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Interaction of carbon dioxide with clean and oxygenated Cu(110) surfaces

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Thermal desorption studies of CO_2 adsorbed on Cu(110) at 85 K and low pressures reveal nearly 100% dissociation on the oxygen-free surface to give adsorbed oxygen and CO. By oxygen predosing a pronounced molecular adsorption state at 100 K is induced with up to a twenty-fold coverage increase, which cannot be explained by simply considering the dissociation equilibrium on the surface. Probably new sites are generated by oxygen as indicated by a pronounced increase of the sticking coefficient. The adsorbed amount of CO_2 in dependence on oxygen dose at 85 K exhibits a maximum, which is tentatively attributed to the dynamics of the surface due to oxygen induced reconstruction $((1\times1)\rightarrow p(2\times1))$. On polycrystalline copper enhanced CO_2 dissociation is observed.

Keywords: Carbon dioxide; oxygenated Cu(110); thermal desorption

1. Introduction

On copper containing methanol synthesis catalysts carbon dioxide is the main precursor to methanol [1–5]. But it could also act as an indirect promoter of the reaction as not only hydrogenation but also dissociation of CO_2 on the copper surface might occur effecting a certain oxygen coverage. As oxygen adsorbed on copper is known to stimulate hydrogenation/dehydrogenation reactions [2,3,6,7] it seemed worthwhile studying the interaction of CO_2 with clean and oxygenated copper surfaces.

Low temperature/low pressure (80 K, 10^{-4} Pa) XPS studies (X-ray photoelectron spectroscopy) of CO_2 adsorbed on oxygen containing copper surfaces (polycrystalline and (211) face) are reported by Copperthwaite et al. [8], while Hadden et al. [9] report on radiolabelling and TPD studies (TPD = temperature programmed desorption) of CO_2 adsorbed on polycrystalline copper (unoxidised and oxidised), after exposure at markedly higher temperatures (room temperature) and pressures (0.1 atm).

The present study reports on low temperature TDS experiments (TDS = thermal desorption spectroscopy) performed mainly on clean and oxygen predosed Cu(110) with a few results obtained with polycrystalline copper.

2. Experimental

Copper single crystals and a polycrystalline sheet (99.999% Cu) were cleaned by UHV standard methods. Structure and chemical composition of the surface were monitored by LEED and Auger electron spectroscopy (AES). While no contaminations could be detected by AES on Cu(110) single crystal faces after the cleaning procedure it was impossible to get completely rid of oxygen on polycrystalline samples by sputter/heating cycles and reduction. Every slight heating induced oxygen again to come up to the surface, probably by grain boundary diffusion, producing an oxygen coverage in the range of a tenth of a monolayer.

At background pressures of less than 10^{-8} Pa the sample could normally be cooled down to 85 K while by reducing the pressure over the liquid nitrogen reservoir of the sample holder a temperature of 70 K could be reached for about 30 min. Exposures of the sample to oxygen and carbon dioxide were performed at pressures between 10^{-4} and 10^{-6} Pa and at different temperatures with the Auger spectrometer switched off in any case to avoid dissociation by the electron beam [8]. The differentially pumped mass spectrometer (QMA 112, Balzers) used for TDS runs was separated from the UHV main chamber. An orifice of 5 mm diameter in the mass spectrometer shielding facing the sample surface acted as inlet for desorbing molecules. The heating rate was 8.4 K s^{-1} in all TD experiments.

Oxygen predosing was performed at 85 and 300 K with varying exposures. For a number of experiments the Cu(110) face was exposed to oxygen at 300 K until the p(2 × 1)O overlayer had completely formed, as monitored by LEED [10].

Coverages of CO_2 were determined by comparison of the TD peak area with the sensitivity corrected TD peak area of the fully developed (2 × 1) overlayer structure of CO (as determined by LEED), which corresponds to a degree of coverage of $\Theta = 0.5$. Therefore CO_2 coverages are relative numbers.

