10]. The technique is of general applicability.

The following sequence of experiments was carried out to study the morphological changes of the copper component of a $Cu/ZnO/Al_2O_3$ catalyst induced by carbon dioxide decomposition.

(i) Initial state morphology produced by hydrogen reduction and desorption

The catalyst (0.5 g) was reduced in a hydrogen/helium stream (5% H_2, 1 bar, 25 cm^3/min), by raising the temperature from ambient to 513 K at 1 K min^{-1} and holding the temperature at 513 K for 16 h under the hydrogen/helium flow. The temperature was then lowered to 77 K under the hydrogen/helium stream. The flow was then switched to helium (25 cm^3/min, 1 bar) and the adsorbed hydrogen removed by temperature programming, at a heating rate of 5 K min^{-1}, from 77 to 513 K under the helium stream. (Lowering the temperature from 513 to 77 K under the helium and temperature programming again from the lower temperature to 513 K produced no further hydrogen desorption.)

The temperature was again lowered to 77 K under

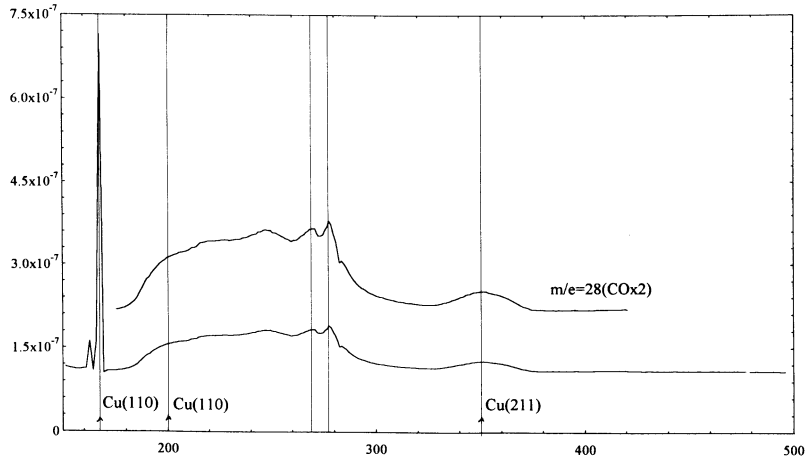

Figure 1. The initial state morphology of the copper component of the $Cu/ZnO/Al_2O_3$ catalyst (i.e. after H_2 reduction (5% H_2 in He, 1 bar, 25 cm^3 min^{-1}, 513 K, 16 h and temperature programmed desorption of the surface hydrogen) characterised by CO TPD. The verticals at 170 and 200 K inidicate the positions of the peak maxima of CO desorbing in a TPD experiment from Cu(110), the temperatures of these maxima having been adjusted from the single crystal heating rate of 5 K s^{-1} to the value used here, 5 K min^{-1}. The vertical at 345 K is assigned in this work to CO desorbing from Cu(211); those at 269 and 275 K are unassigned.

the helium stream and the carbon monoxide was dosed on to the catalyst by switching the flow from helium to a CO/He (10% CO, 1 bar, 25 cm^3 min^{-1}) stream. After breakthrough of the CO, the CO/He stream was passed for a further 5 min, and then switched again to helium, to sweep out all gaseous carbon monoxide ($\sim$ 20 min). The physisorbed and chemisorbed carbon monoxide was desorbed by temperature programming at a heating rate of 5 K min^{-1} from 77 to 513 K under the helium stream.

The CO desorption spectrum so obtained is shown in figure 1. The lower temperature physisorbed peak which dominates the spectrum and overlaps the Cu(111) peak at 145 K is removed for clarity. The positions of the CO peak maxima from Cu(110), recalculated on the basis of the lower heating rate used here, are indicated on the figure. The CO desorbing with a peak maximum temperature of 344 K is assigned to have derived from desorption from the (211) face of copper. This assignment is made on the basis of the identification, using DRIFTS, of the development of this face by adsorbed oxygen driven reconstruction of the Cu(110) face. A CO desorption peak maximum at this temperature was observed as the Cu(211) face developed [4].

