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Inverted Temperature Dependence of the Decomposition of Carbon Dioxide on Oxide-Supported Polycrystalline Copper

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The paper reports an investigation of the decomposition of carbon dioxide on an industrial (I.C.I.) methanol synthesis catalyst, which in effect is oxide-supported polycrystalline copper. In the temperature range 173 to 333 K using the technique of reactive frontal chromatography it is shown that (i) the rate of decomposition of carbon dioxide increases on decreasing the dosing temperature, and (ii) the extent of oxidation of copper by the decomposition of carbon dioxide increases on decreasing the dosing temperature. The former result is in agreement with an earlier conclusion that carbon dioxide decomposition on unsupported polycrystalline copper was precursor-state moderated. The "negative" activation energy obtained is in fact the difference in energy between the heat of adsorption of the precursor state and the surface decomposition activation energy of the adsorbed precursor state, which is the same argument as that used by G. Ertl [*in* "Catalytic Ammonia Synthesis" (J. R. Jennings, Ed.), p. 123, Plenum, New York, 1991] to explain the negative activation energy for the nitrogen sticking probability on potassium-promoted single crystal iron. The inverted temperature dependence of the extent of the oxidation of copper by the decomposition of carbon dioxide is rationalised on the basis that the oxided copper surface reconstructs in an activated way to an unreactive state. The energy barrier to that reconstruction is too high for it to occur at 173 K (the lowest temperature studied) where the extent of surface oxidation (25% of a monolayer) is therefore solely a function of oxygen poisoning of the reactive surface. The CO/CO_2 reactive frontal lineshape at 173 K is exactly the same as that of the N_2/N_2O lineshape at 333 K; the lower oxygen coverage at cessation of reaction by oxygen poisoning for the CO/CO_2 reaction shows the reaction to be structure sensitive. Infrared spectroscopic data show the reconstruction to involve the loss of the (110) face and the growth of the (211) face while CO desorption data confirm the activated nature of the reconstruction. © 1995 Academic Press, Inc.

INTRODUCTION

One of the more surprising recent results of surface science has been the discovery of the remarkable reactivity of carbon dioxide on copper. Indeed, the degree to which it was both unexpected and to some extent disbelieved, even by those who discovered it, is reflected in the fact that its first reporting was hidden deep in the recesses of one of two appendices of a paper on the oxidation of methanol on copper(110). It was there in 1978 that Wachs and Madix noted that greater than 99% of the carbon dioxide molecules adsorbed at 180 K on Cu(110) dissociated to carbon monoxide and surface oxygen (1).

The relevance of this to the mechanism of the copper-catalysed forward and reverse water–gas shift reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$) lay undetected until Hadden and co-workers reported the adsorption and decomposition of carbon dioxide on polycrystalline copper (2). They concluded that the CO_2/Cu reaction was structure sensitive and that it was precursor-state moderated. The latter conclusion was arrived at in stopped-flow experiments where the amount of carbon dioxide found to decompose increased on decreasing the adsorption temperature.

These conclusions, however, were met with some scepticism to the extent that Nakamura *et al.* wrote a paper entitled "Does CO_2 dissociatively adsorb on Cu surfaces?" (3). Their conclusion was that it did on Cu(110) with an overall activation energy of 67 kJ mol^{-1} or a reaction probability of 10^{-9} to 10^{-11} per collision at 400 to 600 K. However, no carbon monoxide was detected in this experiment, the decomposition of the CO_2 being inferred from the oxygen coverage of the Cu(110) after exposure to the carbon dioxide (3).

In direct contradiction to this, Schneider and Hirschwald found that CO_2 decomposition on Cu(110) was facile, occurring at 85 K with the CO produced desorbing between 200 and 220 K (4). This was hotly contested by Campbell (5), forcing Schneider and Hirschwald to concede that their observed, but small, reactivity may have been due to defects in their Cu(110) face (6).

This latter admission is in accord with the work of Fu and Somorjai (7, 8). At 180 K they found that carbon dioxide neither decomposed nor adsorbed on Cu(110). They did, however, find that it both adsorbed and decomposed on Cu(311). In addition, Bonicke *et al.* have found

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recently that another stepped copper surface (Cu(332)) also catalyses carbon dioxide decomposition (9). [Note: The Cu(110) surface is a corrugated surface and in this respect can be regarded as highly stepped, there being access to the subsurface atoms. The Cu(311) surface has two-atom-wide (111) terraces separated by single-atom steps of (100) orientation and can be viewed as less stepped than the Cu(110) surface. The Cu(332) surface has six-atom-wide (111) terraces with single-atom steps of (111) orientation. It is considerably less stepped that the Cu(110) and Cu(311) surfaces.]

It is generally agreed that the flat Cu(111) face does not decompose carbon dioxide (10, 11) so it might reasonably be concluded that stepped (or defected) copper surfaces are a prerequisite for the decomposition of carbon dioxide. This conclusion, however, is contradicted by the findings of Taylor and co-workers (12), who discovered that carbon dioxide decomposed on the flat Cu(100) surface. Their study showed that this decomposition had an activation energy of 93 kJ mol^{-1} in the temperature range 475 to 550 K at a CO_2 pressure of 990 mbar.

The situation with respect to carbon dioxide decomposition on copper is therefore confused. There is disagreement about whether the process is activated and about whether it is structure sensitive. The purpose of this paper is to investigate both of these aspects of carbon dioxide decomposition on copper. The reaction has accordingly been studied on a standard industrial methanol synthesis catalyst whose surface morphology had previously been determined (13). The extent of decomposition will be related to the surface population of stepped surfaces and the activation energy will be determined by measuring the rate of decomposition in the temperature range from 77 to 333 K at a CO_2 prressure of 10 mbar.

