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A study of the activated decomposition of CO_2 on the Cu component of a $Cu/ZnO/Al_2O_3$ catalyst

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The decomposition of CO_2 over the Cu component of two ZnO/Al_2O_3 supported Cu catalysts, having different Cu areas, has been studied over the temperature range 393–513 K. The time dependence of the evolution of CO from a CO_2/He stream (10% CO_2, 101 kPa) which was dosed continuously over the catalyst showed two peak maxima, the first of which moved to shorter times on raising the temperature. The activation energy for the decomposition of CO_2 on the ZnO/Al_2O_3 supported polycrystalline copper was obtained from a plot of the logarithm of the time to the peak maximum of the first peak against the reciprocal of the dosing temperature. The value so obtained was $83 \pm 10\,\mathrm{kJ\,mol^{-1}}$ (catalyst A) and $86 \pm 10\,\mathrm{kJ\,mol^{-1}}$ (catalyst B) for fresh catalysts reduced in H_2 at 513 K. This value fell to $49 \pm 4\,\mathrm{kJ\,mol^{-1}}$ (catalyst A) and $55 \pm 5\,\mathrm{kJ\,mol^{-1}}$ (catalyst B) after CO reduction at 473 K of the Cu which had been oxidised by the decomposition of the CO_2. This lowering of the activation energy for the second CO_2 decomposition is considered to be due to the original morphology of the Cu not being restored by reduction in CO after the oxygen-driven reconstruction of the Cu deriving from the decomposition of the CO_2.

KEY WORDS: carbon dioxide; decomposition; copper; structure sensitive; surface reconstruction.

1. Introduction

The possibility that CO_2 decomposes over Cu proves to be a continuous source of controversy. Arguments which are presented in support of the view that it cannot occur are thermodynamic and are the same as those forwarded earlier to deny the occurrence of the decomposition of H_2O on Cu [1]; they are that the heats of formation of bulk CuO ($\Delta H_f = -155.2\,\mathrm{kJ\,mol^{-1}}$) or Cu_2O ($\Delta H_f = -166.7\,\mathrm{kJ\,mol^{-1}}$) are insufficient to drive the decomposition of either CO_2 ($\Delta H_f = -393.5\,\mathrm{kJ\,mol^{-1}}$) to CO ($\Delta H_f = -105\,\mathrm{kJ\,mol^{-1}}$) or the decomposition of H_2O ($\Delta H_f = -241.8\,\mathrm{kJ\,mol^{-1}}$) to H_2. Reactions (1)–(4) are all highly endothermic:

$$\Delta H\ (\mathrm{kJ\,mol^{-1}})$$

$$H_2O + Cu \rightarrow H_2 + CuO_{bulk} \qquad +86.6 \tag{1}$$

$$H_2O + 2Cu \rightarrow H_2 + Cu_2O_{bulk} \qquad +75.1 \tag{2}$$

$$CO_2 + Cu \rightarrow CO + CuO_{bulk} \qquad +127.8 \tag{3}$$

$$CO_2 + 2Cu \rightarrow CO + Cu_2O_{bulk} \qquad +115.3 \tag{4}$$

confirming that neither H_2O nor CO_2 will oxidise Cu metal to bulk CuO or Cu_2O. However, it is possible for CO_2 and H_2O to oxidise the surface of Cu on specific (possibly stepped) sites, even in the energetically most demanding case of CO_2 oxidation of the Cu surface, if the heat of adsorption of an oxygen atom on the surface of the Cu is 288 kJ per mol O adsorbed—the difference in the heats of formation of CO_2 and CO.

The literature on the heat of adsorption of O_2 on Cu is not entirely helpful. In a seminal paper, Dell *et al.* [2] measured the limiting low coverage heat of adsorption of O_2 on polycrystalline Cu to be $-460\,\mathrm{kJ\,(mol\ O_2)^{-1}}$ (-230 kJ per mol O adsorbed). The measurement was carried out on 6–12 g of polycrystalline Cu in an adiabatic calorimeter using a Pt/Pt-Rh thermocouple. They obtained the same heat of adsorption per mol O atoms when N_2O was used as the oxidant.