Table 1 lists the clearly identifiable CO desorption peak maxima observed as a function of different pretreatments (figures 1, 4, 5 and 6) together with the amount of CO adsorbed on these states. The numerous peaks in the temperature range 230 to 250 K, are not resolved and so no attempt is made to deconvolute and integrate these. These numerous, but ill-defined states, could reside on the copper surface at the copper zinc oxide interface. The broad unassigned CO stretching frequency at 2058 cm^{-1} observed previously [11] could also have originated from CO adsorbed on these ill-defined states. Where there are clearly identifiable peaks, e.g. at 168 and 178 K, 200 to 220 K, 260 to 269 K, 275 and 345 K, they are integrated simply by dropping verticals at the obvious minima at either side of the maxima.

The initial state morphology determined by the CO TPD data presented here which excludes the Cu (111) face is of a surface comprising the Cu(110) face (12% of a monolayer) with a lesser amount of the Cu(211) face (2%

Table 1
Amount of carbon monoxide desorbed by temperature programmed desorption from figure 1

Figure	CO desorbed (molecule $\times 10^{18}$)				
	T_m = 169 and 178 K E_d = 11.4 [a] kcal mol^{-1} Cu(110)	T_m = 200–220 K E_d = 15.0 [a] kcal mol^{-1} Cu(110)	T_m = 260 and 269 K E_d = 17.8 kcal mol^{-1}	T_m = 275 K E_d = 18.0 [a] kcal mol^{-1}	T_m = 345 K E_d = 22.8 [a] kcal mol^{-1} Cu(211)
1	4.5	13.3	4.1	8.4	3
4	0	9.7	5.0	9.5	15
5	0	7.0	6.0	9.5	17
6	1.5	11.9	3.8	7.6	< 3.0

[a] Calculated from the peak maximum temperature for an assumed value of 10^{13} s^{-1} for the desorption pre-exponential. The total number of copper sites is approximately 1.5×10^{20}.

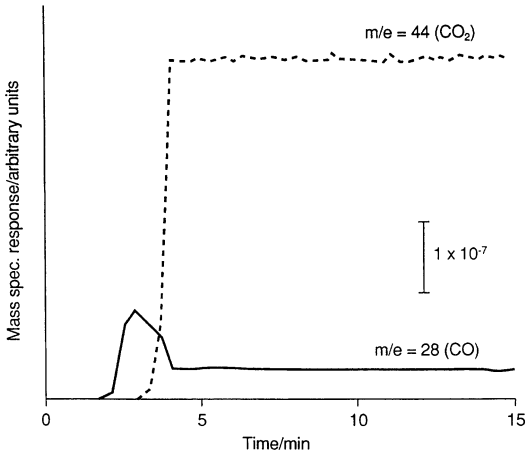

Figure 2. The reactive frontal chromatogram of CO_2 decomposition on the copper component of the $Cu/ZnO/Al_2O_3$ catalyst at 213 K.

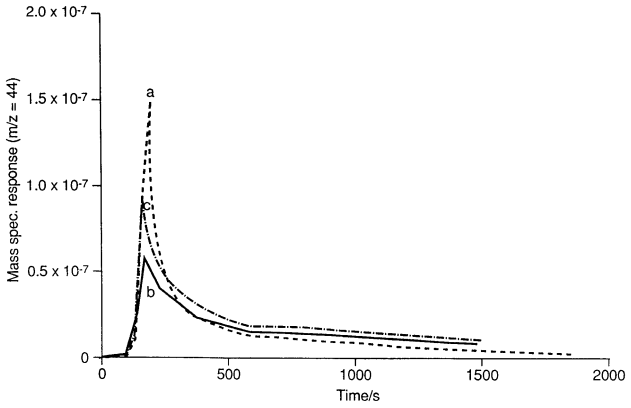

Figure 3. The time dependence of the rate of reduction by CO at 493 K of the surface oxidised copper component of the $Cu/ZnO/Al_2O_3$ catalyst: curve a, after the initial CO_2 decomposition at 213 K; curve b, after the second CO_2 decomposition at 213 K; curve c, after treatment in hydrogen (5% H_2 in He, 1 bar, 25 cm^3 min^{-1}, 513 K, 16 h) surface hydrogen desorption, by TPD, and CO_2 decomposition at 213 K.

of a monolayer). Surfaces producing CO desorption peak maxima of 260 and 275 K occupy 3 and 6% of the total copper area. This surface morphology of the copper is in marked contrast to that of the bulk which has been found by in situ X-ray diffraction to comprise only (111) and (200) phases [12].