EXPERIMENTAL

Microreactor

The multipurpose microreactor has been described in detail previously (14). It is a single tube reactor (20 cm long, 0.4 cm i.d.) connected via a heated capillary to a mass spectrometer (Hiden Analytical, Warrington, England). In this work it was used in the following types of experiments: (i) N_2O and CO_2 reactive frontal chromatography, (ii) CO and H_2 temperature-programmed reduction, (iii) temperature-programmed desorption, and (iv) total area measurements by nitrogen uptake and desorption (BET) at 77 K.

Catalyst Preparation and Pretreatment

The catalyst was a typical commercial $Cu/ZnO/Al_2O_3$ (60:30:10) methanol synthesis catalyst (ICI). It was prepared by coprecipitation from a mixed nitrate solution of copper, zinc, and aluminium by sodium carbonate. The precipitate was washed, dried, and calcined. A weighed amount (0.5 g) was loaded into the microreactor where it underwent the following pretreatments: (i) heating to 643 K under a helium stream (25 cm^3 min^{-1}) to decompose any residual carbonates and to desorb any adventitiously adsorbed water, (ii) reducing under a hydrogen/helium stream (5% H_2, 1 bar, 25 cm^3 min^{-1}) by temperature programming in that stream from room temperature to 513 K (heating rate, 1 K min^{-1}), holding the catalyst at that temperature under that flow for 16 h, (iii) switching flows from hydrogen/helium to helium (1 bar, 25 cm^3 min^{-1}) and holding the temperature at 513 K for 1 h, (iv) lowering the temperature to ambient under the helium flow and then temperature programming to 513 K to desorb any residually adsorbed hydrogen.

The total surface area of the reduced catalyst measured by nitrogen uptake and by BET was 65 m^{2}g^{-1} and the copper metal area measured by N_2O reactive frontal chromatography was 30 m^2/g (loaded catalyst).

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS): Equipment and Technique

DRIFTS experiments were carried out using a Nicolet Magna-IR550 spectrometer equipped with a mercury cadmium telluride detector together with a "praying mantis" model diffuse reflectance attachment (Harrick Scientific) and a Harrick high-vacuum-chamber diffuse reflectance cell (HVC-DR2 low-pressure model).

The following procedure was used in these experiments:

(i) the catalyst was first reduced in the microreactor as described above;

(ii) the catalyst was passivated by reaction with a nitrous oxide/helium stream (5% N_2O, 1 bar, 25 cm^3 min^{-1}, 333 K);

(iii) the passivated material was diluted with KBr (10% by weight catalyst) and loaded into the diffuse reflectance cell;

(iv) the solid was rereduced in the diffuse reflectance cell with a carbon monoxide/helium stream (2% CO, 1 bar, 25 cm^3 min^{-1}) by heating the solid from ambient temperature to 513 K (heating rate 5 K min^{-1}) and holding the temperature at that value for 3 h;

(v) the carbon monoxide/helium stream was then switched to a helium flow (1 bar, 25 cm^3 min^{-1}) and the solid was held under that stream at 513 K for 30 min before cooling to ambient in the helium;

(vi) the helium stream was then switched to a carbon dioxide flow (1 bar, 25 cm^3 min^{-1}) and the infrared spectra were recorded.

Gases

Helium was supplied by Linde and was 99.998% pure. Before use it was passed through a Chromapack Gas Clean