Fubini and co-workers [3], using a Tian-Calvet calorimeter and N_2O as the oxidant, found the heat of adsorption of oxygen on Cu to be $-234.1\,\mathrm{kJ\,(mol\ O\ atom)^{-1}}$, a value which was constant over the whole range of coverage. They also reported no temperature dependence on the decomposition of N_2O. Scholten and Konvalinka [4], however, reported an activation energy of $80\,\mathrm{kJ\,mol^{-1}}$ for the decomposition of N_2O on Cu. In a series of papers, Habraken and co-workers [5–7] reported that N_2O decomposed on Cu(111) and Cu(100) with activation energies of 44 and $13.4\,\mathrm{kJ^{-1}}$ respectively and with an apparent negative activation energy on Cu(110). The situation therefore is not clear.

By monitoring the time/temperature dependence of the H_2 produced when the H_2O/He stream is diverted over reduced polycrystalline Cu in the temperature range 316–507 K, we have shown unambiguously: (i) that H_2O decomposes over Cu, (ii) that it is an activated

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process having an activation energy of 38 kJ mol^{-1} and (iii) that the reaction is probably structure-sensitive, since it self-poisons after only 7–8% of a monolayer of oxygen is deposited on the surface of the Cu [8]. The fact that the reaction proceeds at between 316 and 507 K, coupled with the smallness of the activation energy, indicates that the reaction is not endothermic. It further demonstrates the inapplicability of the thermodynamic arguments based on bulk CuO/Cu_2O with respect to the feasibility of H_2O decomposition on Cu.

We first reported on the decomposition of CO_2 on polycrystalline Cu in 1988 where, because the extent of the reaction increased with decreasing temperature, we concluded that the reaction was precursor state mediated [9]. Here, as with the decomposition of H_2O on Cu, because the oxygen coverage of the Cu at the end of the reaction was never greater than 20% of a monolayer, we further concluded that the reaction was structure-sensitive. This study was followed up with a second paper in which we investigated the precursor-state-mediated decomposition of CO_2 on Cu in greater detail [10]. The reaction was studied by the technique of reactive frontal chromatography [11], monitoring the CO produced using on-line mass spectrometry at 173, 213, 297 and 333 K. (CO was detected at 173 and 213 K before CO_2 breakthrough.) We found an oxygen balance between the CO produced and the oxygen coverage of the Cu, the latter decreasing from 26% of a monolayer at 173 K to a minimum value of 11% of a monolayer at 333 K. These results show unambiguously that the decomposition of CO_2 on the surface of polycrystalline Cu cannot be endothermic and that thermodynamic arguments relating to bulk CuO or Cu_2O are invalid.

Our first paper provoked an immediate response in the surface science literature. Schneider and Hirschwald [12] found that CO_2 decomposition on Cu(110) was facile, occurring at 85 K with the CO produced desorbing between 200 and 220 K. Fu and Somorjai [13] found that CO_2 neither adsorbed nor decomposed on Cu(110) at 180 K but that it did both at 180 K on Cu(311). Campbell and co-workers [14] found that CO_2 did not decompose on Cu(110) at 85 K but that it did between 400 and 600 K with an overall activation energy of 67 kJ mol^{-1} or a reactive sticking probability of 10^{-9} to 10^{-11} per collision.

The purpose of the present paper is to determine whether, as indicated by the conflicting reports above, two mechanisms exist for CO_2 decomposition on Cu: (i) a precursor-state-mediated mechanism at low temperature (between 173 and 333 K) and (ii) an impulsive mechanism, at temperatures >333 K, in which the CO_2 decomposes on collision with the Cu surface, the probability of which is determined by whether it has the necessary kinetic or vibrational energy. The apparatus, the catalyst, the catalyst pre-treatment and the experimental techniques employed in the present paper are identical to those used in our earlier paper [10] so that the results of both papers can be compared directly.