(ii) CO_2-oxidation/CO-reduction induced morphology

The initial state morphology was changed by oxidising the copper component of the catalyst by decomposing CO_2 at 213 K. This was done by the technique of reactive frontal chromatography which has been described previously [7]. In this case, however, the flows were switched from helium to CO_2/He (10% CO_2, 1 bar, 25 cm^3 min^{-1}) at 213 K, following the $m/z = 44$ (CO_2) and 28 (CO) continuously on the mass spectrometer. (The reactive frontal chromatogram produced by this technique, shown in figure 2, bears a remarkable resemblance to that produced by N_2O decomposition at 333 K [7].) The chemisorbed CO_2 (bonded as a carbonate on both the Cu and ZnO) was desorbed by temperature programmed desorption in a helium stream, raising the temperature from 213 to 513 K at 5 K min^{-1}. The CO_2 surface oxidised copper was then reduced at 473 K in a CO/He stream (10% CO, 1 bar, 25 cm^3 min^{-1}), the time dependent production of CO_2 being shown in figure 3, curve a.

The morphology of the copper produced by this CO_2-oxidation/CO-reduction cycle was determined by re-adsorbing CO at 77 K by frontal chromatography and then desorbing the CO by temperature programming in a helium stream from 77 to 513 K. The CO desorption spectrum is shown in figure 4.

Figure 5 is the fingerprint of the morphology of the copper component of the catalyst after a repeat of CO_2-

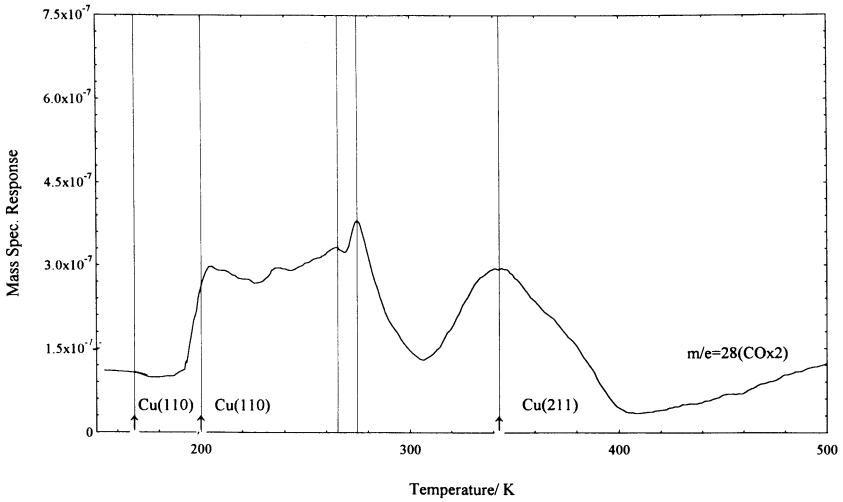

Figure 4. The morphology of the copper component of the $Cu/ZnO/Al_2O_3$ catalyst characterised by CO TPD, after the initial CO_2 decomposition at 213 K and CO reduction at 473 K of the resulting oxidised surface.