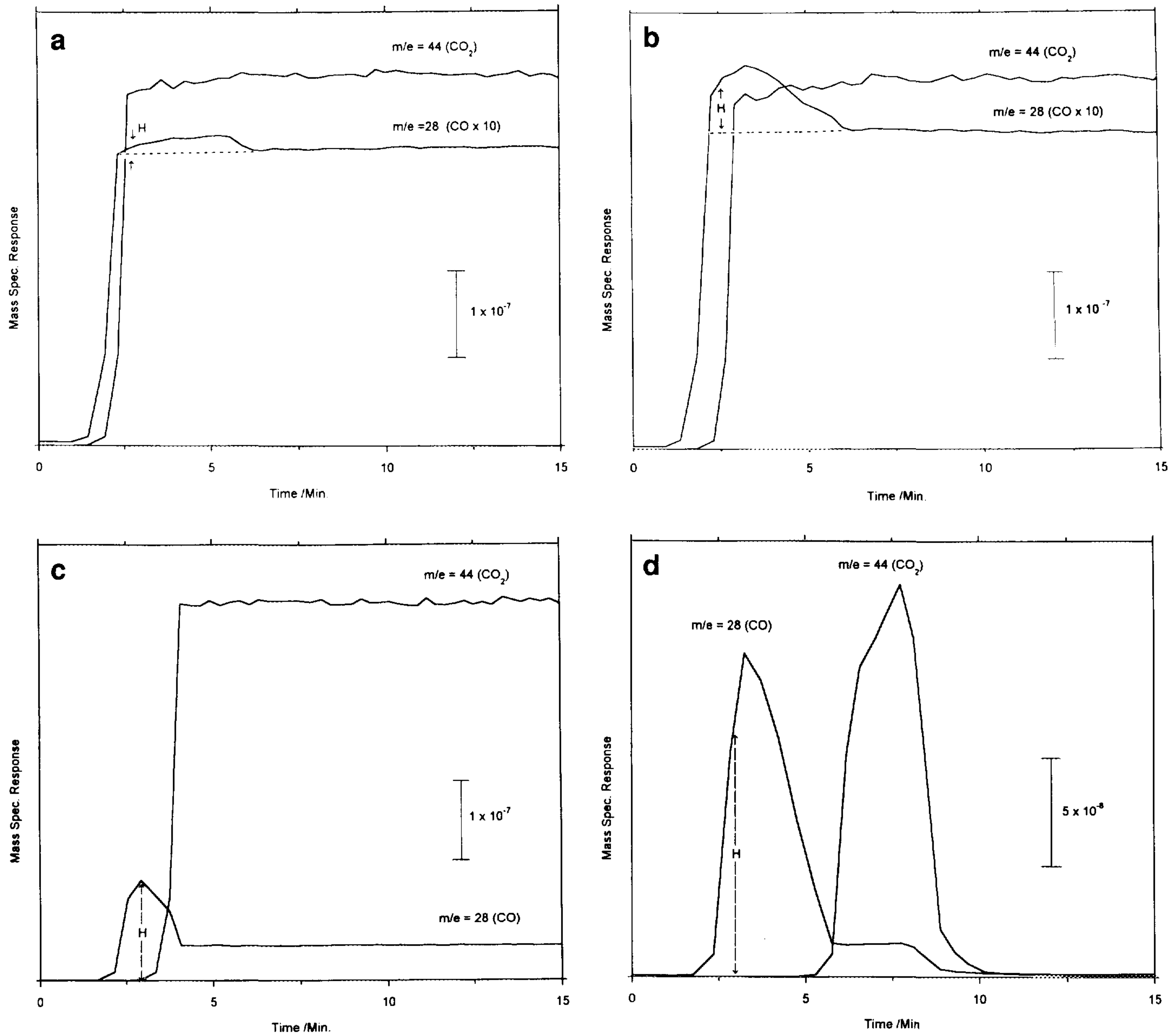

FIG. 1. Time dependence of the rate of carbon dioxide decomposition at 333 (a), 299 (b), 213 (c), and 173 K (d). Mass spectrometer response is in arbitrary units.

Moisture filter. Hydrogen (British Oxygen Co.) was 99.995% pure and was used direct from the cylinder.

Carbon dioxide (Electrochem Ltd.) was 99.995% pure; the hydrogen/helium (5% H_2 in He), the nitrogen/helium (10% N_2 in He), and the nitrous oxide/helium (5% in N_2O in He), all supplied by Electrochem, were all 99.999% pure and were all used direct from the cylinders. The carbon monoxide/helium (9.97% CO in He) was also supplied by Electrochem and contained nitrogen (200 ppm) and argon (100 ppm) as impurities. It was used direct from the cylinder.

RESULTS AND DISCUSSION

The Temperature Dependence of the Decomposition of Carbon Dioxide on Oxide (ZnO/Al_2O_3) Supported Polycrystalline Copper

It must be stated at the outset that the carbon dioxide decomposition on the $Cu/ZnO/Al_2O_3$ catalyst reported in Figs. 1a–1d and in Table 1 is confined to the copper component of the catalyst. No decomposition has been observed on zinc oxide or alumina; as indicated above, however, it has been previously established that carbon

TABLE 1

Temperature Dependence of the Rate of CO_2 Decomposition and of the Oxygen Coverage of the Copper Resulting from the CO_2 Decomposition

Temperature (K)	CO evolved (molecule × 10^{19})	CO_2-deposited surface oxygen measured by titration with CO at 473 K (atom × 10^{19})	Oxygen atom coverage (monolayer)	Rate of CO_2 decomposition (molecule cm^{-2} s^{-1} × 10^{12})
333	1.6	1.7	0.11	0.56
299	2.3	2.4	0.16	0.69
213	2.9	3.3	0.19	1.84
173	3.8	3.9	0.25	2.43

dioxide does decompose on polycrystalline copper (2) and on various single crystal faces (1, 3, 4, 7–9).

Figure 1a shows the time dependence of the rate of carbon dioxide decomposition at 333 K. The carbon dioxide/helium flow replaced the helium flowing over the reduced catalyst 60 s after time zero. The carbon monoxide produced is observed initially after ~90 s after time zero, approximately 20 s before the carbon dioxide breakthrough. Carbon dioxide decomposition proceeds for a further ~150 s at which point the carbon monoxide signal in the mass spectrometer (*m*/*e* = 28) falls to the value of the carbon dioxide cracking fraction.