2. Experimental

2.1. The apparatus

The multipurpose tubular microreactor used in these experiments has been described in detail previously [15]. 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.

2.2. The gases

The gases CO/He (10% CO), CO_2/He (10% CO_2) and H_2/He (5%) were all 99.9995% pure and were used directly from the cylinder.

2.3. The catalysts

The two catalysts studied were typical commercial $Cu/ZnO/Al_2O_3$ (60 : 30 : 10) methanol synthesis catalysts which were supplied by ICI. Their total surface areas were found to be 80 and 68 m^2g^{-1} by N_2 adsorption at 77 K and their copper metal areas were determined to be 25 and 33 m^2g^{-1} by nitrous oxide reactive frontal chromatography. Since the data obtained for both catalysts was found to be virtually identical, for brevity, the figures relating to the catalyst with the copper metal area of 25 m^2g^{-1} (designated CAT A) only will be shown. The results for the second catalyst (CAT B) are listed in table 1.

3. Experimental method

The procedure used for the reduction of the catalyst and subsequent decomposition of CO_2 was as follows:

1. The catalyst (0.5 g, 300–350 μm finings) was loaded into the reactor tube and held in place by glass wool plugs with a thermocouple located in the middle of the catalyst plug. The catalyst was then heated in a He stream (25 cm^3 min^{-1}, 101 kPa) from ambient to 553 K where it was held for 1 h. This was done to desorb any adventitious adsorbates, *e.g.*, CO_2, H_2O.
2. Having cooled the catalyst from 553 K to ambient in the He stream, the flow was switched to a H_2/He stream (5% H_2, 25 cm^3 min^{-1}, 101 kPa) and the temperature was raised from ambient to 513 K at 1 K min^{-1}, holding the temperature at 513 K under the H_2/He stream at the temperature for 16 h to ensure complete reduction.
3. The gas flow was then switched from H_2/He to He at 513 K and the temperature was held at 513 K under the He flow for 1 h to desorb H_2 and H_2O, after which the temperature was lowered under the He stream to any of the five temperatures 393, 413, 433,

Table 1
Parameters for the first and second set of decompositions for CO_2 on CAT A and CAT B in the temperature range 393 to 513 K

Temperature (K)	CAT A ($25\,m^2/g$)			CAT B ($33\,m^2/g$)		
	Time to the maximum rates of CO evolution (min)	CO evolved (molecule × 10^{19})	θ_O [a]	Time to the maximum rates of CO evolution (min)	CO evolved (molecule × 10^{19})	θ_O [a]
First decomposition						
393	2.32, 5.97	1.08	0.05	2.96, 5.62	1.31	0.06
413	1.02, 5.95	1.62	0.07	0.95, 5.61	1.19	0.05
433	0.20, 5.97	2.59	0.11	0.23	0.91	0.03
473	0.23, 5.88	3.21	0.14	0.43, 5.19	2.62	0.11
513	0.35, 6.79	4.69	0.20	0.35, 5.82	3.87	0.16
Second decomposition						
393	2.13	0.91	0.04	2.33	0.97	0.04
413	1.03	1.30	0.06	0.86	0.82	0.04
433	0.24	2.00	0.09	0.50	0.68	0.03
473	0.20	2.99	0.13	0.28, 6.26	2.60	0.11
513	0.35	2.97	0.13	0.29	2.97	0.13

[a] The oxygen coverage is calculated from the number of CO molecules evolved. (The oxygen coverage measured by CO reduction of the oxidised surface at 473 K was within 10% of these values.) The times for the first appearance of CO at the detector are 2 min (figure 1), 2.74 min (figure 2), 2.56 min (figure 3) and 2.82 min (figure 4). These are the zero times used for the measurement of the time to the maximum rate of CO evolution.

473 or 513 K at which the decomposition of CO_2 was studied.