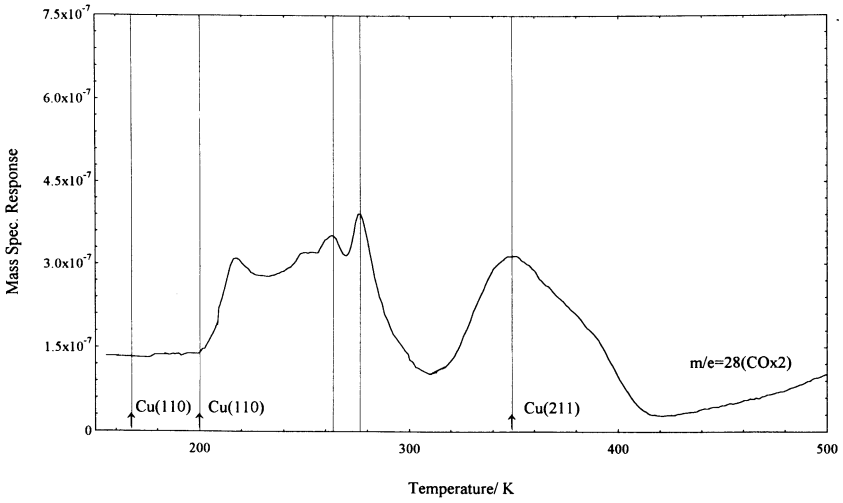

Figure 5. The morphology of the copper component of the $Cu/ZnO/Al_2O_3$ catalyst characterised by CO TPD after the second CO_2 decomposition at 213 K and CO reduction at 473 K of the resulting oxidised surface.

oxidation at 213 K/CO-reduction at 473 K described above, the time dependent reduction, by CO, of the CO_2 surface oxidised copper being shown in figure 3, curve b. As in figure 1, the verticals in figures 4 and 5 at 269 and 275 K are of unassigned CO desorption peak maxima.

Figure 4 shows that the CO_2-oxidation/CO-reduction cycles produce a surface which no longer desorbs CO with a peak maximum to temperature, T_m of 169 K, and a 38% reduction in the CO desorption peak maximum state of 200 K – first CO_2-oxidation/CO-reduction cycle. On the second CO_2-oxidation/CO-reduction cycle there is a further 28% reduction in the 200 K CO desorption peak state. The Cu(110) face associated with the 169 K state is completely lost and the population of the Cu(110) face associated with the 200 K state is halved. However, the 345 K state assigned to the Cu(211) face has undergone a five-fold increase in its population (table 1). Additionally, figures 4 and 5 and table 1 show that the loss in the surface area associated with the Cu(110) face is compensated by the increase in the area of the Cu(211) face. Cu(110) would therefore appear to have reconstructed to the Cu(211) face as had been concluded by our infrared studies [4].

The important conclusion to be made here is that the reconstructed copper surface produced by adsorbed oxygen from CO_2 decomposition does not relax back to its original morphology upon the removal of the adsorbed oxygen by reducing CO reduction at 473 K. Furthermore, since there is a good oxygen balance (within 10%, which is an indication of the experimental error) between the CO evolved by CO_2 decomposition and the CO_2 produced by CO reduction of the surface oxygen at 473 (table 2), the reconstructed surface is therefore not prevented from relaxing back to its original morphology by surface oxygen.

It can also be seen by comparison of curves a and b in figure 3 that the surface produced after CO reduction of the CO_2 oxidised copper (the surface which has largely lost the Cu(110) face, having replaced it by the Cu(211) face) is now considerably less active for the decomposition of CO_2. This confirms our previous finding that the Cu(110) face is active in the composition of CO_2 [4] in agreement with the work of Schneider and Hirschwald [9] but disagreeing with Fu and Somorjai [5] who found the Cu(110) face to be inactive in CO_2 decomposition.

Morphology produced by prolonged, high temperature treatment in hydrogen

Figure 6 is a carbon monoxide desorption spectrum exemplifying the morphology produced by treating the CO_2-oxidised/CO-reduced surface of figure 5 with hydrogen in an identical manner to that used to reduce the catalyst initially, i.e. by heating from ambient to

Table 2
The amount of oxygen atoms deposited on the copper (CO evolved) by CO_2 decomposition and the amount of oxygen removed by CO reduction at 473 K

	CO evolved (molecule $\times 10^{19}$)	CO_2-deposited surface oxygen measured by titration with CO at 473 K (atom $\times 10^{19}$)	Oxygen coverage/ monolayer
curve a	3.2	3.5	0.21
curve b	2.2	2.2	0.15
curve c	2.9	3.2	0.19