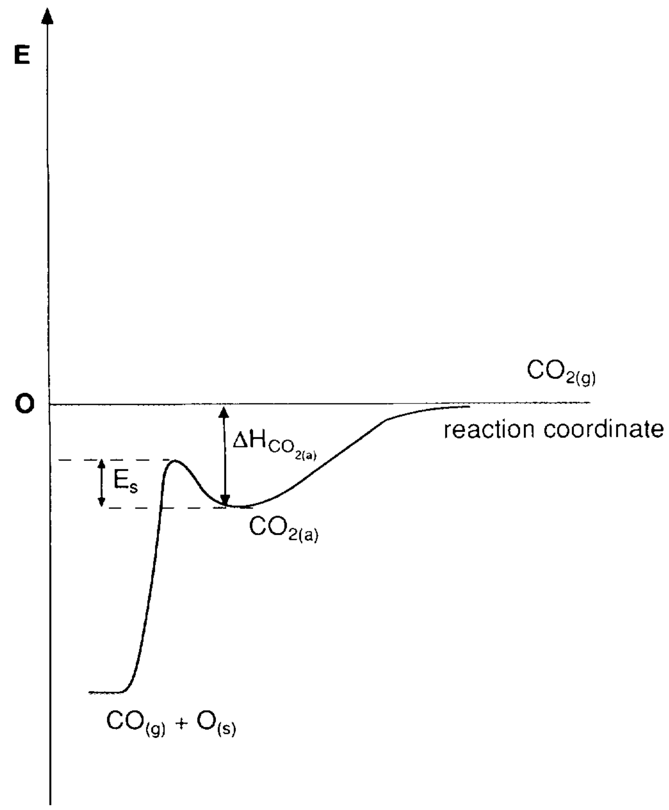

FIG. 2. Simplified potential energy diagram of the precursor state moderated (copper catalysed) decomposition of adsorbed carbon dioxide. The subscripts "(g)", "(a)," and "(s) refer to species which are gas phase, adsorbed, and on the surface, respectively.

Figures 1b, 1c, and 1d are a repeat of the above experiment at 299, 213, and 173 K, respectively, with a new amount of catalyst being used for each experiment. The measurements of the rate of carbon monoxide production were made 90 s after the initial appearance of carbon monoxide (see Figs. 1a to 1d), due allowance being made for the contribution of the *m*/*e* = 28 cracking fraction from any carbon dioxide present. The extent of surface oxidation by carbon dioxide decomposition and the temperature dependence of the rate of decomposition are shown in Table 1.

Inverted Temperature Dependence of the Rate of CO_2 Decomposition

Concentrating initially on the inverted temperature dependence of the rate of decomposition, this can be understood on two conditions: (i) if the rate of decomposition requires a high population of a weakly held precursor state as has been previously suggested (2), and (ii) if the activation energy for the decomposition of this weakly held precursor carbon dioxide were lower than its heat of adsorption. (A highly simplified two-dimensional potential energy diagram describing this condition is shown in Fig. 2. The position of zero potential energy on the diagram should be at −393.5 kJ, the heat of formation of carbon dioxide.)

On this basis the rate expression for the rate of production of carbon monoxide would be given by

$$\frac{d(P_{CO})}{dt} = k_s\theta_{CO_2}, \qquad [1]$$

where $k_s = A_s e^{-E_s/RT}$ is the surface rate constant for the decomposition of adsorbed CO_2 and $\theta_{CO_2} = \dfrac{KP_{CO_2}}{1 + KP_{CO_2}}$ is

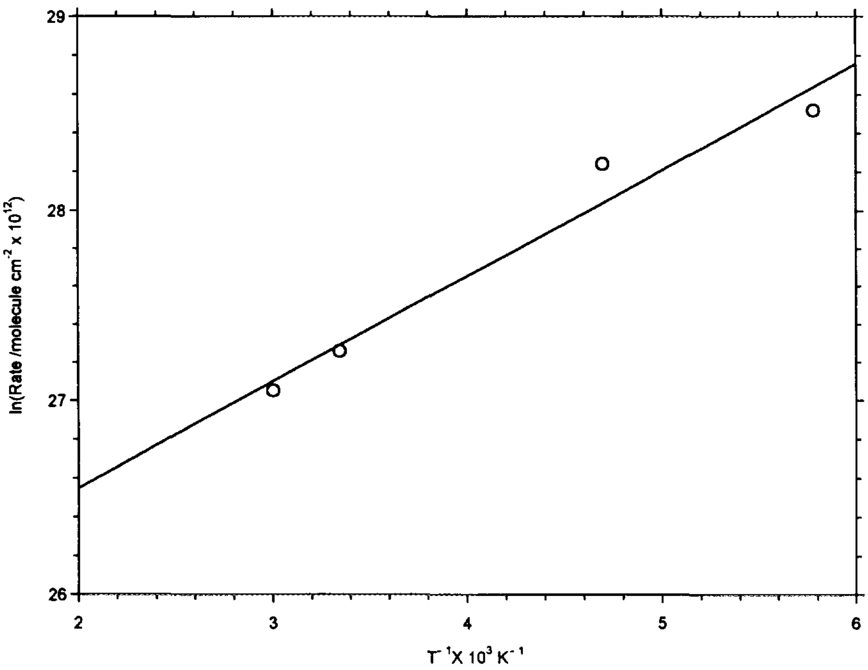

FIG. 3. The dependence of the logarithm of the rate of carbon dioxide decomposition on reciprocal temperature.

the fraction coverage of adsorbed CO_2, with $K = Ae^{\Delta H_{CO_2}/RT}$ being the adsorption equilibrium constant for the weakly held precursor state. Since the precursor state is weakly held, $1 + KP_{CO_2} \approx 1$ so that Eq. [1] reduces to

$$\frac{d(P_{CO})}{dt} = k_s K P_{CO_2} \qquad [2]$$

or

$$\frac{d(P_{CO})}{dt} = A_s A e^{(\Delta H_{CO_2} - E_s)/RT} P_{CO_2}. \qquad [3]$$

The "activation energy" for the rate of production of CO is $(\Delta H_{CO_2} - E_s)$ so that if $\Delta H_{CO_2} > E_s$ an inverted temperature dependence obtains. (This is exactly analogous to the argument proposed by Ertl and co-workers for the "negative" activation energy observed for the sticking probability of nitrogen on potassium-promoted iron single crystals (15).)