4. Having reached the desired temperature, the He flow was switched to a CO_2/He stream (10% CO_2, $25\,cm^3\,min^{-1}$, 101 kPa) for 30 min, following $m/z = 2(H_2)$, $18(H_2O)$, 28(CO) and $44(CO_2)$ on the mass spectrometer. At the end of the 30 min CO_2/He flow, the system was flushed with He for 30 min, following which the temperature was raised at $5\,K\,min^{-1}$ to 513 K.
5. The catalyst was cooled to 473 K and the flow switched to a CO/He stream (10% CO, $25\,cm^3\,min^{-1}$, 101 kPa) for 30 min, monitoring the CO_2 produced by the reduction of the surface oxygen continuously on the mass spectrometer. After the 30 min CO/He flow, the flow was then switched to He for 30 min at 473 K before lowering the temperature to ambient.
6. Steps 4 and 5 were repeated.

Each set of CO_2 decomposition experiments (steps 1–5 above) was carried out on a fresh batch of catalyst for every temperature studied.

4. Results and discussion

Figure 1 shows the time dependences of CO evolution at 393 (curve (a)), 413 (curve (b)), 433 (curve (c)), 473 (curve (d)) and 513 K (curve (e)) for catalyst A. (The $m/z = 28$ cracking fraction of the CO_2 signal is subtracted from these curves.) Figure 2 shows the second set of time dependences for CO evolution from CO_2 decomposition which had previously undergone CO_2 decomposition at the given temperatures, the oxidised Cu surface produced by this first CO_2 decomposition having reduced by CO at 473 K. Table 1 lists the time to the maximum rates of CO evolution, and the amount of CO evolved the oxygen coverage of the Cu for both catalysts for the first and second CO_2 decompositions at each of the temperatures studied.

In contradistinction to our previous study of CO_2 decomposition on the same catalyst in the temperature range 173–333 K where the CO product appeared before the CO_2 [10], here there is a temperature-dependent delay after the CO_2 breakthrough before the CO appears. The length of time of the delay for a fixed conversion at a given temperature depends upon the

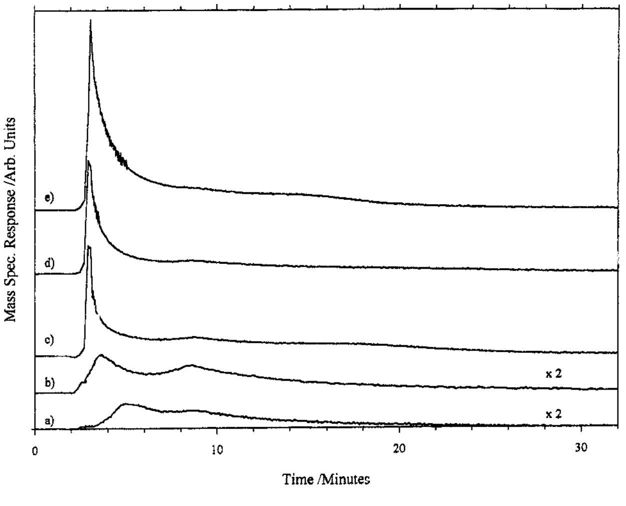

Figure 1. The time dependence of the evolution of CO from the first CO_2 decomposition on the $Cu/ZnO/Al_2O_3$ catalyst (catalyst A) at 393 (curve a), 413 (curve b), 433 (curve c), 473 (curve d) and 513 K (curve e).