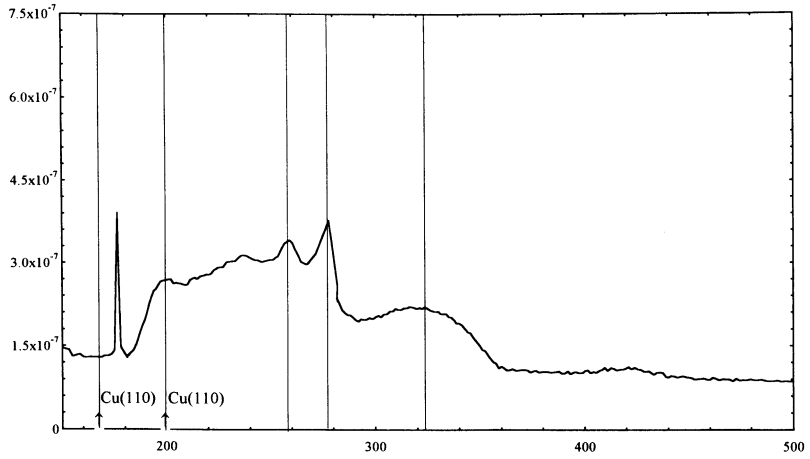

Figure 6. The morphology of the copper component of the $Cu/ZnO/Al_2O_3$ catalyst characterised by CO TPD after hydrogen treatment (5% H_2 in He, 1 bar, 25 cm^3 min^{-1}, 513 K, 16 h and desorption of the surface hydrogen by TPD in He).

513 K in a H_2/He stream (5% H_2, 1 bar, 25 cm^3 min^{-1}, 1 K min^{-1}) and holding the catalyst at 513 K under that stream for 16 h, finally desorbing the hydrogen by heating from 77 to 513 K in a helium stream. Table 1 shows that, to a large extent, the initial morphology is restored. Most dramatically the high temperature (345 K) CO desorption state assigned to the Cu(211) face is removed to a level lower than that found initially. The 200 K Cu(110) peak is restored almost completely and the 178 K Cu(110) surface is also restored but at a lower level ($\sim$ 30%) compared with that found initially. Additionally, the activity of the surface for the decomposition of CO_2 is now 90% of that found initially, 2.9×10^{19} molecules of CO now being produced from CO_2 decomposition compared with 3.2×10^{19} molecules CO initially (figure 3, curve c; table 2).

Single crystal studies have shown hydrogen to adsorb and then migrate into the subsurface layer of the copper where it causes the subsurface copper atoms to reconstruct [13]. The initial state morphology of the copper therefore derives from hydrogen absorption in which the subsurface hydrogen underpins and stabilises the observed surface structure. We have shown hydrogen to be absorbed both by $Cu/ZnO/Al_2O_3$ and Cu/Al_2O_3 catalysts [14,15]. The hydrogen has been shown to be locked into the subsurface layers by the oxygen driven reconstruction produced by N_2O decomposition [15]. Removal of this surface oxygen by reduction of CO and 473 K allows the explosive release of the subsurface hydrogen [15]. Figure 7 shows that CO reduction of the oxide overlayer here, which has driven a reconstruction of the initial morphology results in the release of the subsurface underpinning hydrogen. The ultimate surface structure obtained therefore is not the initial (H-under-

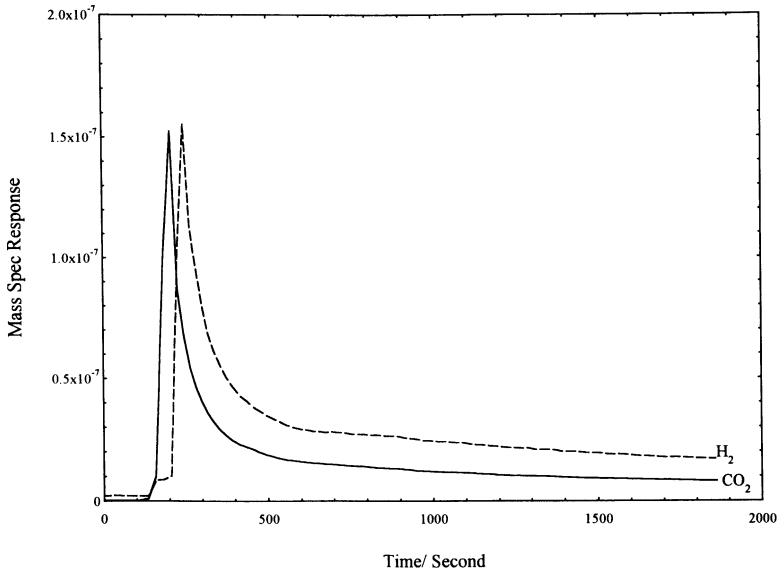

Figure 7. Explosive release of subsurface hydrogen in the copper by CO reduction at 473 K of the CO_2-surface oxidised copper. The time dependent CO_2 evolution shown here is by reduction of the copper after the initial CO_2 decomposition at 213 K – figure 3, curve a.

pinned) morphology, but one which is a minimum energy configuration determined by Cu–Cu interactions.