A plot of the logarithm of the rate of production of carbon monoxide versus reciprocal temperature is shown in Fig. 3. (The rate is calculated 90 s after the initial appearance of carbon monoxide.) The figure shows enthalpic-type behaviour, i.e., the rate decreases with increasing temperature. The temperature dependence is determined by the difference in energy between the heat of adsorption of carbon dioxide, ΔH_{CO_2}, and the activation energy for the decomposition of the adsorbed carbon dioxide E_s (Fig. 2, Eq. [3]). This difference in energy obtained from Fig. 3 is 4 kJ mol^{-1}; therefore, $\Delta H_{CO_2} - E_s = 4$ kJ mol^{-1}. The heat of adsorption of carbon dioxide, ΔH_{CO_2}, on partially oxidised copper has been found to be 18 kJ mol^{-1} (16) so that the surface activation energy E_s, is 14 kJ mol^{-1}. This value is obviously at odds with activation energies of 67 and 93 kJ mol^{-1} reported for the Cu(110) and Cu(100) surfaces (3, 12). However, those experiments were carried out at temperatures above 400 K so that they would not be probing the weakly held precursor route to the decomposition of carbon dioxide. The mechanism being probed in these experiments is either that of surmounting a translational energy barrier or populating an excited vibrational state whose sticking decompositional probability was unity. On the basis of the latter argument the population of the $v = 3$ state of carbon dioxide at 600 K is 10^{-9} of the ground state, which is exactly the same as the reaction probability per collision reported by Nakamura *et al.* (3), strongly suggesting that population of the higher vibrational state (the $v = 3$ state) may be the route to dissociation in the higher temperature range.

Inverted Temperature Dependence of the Degree of Surface Oxidation

The oxygen coverage of the copper after decomposition of the carbon dioxide is obtained by titration with a carbon monoxide/helium stream (9.97% CO, 1 bar, 25 cm^3 min^{-1}) at 473 K. The time-dependent evolution of the CO_2 produced by this reduction of the catalysts which had pre-

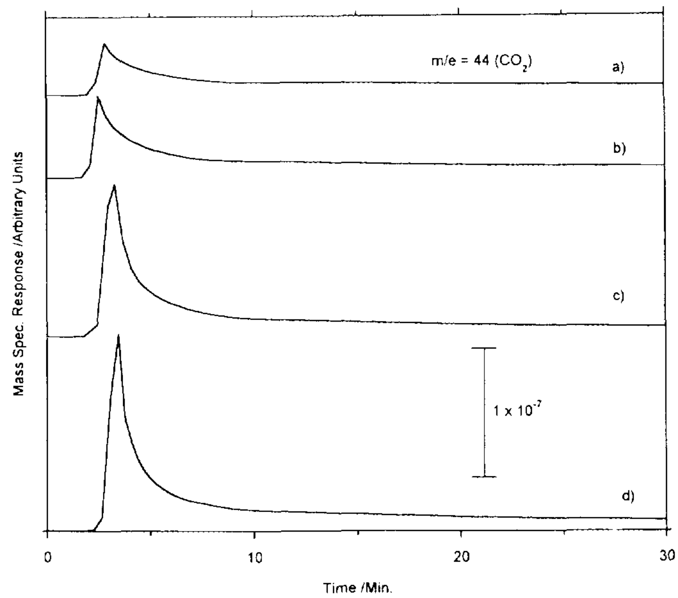

FIG. 4. Oxygen coverage on copper after carbon dioxide decomposition by titration with CO/He (9.97% CO, 1 bar, 473 K).

viously decomposed carbon dioxide at 333, 299, 213, and 173 K are shown in Fig. 4, curves a, b, c, and d, respectively. The total oxygen coverage, expressed as atoms or fractions of a monolayer, is listed in Table 1, from which it can be seen that a good oxygen balance is obtained when the oxygen coverage is compared with the amount of carbon monoxide evolved. This can only be true if there is no strongly held carbon monoxide remaining on the surface of the copper after cessation of the decomposition, a fact which is confirmed on temperature programming under helium from the decomposition temperature to 473 K (prior to reduction in the CO/He stream) when no carbon monoxide is observed to desorb. This experiment, however, confirms that the carbon dioxide decomposition is confined solely to the copper since the interaction of CO at 473 K does not reduce the zinc oxide.

The oxygen coverage at the cessation of carbon dioxide decomposition rises from 11% of a monolayer of the copper at 333 K to 25% of a monolayer at 173 K. Saturation coverage of polycrystalline copper by oxygen atoms at 333 K, measured by N_2O decomposition, is 50% of a monolayer (17) so that this observed "self-poisoning" cannot result from saturation of all of the available oxygen sites.

It could result, however, from a combination of two effects: (i) from the CO_2/Cu reaction being structure sensitive and confined to the stepped sites; and (ii) from the oxided stepped sites reconstructing in an activated manner to an unreactive (possibly planar) state with the result that reconstruction is facile at 333 K, but becomes increasingly inhibited as the temperature is lowered to such an extent that it does not take place at 173 K. Scanning tunnelling microscopy experiments have shown that the Cu(110) surface on oxidation reconstructs in a time-dependent, and