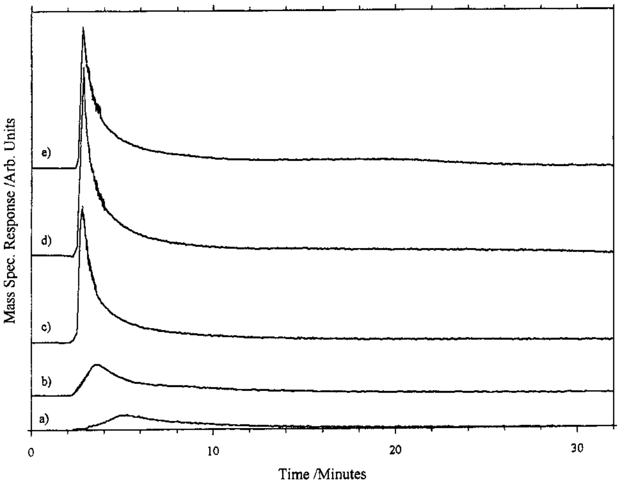

Figure 2. The time dependence of the evolution of CO from the first CO_2 decomposition on the $Cu/ZnO/Al_2O_3$ catalyst (catalyst A) at 393 (curve a), 413 (curve b), 433 (curve c), 473 (curve d) and 513 K (curve e).

activation energy for the reaction through the Frenkel equation [8]

$$\tau = \frac{e^{E/RT}}{A},$$

where τ is the time in seconds to a given amount of decomposition, E ($J\,mol^{-1}$) is the activation energy for reaction, R ($J\,mol^{-1}\,K^{-1}$) is the gas constant, T (K) is the temperature, and A (s^{-1}) is the pre-exponential term.

For the first CO_2 decomposition on the copper surface produced by reduction in H_2, two distinct maxima are seen in the rate of CO_2 decomposition at all temperatures for the catalyst. The time of the maximum of the first peak moves to shorter values as the temperature is increased. Since the amount of CO_2 decomposition at the maxima is roughly the same at 393, 413 and 433 K, it is permissible to use the Frenkel equation to calculate the activation energy for the decomposition.

A plot of $\ln \tau$ *versus* the reciprocal of $1/T$ gives the activation energy for CO_2 decomposition without any assumptions about the value of the pre-exponential term. The activation energies obtained are $83 \pm 10\,kJ\,mol^{-1}$ for catalyst A and $86 \pm 10\,kJ\,mol^{-1}$ for catalyst B. These activation energies are higher than the value ($67\,kJ\,mol^{-1}$) obtained by Campbell and co-workers [14] for Cu(110) but similar to that ($93\,kJ\,mol^{-1}$) obtained by Taylor *et al.* [16] for Cu(100). The Cu component of these $Cu/ZnO/Al_2O_3$ catalysts is a polycrystalline solid comprising predominantly the low-index faces—the (111), (110) and (100) surfaces. It is known that CO_2 does not decompose on Cu(111) [17,18] and so an active surface containing a 4 : 1 ratio of the (100) : (110) faces would account for the activation energy for CO_2 decomposition found here.

As explained in the experimental section, the oxygen which was deposited on the surfaces of the Cu by the decomposition of the CO_2 was removed by reduction in CO at 473 K for 30 min. The reduced Cu surface so produced was then exposed to the CO_2/He stream again (10% CO_2, $25\,cm^3\,min^{-1}$, 101 kPa) for 30 min at 393, 413, 433, 473, and 513 K. The time dependences of the CO evolved at these temperatures for the second CO_2 dosing is shown in figure 2. (The times to the evolution of the maximum rates of CO, the amounts of CO evolved and the fractional coverages of the Cu by adsorbed oxygen for both catalysts for all temperatures for both the first and second CO_2 dosing are listed in table 1.)

Three points should be noted about the second set of CO_2 decompositions. They are:

1. The total amount of CO_2 decomposed is roughly the same as that of the first decomposition at all temperatures for catalyst B. For catalyst A the amount of CO_2 decomposing in the second decomposition is slightly less than the first. (It should also be noted that the fractional coverage of the Cu by oxygen for both catalysts lies in the range of 6% of a monolayer at 393 K to 20% of a monolayer at 513 K, this low value suggesting that the reaction is structure-sensitive.)
2. The times to the evolution of the first CO peak maxima are shorter for the second CO_2 decomposition.
3. The CO second peak disappears on the second CO_2 dosing for catalyst A and is only barely discernible for the second CO_2 dosing on catalyst B at 473 K.