3. Results and discussion

Fig. 1 gives an overview of the behavior of the two surfaces (clean Cu(110) and Cu(110)-p(2 × 1)O) and the influence of oxygen. It is obvious from fig. 1a that molecular adsorption of CO_2 on clean Cu(110) is very small (about 0.3% of a monolayer) compared to dissociative adsorption yielding adsorbed CO and oxygen. The oxygen built up in the course of CO_2 adsorption sequences was

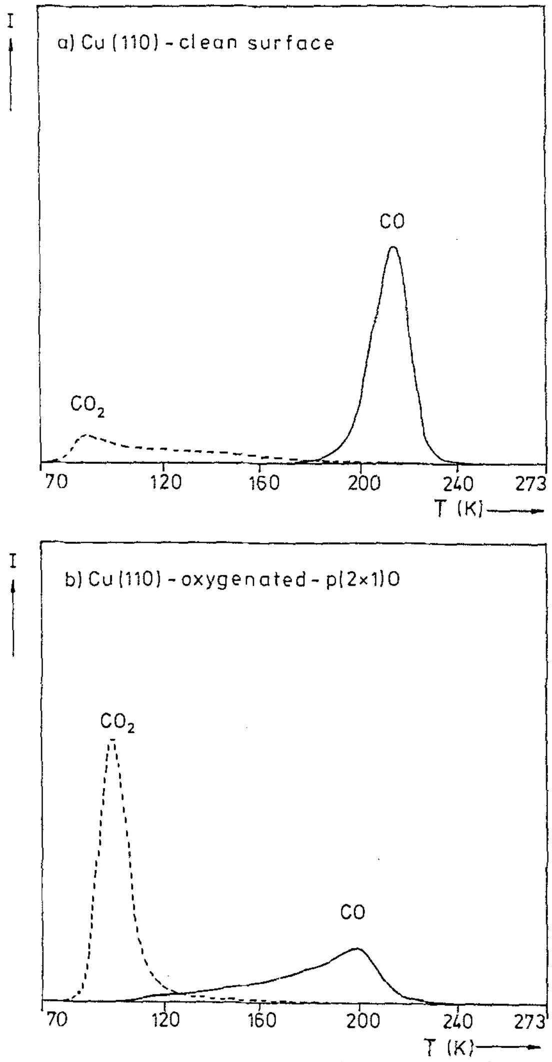

Fig. 1. Desorption of CO_2 and CO following CO_2 adsorption (1 L) at 85 K on clean (a) and oxygenated (b) Cu(110). (Oxygen coverage: $\Theta_0 = 0.5$.)

followed by AES. This behavior is reversed on the oxygen predosed surface (fig. 1b) where molecular adsorption prevails, with the CO peak not only being largely reduced but also shifted to lower temperatures indicating the formation of new less stable states due to the influence of preadsorbed oxygen and/or coadsorbed CO_2.

The dependence on CO_2 exposure is shown for the clean surface in fig. 2 with a peak at 100 K and a pronounced tail which extends to more than 200 K indicating more than one state for molecularly adsorbed CO_2. The CO peak at 215 K which originates from CO_2 dissociation corresponds to the CO peak

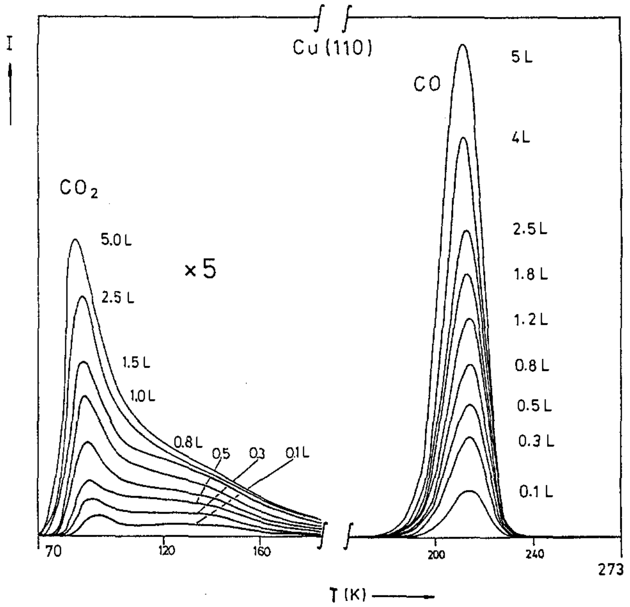

Fig. 2. Dose dependence of CO_2 and CO desorption from clean Cu(110) following CO_2 exposure at 85 K. (CO_2 desorption curves magnified by a factor of 5.) Exposure to $C^{18}O_2$ and detection of masses 48 and 30.