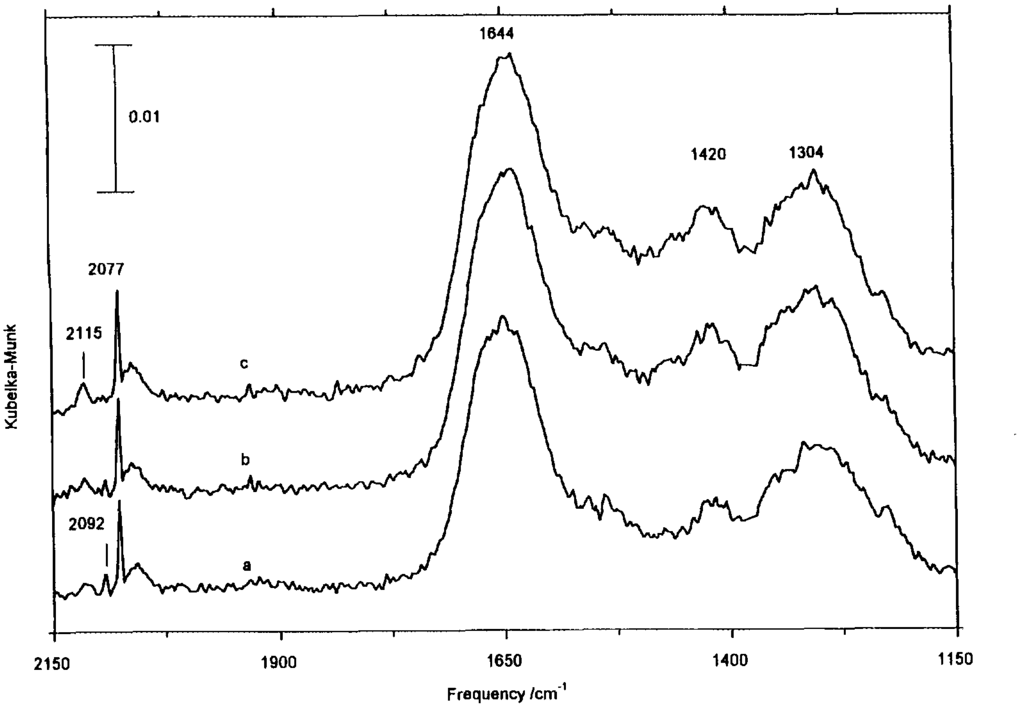

FIG. 5. Infrared spectra obtained on exposing CO_2 to the reduced catalyst at 295 K after 1 (a), 15 (b), and 60 min (c). DRIFT spectra expressed as the Kubelka–Munk function in arbitrary units.

therefore activated, way to a (2 × 1)O–Cu(110) overlayer at 300 K (28). We shall also present below both infrared and thermal desorption evidence which shows that the oxide-supported polycrystalline copper of the industrial catalyst is involved in an activated reconstruction.

Infrared Evidence for the Activated Reconstruction of the Oxided Copper Surface

Figure 5 shows the infrared spectra obtained by the diffuse reflectance technique after exposing the reduced catalyst to carbon dioxide (1 bar, 25 cm^3 min^{-1}, 295 K) for 1 min (spectrum a), 15 min (spectrum b), and 60 min (spectrum c). The peaks observed at 1644 and 1420 cm^{-1} correspond to those obtained for hydrogeno-carbonate on zinc oxide while the peak at 1304 cm^{-1} corresponds to that of a high-coverage bidentate carbonate on zinc oxide (19).

The peaks at 2077, 2092, and 2115 cm^{-1} are the CO stretch on Cu(111) (20), Cu(110) (21), and Cu(211) (22). [The Cu(211) surface has three-atom wide (111) terraces separated by single-atom steps of (100) orientation; it therefore has a lower step density than the Cu(110) and Cu(311) surfaces.] The intensity of the 2077 cm^{-1} peak is invariant with time so that there is no change in the surface population of the Cu(111) face. However, in moving from curve (a) to (c) (increasing time of exposure), the intensity of the 2092 cm^{-1} peak (the (110) face) decreases roughly linearly with the increase in intensity of the 2115 cm^{-1} peak (the (211) face). This time-dependent change in these peaks, however, is clear evidence of an activated reconstruction of the surface of the copper under oxidising conditions; exposure to carbon monoxide alone does not produce this reconstruction.

The time dependence of the loss in the ability of the catalyst to decompose carbon dioxide at 299 K (Fig. 1b) is paralleled by the rate of loss of the (110) face of the copper and in the rate of appearance of the (211) face at this temperature. It is reasonable to conclude therefore that the (110) face is the active surface for carbon dioxide decomposition, in agreement with the findings of Schneider and Hirschwald (4), and that the flat (111) and the lower step density (211) surfaces are inactive for this reaction. The (311) surface (two-atom wide (111) terrace separated by single-atom steps of (100) orientation) which is more highly stepped than the (211) surface and which Fu and Somorjai have found to be active for carbon dioxide decomposition was not found on this catalyst under these conditions, although it has been seen previously on the same catalyst in a CO_2/H_2 stream (30 bar) at 413 K (13). The difference in the surface crystallography between two samples of the same catalyst is not too surprising in view of our finding in this paper of the overriding influence of surface reaction and temperature in determining the surface morphology of the catalyst.