Using the temperature dependence of the logarithm of the time to the CO peak maximum for the second CO_2 dosing to obtain the decomposition activation energy as before gives values of $49 \pm 4\,kJ\,mol^{-1}$ for catalyst A and $55 \pm 5\,kJ\,mol^{-1}$ for catalyst B. These values are now lower than for the first CO_2 dosing and are lower than that found by Campbell and co-workers [14] for Cu(110). It is clear therefore that the Cu surface produced by CO_2 decomposition and CO reduction has been reconstructed from its original morphology produced by H_2 reduction to one which is more reactive for CO_2 decomposition. We have shown previously that CO_2 oxidation of Cu followed by reduction of the oxidised surface with CO at 473 K results in an increase in the area of the surface covered by the (211) face of Cu [19]. It is evident from these results that the Cu(211) face has a low activation energy of $\sim 50\,kJ\,mol^{-1}$ for the decomposition of CO_2.

We had argued previously that the activation energy for CO_2 resulted from the requirement of the CO_2 to be in a vibrationally excited state [10]. Our observation here of a dramatic reduction in the activation energy for the decomposition of the CO_2 as a result of different methods of pretreating the Cu, producing different Cu surface morphologies, shows that the energy barrier to CO_2 decomposition is determined by the surface structure of the Cu and not by the reaction dynamics.

It is difficult to explain the origin of the second CO peak in the rate of CO_2 decomposition on the first CO_2 decomposition. This decomposition takes place on the Cu morphology produced by H_2 reduction. It is also difficult to explain why the time to the maximum of the second peak in CO_2 decomposition is constant over the whole temperature range.

Oxidation of the Cu(110) surface is known to cause reconstruction of that surface [20]. It is also probable that oxidation of the other low-index faces will by its very nature cause reconstruction. It appears therefore that oxidation of the original morphology produced by reduction in H_2 results in an overall surface which after the initial oxidative reconstruction produces a new surface (possibly by the growth of Cu on top of the oxide) on which a second oxidation can occur. The morphology of the Cu produced by CO reduction at 473 K of the CO_2 oxidised surface now contains a significant fraction of the (211) face. This surface does not allow any secondary oxidation evidenced by the absence of a second CO peak.

It is clear from these data that the decomposition of CO_2 on polycrystalline Cu in the temperature range 393–513 K is activated in contradistinction to that observed in the temperature range 173–333 K, where there is an apparent negative activation energy, deriving from the reaction being precursor-state mediated [10]. Since both sets of data were carried out on identical catalysts which had undergone identical pre-treatments, it is permissible to combine them. Figure 3 shows the oxygen coverage of the Cu after dosing CO_2 (10% in He, 101 kPa, 30 min) over a range of temperature from 173 to 513 K. Its value falls from 26% of a monolayer at 173 K to ~6% of a monolayer at 393 K and then rises again on increasing the temperature to 20% of a monolayer at 513 K.

There are several important points that should be made from this. These are:

1. The oxygen coverage is self-evidently a function of temperature.
2. The CO_2 decomposition stops (self-poisons) well within the duration (30 min) of CO_2 exposure and so the final coverage is not a result of insufficient time of exposure at any temperature.
3. The largest oxygen coverage is found at the lowest temperature of exposure to CO_2 (173 K) and so the incorporation of oxygen onto the Cu surface cannot be rate determining.
4. The submonolayer coverages of the Cu by oxygen at the cessation of reaction suggests that the CO_2 decomposition on Cu is dependent on the initial coverage of given crystal faces and so can be considered to be "structure sensitive".
5. It is evident from the STM video of the time dependence of the room temperature oxygen-driven reconstruction of Cu(110) [21] that the reconstruction is activated. Depending on the size of the activation energy it is possible that the reconstruction may not occur (or will occur to a negligible extent) at 173 K. Assuming that the decomposition of the CO_2 is confined to the (110) face of Cu and that negligible oxygen-driven reconstruction occurs at 173 K, then it is likely that the adsorbed oxygen atoms sit on top of the Cu at 173 K. An oxygen coverage of 26% of a monolayer from CO_2 decomposition at 173 K would then represent the surface coverage of the polycrystalline Cu by the (110) face. The room temperature oxygen-driven reconstruction of Cu(110) produces a (2 × 1)O-Cu(110) overlayer so that the maximum oxygen coverage at complete reconstruction of Cu(110) at room temperature will be half a monolayer. If the surface population of the polycrystalline Cu by the Cu(110) face is 26% of a monolayer, then the oxygen coverage of the polycrystalline Cu resulting from the room temperature oxygen-driven reconstruction from CO_2 decomposition will be 13% of a monolayer. We found an oxygen coverage of the polycrystalline Cu by CO_2 decomposition at 333 K of 11% of a monolayer in good agreement with the above arguments. The higher intermediate oxygen coverages at cessation of CO_2 decomposition occurring between 333 and 173 K probably derive from a combination of incomplete reconstruction of the Cu(110) face and by on-top oxygen adsorption on the unreconstructed Cu(110).