between 200 and 220 K which is obtained after CO interaction with clean Cu(110) [11]. In order to avoid background effects, CO desorption after CO_2 adsorption was performed with $C^{18}O_2$, so that $C^{18}O$ with mass 30 was monitored with the mass spectrometer.

Corresponding TD spectra for the Cu(110)–p(2 × 1)O surface are shown in fig. 3 which reveals again the pronounced increase in molecular CO_2 adsorption due to oxygen predosing. The reduction – but not complete suppression – of dissociative adsorption and the development of new states at $T_p = 125$ and 180 K for adsorbed CO are also demonstrated by the spectra in fig. 3. The oxygen induced CO states which may well correspond to the adsorption states of excited and stabilised CO_2 (CO_2^-, CO_3 and $[CO_2^- \cdot CO_2]$) as suggested by Copperthwaite et al. [8] will be discussed in more detail in a separate publication to follow. The sticking coefficient of CO_2 being a function of exposure increases at 85 K by a factor of about 40 at low exposures due to oxygen predosing. On polycrystalline samples dissociation of CO_2 was markedly enhanced compared to the single crystal surface as determined by AES. As adsorbed oxygen is produced by this process an autocatalytic site generation for CO_2 adsorption occurs. Furthermore – as mentioned above – oxygen diffused from the bulk to the clean surface in a fast process in the course of thermal desorption runs. Therefore the polycrystalline surface behaved already in the first TD run like a slightly oxygen predosed surface while the following TD runs exhibited already

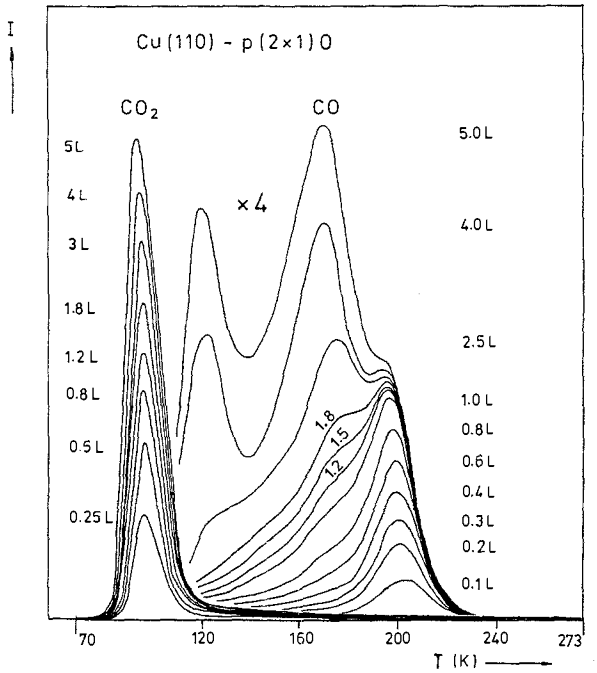

Fig. 3. Dose dependence of CO_2 and CO desorption from oxygenated Cu(110)[p(2×1)O] following CO_2 exposure at 85 K. (CO desorption curves magnified by a factor of 4.) Exposure to $C^{18}O_2$ and detection of masses 48 and 30.

the same behavior as the Cu(110)–p(2 × 1)O surface concerning peak position and coverage (with the uncertainty of the absolute area of the polycrystalline surface).