Industrially, methanol is produced from $CO/CO_2/H_2$ (10 : 10 : 80) mixtures over a $Cu/ZnO/Al_2O_3$ catalyst. The surface of the operating catalyst therefore will be in dynamic time averaged steady state, involving continuous reconstruction of the surface of the active component of the catalyst – the copper component. The initial morphology of the surface of the copper produced by hydrogen reduction will be transformed upon changing to the reactant mixture. Methanol is produced from the CO_2 component of the $CO_2/CO/H_2$ mixture [16], and so an oxygen atom will be left on the surface for each methanol molecule produced. This surface oxygen atom will drive a reconstruction, the extent of which is determined by its surface coverage. This latter is determined by the rate of reduction of the surface copper oxide by the CO and H_2 components of the reactant mixture. Carbon monoxide has been shown to be a stronger reducing agent than hydrogen [17] and so the oxide driven reconstruction will be changed to a new structure by preferential reduction of the oxided surface by the CO molecule with the concomitant release of sub surface hydrogen. Continuous adsorption and re-incorporation of hydrogen into the bulk of the copper will partially re-establish the original morphology. It is evident therefore that, depending on the conditions, this system has the potential to exhibit chaotic behaviour.

References

[1] G. Ertl, Catal. Lett. 9 (1991) 219.
[2] D.J. Coulman, J. Winterlin, R.J. Behm and G. Ertl, Phys. Rev. Lett. 64 (1990) 1761.
[3] F. Bessenbacher, P.T. Sprunger, L. Ruan, L. Olesen, I. Stensgaard and E. Loesgaard, Topics Catal. 1 (1994) 325.
[4] A.J. Elliot, R.A. Hadden, J. Tabatabaei, K.C. Waugh and F.W. Zemicael, J. Catal. 157 (1995) 153.
[5] S.S. Fu and G.A. Somorjai, Surf. Sci. 237 (1990) 87.
[6] K.C. Waugh, Catal. Today 15 (1992) 51.
[7] G.C. Chinchen, C.M. Hay, H.D. Vandervell and K.C. Waugh, J. Catal. 103 (1987) 79.
[8] P.A. Redhead, Trans. Faraday Soc. 57 (1961) 641.
[9] T. Schneider and W. Hirschwald, Catal. Lett. 14 (1992) 197.
[10] R. Schlögl, R.C. Schoonmaker, M. Muhler and G. Ertl, Catal. Lett. 1 (1988) 237.
[11] S. Bailey, J.W. Snoeck, G. Froment and K.C. Waugh, Catal Lett. 30 (1995) 99.
[12] B.S. Clausen, G. Steffensen, B. Fabius, J. Villadsen, R. Feidenhans'l and H. Topsøe, J. Catal. 132 (1991) 524.
[13] C.H. Rieder and W. Stocker, Phys. Rev. Lett. 57 (1986) 2548.
[14] M. Bowker, R.A. Hadden, H. Houghton, J.N.K. Hyland and K.C. Waugh, J. Catal. 103 (1987) 79.
[15] A.J. Elliott, B. Sakakini, J. Tabatabaei, K.C. Waugh, F.W. Zemicael and R.A. Hadden, J. Chem. Soc. Faraday Trans. 91 (1995) 3659.
[16] G.C. Chinchen, P.J. Denny, D.G. Parker, G.D. Short, M.S. Spencer, K.C. Waugh and D.A. Whan, Reprint ACS Div. Fuel Chem. 29 (1984) 178.
[17] G.C. Chinchen, M.S. Spencer, K.C. Waugh and D.A. Whan, J. Chem. Soc. Faraday Trans. I 83 (1987) 2193.