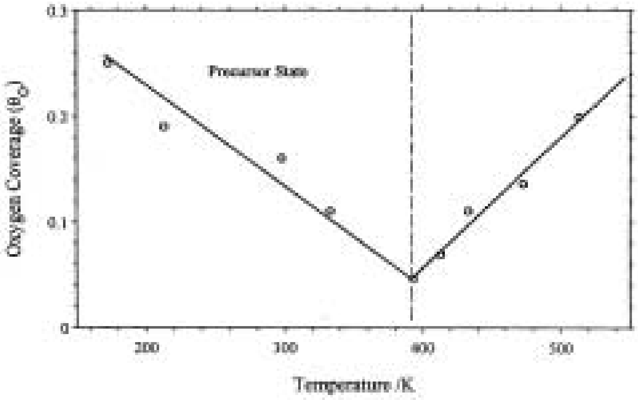

Figure 3. The oxygen coverage of the Cu component of the $Cu/ZnO/Al_2O_3$ catalyst as a function of temperature. (The precursor-state coverages are reported in ref. [10].)

The increase in oxygen coverage at cessation of reaction between 393 K and 513 K reported here by the argument detailed above cannot therefore result from incomplete reconstructive overlayer of the Cu(110) surface. It must result from a second Cu growth over the (2 × 1)O-Cu(110) surface. This has been seen by STM. This new surface must also allow oxidation to occur on it and we have seen evidence of this here in a second peak in CO production on the first CO_2 decomposition.

5. Conclusions

1. The decomposition of CO_2 on Cu occurs in two distinctly different modes: (i) in a precursor-state-mediated mode at temperatures below 333 K and (ii) in a direct impulsive mode at temperatures above 393 K.
2. The decomposition of CO_2 over the Cu component of $Cu/ZnO/Al_2O_3$ catalysts is a significantly activated process in the temperature range 393–513 K. The value of the activation energy depends on the pre-treatment of the Cu. For a Cu surface produced by H_2 reduction at 513 K of bulk copper oxide its value is $83 \pm 10\,\mathrm{kJ\,mol^{-1}}$ (catalyst A) and $86 \pm 10\,\mathrm{kJ\,mol^{-1}}$ (catalyst B). For a Cu surface produced by CO reduction at 473 K of a surface oxidised Cu its value is $49 \pm 4\,\mathrm{kJ\,mol^{-1}}$ (catalyst A) and $55 \pm 5\,\mathrm{kJ\,mol^{-1}}$ (catalyst B).
3. The value of the activation energy for CO_2 decomposition on Cu depends on the morphology of the Cu and is not determined by the reaction dynamics, *i.e.*, by the CO_2 being required to be in a vibrationally excited state as had been previously suggested [10].
4. The oxidation of the Cu resulting from CO_2 decomposition takes place in two steps on the Cu surface produced by H_2 reduction of copper oxide but in one step on the Cu surface produced by CO reduction of surface-oxidised Cu.

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