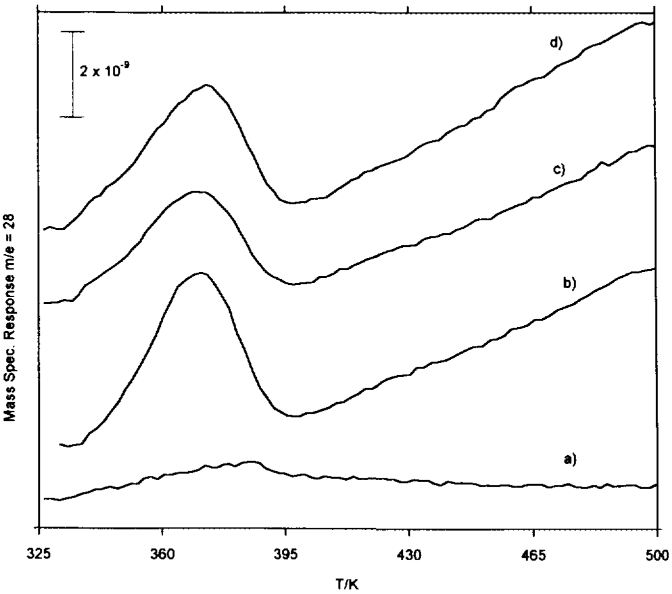

FIG. 6. Carbon monoxide desorption profiles obtained after repeated carbon dioxide decomposition experiments at 333 K; (a) first decomposition, (b) second decomposition, (c) third decomposition, and (d) fourth decomposition.

Carbon Monoxide Thermal Desorption Evidence for Activated Reconstruction of the Oxided Copper Surface

Figures 6, 7, and 8 show the CO desorption profiles obtained upon repeating the following experiment at 333,

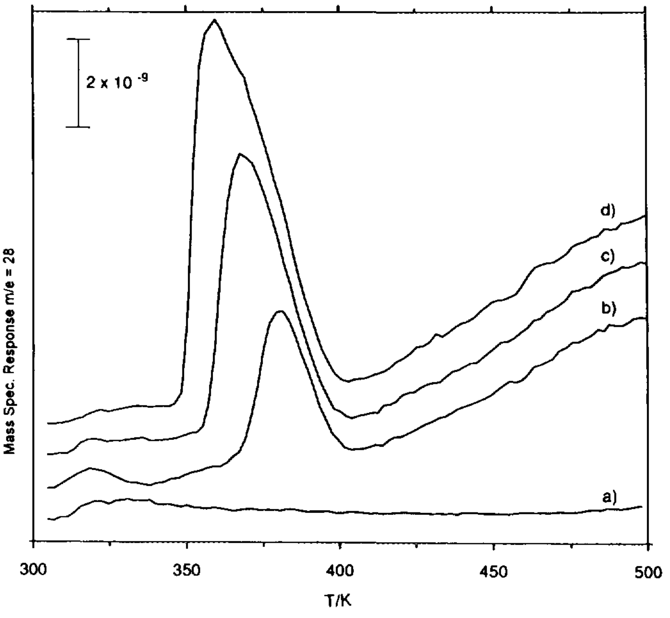

FIG. 7. Carbon monoxide desorption profiles obtained after repeated carbon dioxide decomposition experiments at 299 K; (a) first decomposition, (b) second decomposition, (c) third decomposition, and (d) fourth decomposition.

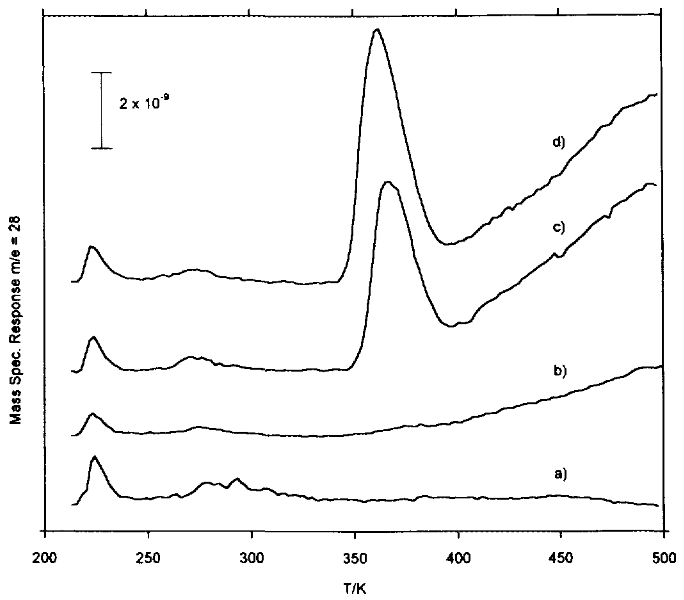

FIG. 8. Carbon monoxide desorption profiles obtained after repeated carbon dioxide decomposition experiments at 213 K; (a) first decomposition, (b) second decomposition, (c) third decomposition, and (d) fourth decomposition.

299, and 213 K, respectively: (i) carbon dioxide decomposition, (ii) thermal desorption under helium, and (iii) carbon monoxide reduction of the oxided overlayer. After the initial carbon dioxide decomposition, shown in Figs. 1a to 1d, when carbon monoxide was observed in the gas phase before and after carbon dioxide breakthrough, on the second and subsequent carbon dioxide dosings carbon monoxide was only observed on temperature programming after carbon dioxide dosing, it was not observed during exposure to the carbon dioxide. Figure 6 (curve a) shows the CO desorption profile after the initial carbon dioxide decomposition and then after subsequent decompositions (curves b, c, and d).

The figure shows that thermal desorption after the initial carbon dioxide decomposition produces no CO desorption (as has been reported earlier). A wide CO_2 peak with a peak maximum of 348 K (an E_d value of 102 kJ mol^{-1} not shown in the figure was also observed); this is not the weakly held precursor state but the decomposition of a surface zinc hydrogeno-carbonate.

The desorption of CO with a peak maximum temperature, T_m of 372 K (E_d = 103 kJ mol^{-1}) appears after the second subsequent CO_2 dosages at 333 K. This carbon monoxide desorption state is exactly the same as that found previously after carbon dioxide decomposition on unsupported polycrystalline copper (2). The total amount of CO desorbing from this state does not change after the second dose. The total amount of CO desorbing from this state is 3.5×10^{18} molecules, which, on the basis of an on-top adsorption indicated by the frequency of the CO infrared spectra, corresponds to a coverage of 2.3% of a monolayer.

As in the decomposition of carbon dioxide at 333 K, at 299 K the desorption spectrum obtained after the first carbon dioxide decomposition shows no CO desorption (Fig. 7). The second and subsequent desorption profiles show the carbon monoxide desorption peak (T_m = 372 K, E_d = 103 kJ mol^{-1}). The coverage of this state increases from 2.0% of a monolayer (second desorption profile) to 3.8% (third), and finally to 4.3% of a monolayer on the fourth profile.

At 213 K, the carbon monoxide desorption peak is seen only after the third carbon dioxide decomposition with a coverage of 2.7% of a monolayer; this value increases to 3.3% of a monolayer on the fourth decomposition (Fig. 8). At 173 K no carbon monoxide desorption peak at 372 K is seen even after four carbon dioxide decompositions.

These results clearly demonstrate a time- and temperature-dependent reconstruction of the copper surface, some of which is irreversible. At 333 K, 10% of a monolayer of oxygen causes a collective reconstruction of the copper surface to a state which no longer decomposes carbon dioxide. Reduction under carbon monoxide at 473 K does not result in a relaxation to the original state. The fraction of the copper area which decomposes the carbon dioxide is now smaller by a factor of 5 with a concomitant development of a high-energy state for carbon monoxide desorption, not seen initially. This smaller value of the active fraction is calculated from the integral of the CO desorption peak (Table 2). As the temperature is decreased, because the oxygen-induced reconstruction is activated, it takes a longer time to reconstruct to the unreactive state so that a larger amount of carbon dioxide decomposes before a combination of oxygen poisoning of the active centres and oxygen-induced reconstruction terminates the decomposition. At 173 K, the temperature is too low to overcome the energy barrier for the oxygen-induced reconstruction so that termination of the carbon dioxide decomposition at this temperature is simply due to oxygen poisoning of the active sites, as has been seen previously for N_2O decomposition on polycrystalline copper (17).

Indeed, the time dependence of the decomposition of carbon dioxide at 173 K on the supported copper is remarkably similar to that of the reactive frontal chromatogram of N_2O decomposition at 333 K (17). Although in the latter case the reaction self-poisons at 50% of a monolayer coverage by oxygen, for carbon dioxide decomposition it self-poisons at 25% of a monolayer. This shows the carbon dioxide decomposition to be structure sensitive. A rough estimate of the relative populations of the (110) and (111) surfaces can be made from the intensities of the 2092 and 2077 cm^{-1} peaks in Fig. 5. Furthermore, if it is assumed that these are the dominant surfaces on the polycrystalline copper, a crude absolute estimate of their coverage can be

TABLE 2

Amount of Carbon Monoxide Evolved by Temperature-Programmed Desorption after Carbon Dioxide Decomposition as a Function of the Number of Repeats of the Carbon Dioxide Decomposition Experiment

	Temperature 333 K		Temperature 299 K		Temperature 213 K	
Decomposition number	CO evolved (molecule × 10^{18})	CO coverage of Cu (% monolayer)	CO evolved (molecule × 10^{18})	CO coverage of Cu (% monolayer)	CO evolved (molecule × 10^{18})	CO coverage of Cu (% monolayer)
1	—	—	—	—	—	—
2	3.45	2.3	3.04	2.0	—	—
3	5.96	4.0	5.68	3.8	3.99	2.7
4	6.62	4.4	6.44	4.3	4.93	3.3

made. On this basis, the (110) surface occupies approximately 20% of the surface, a value which is in reasonably good agreement with the level of oxygen coverage at self-poisoning. This is corroborative evidence that it is the (110) surface which decomposes carbon dioxide at 173 K; the extent of the oxidation of this surface at cessation of reaction indicates that defects on this surface are not responsible for this reaction, as has been suggested previously (5, 6).

CONCLUSIONS

1. The inverted temperature dependence observed for the rate of decomposition of carbon dioxide on oxide-supported polycrystalline copper derives from the reaction proceeding through a weakly held precursor state, the activation energy for the surface decomposition of which is itself smaller than the heat of adsorption of the precursor state.

2. The reactive frontal chromatogram observed for the reaction of carbon dioxide with copper at 173 K is remarkably similar to that observed for the reaction of nitrous oxide with copper at 333 K. The oxygen coverage of the copper at the cessation of reaction by oxygen poisoning for the reaction with carbon dioxide is roughly half that obtained after reaction with nitrous oxide. The latter reaction is structure insensitive, implying that the reaction with carbon dioxide is also structure sensitive.

3. The structure sensitivity of the decomposition of carbon dioxide on copper has been found in this work to be due to the reaction taking place on the (110) surface, a highly stepped surface. The (211) surface, a less highly stepped face than the (110) surface, and the flat (111) surface have been found to be inactive toward the decomposition of carbon dioxide.

4. The oxide overlayer on the copper produced by the decomposition of carbon dioxide drives an activated reconstruction of the surface of the copper from the (110) to the (211) surfaces; reduction of the reconstructed copper oxide overlayer does not result in a relaxation to its original configuration.

5. The observation that carbon dioxide decomposes on a flat Cu(100) surface in the temperature range 475 to 550 K can be explained on the basis that the reaction is an impulsive one, with a vibrationally excited carbon dioxide (v = 3) decomposing on collision with the copper surface.

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