As preadsorbed oxygen obviously plays an important role in CO_2 adsorption its influence was studied in more detail. In fact this influence is not trivial in that it just reduces dissociation to make molecular CO_2 adsorption more probable. Oxygen induced CO_2 coverages up to 18% of a monolayer can be achieved while the corresponding value for CO from dissociation of CO_2 on the clean surface is less than 6%.

In fig. 4 CO_2 coverages versus oxygen exposure (at either 300 or 85 K) after 5 L CO_2 exposure at 85 K are plotted. The coverage numbers were obtained from the quantitative evaluation of 32 TD spectra recorded with stepwise increase of oxygen coverage. While the curve for the higher oxygen exposure temperature (300 K) shows a continuous increase in CO_2 coverage with saturation between 8% and 9% of a monolayer, the curve at $T_{ad(O)} = 85$ K exhibits a maximum coverage of 18% at 1.5 L oxygen dosage. With increasing oxygen exposure the CO_2 coverage decreases to the value obtained with the p(2 × 1)O surface. This striking difference of the two curves indicates a sensible dependence of CO_2 adsorption on the state of the oxygen on the surface. As oxygen induces

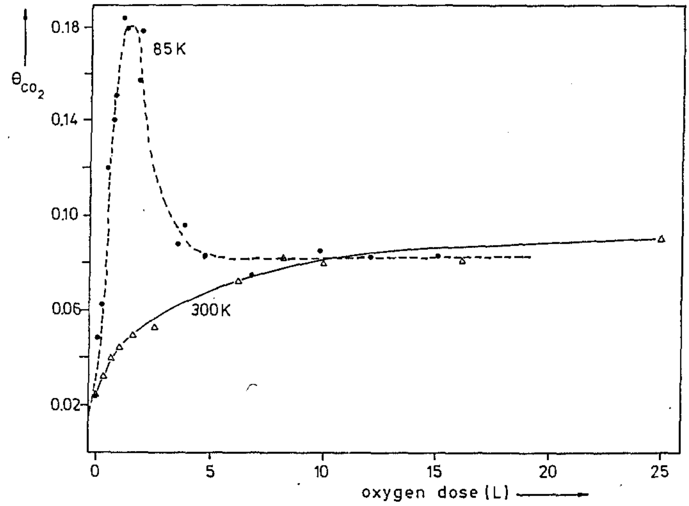

Fig. 4. CO_2 coverage (after 5 L CO_2 at 85 K) as a function of preceding oxygen exposure at two different temperatures. (— — —) $T_{ad(O)}$ = 85 K; (———) $T_{ad(O)}$ = 300 K.

reconstruction on the surface yielding the p(2 × 1)O structure at lower exposures, the experimentally established difference may well be due to structural effects. A possible support for this assumption comes from work function measurements by Spitzer and Lüth [12] and Sass and co-workers [13]. Both groups report on a maximum of the work function change of Cu(110) in dependence on oxygen exposure at 110 K. The maximum of $\Delta\Phi$ is located between 1.0 and 1.5 L oxygen dose in agreement with our observations.

This can be interpreted in terms of local reconstruction which takes partially place already at low temperature. The removal of atomic rows ("missing row" model [14]) or the addition of atomic rows ("added row" model) as proven recently by scanning tunnelling microscopy (STM) [15] induces the formation of new and energetically favourable sites in the course of the transition from (1 × 1) to p(2 × 1). In this dynamic state the surface will be especially active for adsorption, giving rise to the maximum of CO_2 coverage. By completion of the reconstruction not only half of the copper surface will be occupied by oxygen atoms but the surface becomes "perfect" again on a long range scale, offering only a limited number of favourable adsorption sites, as observed, when starting the adsorption experiments from the beginning with the p(2 × 1)O surface. So, both surfaces end up with the same CO_2 "saturation" coverage of 8% to 9% of a monolayer. But this is only a relative value derived from the comparison with LEED calibrated CO adsorption. Furthermore one has to consider an additional 50% coverage by oxygen corresponding to the p(2 × 1)O structure. The near neighbourhood of adsorbed CO_2 and oxygen on the Cu(110)-p(2 × 1)O surface will most probably induce interaction between CO_2 and oxygen, adsorbed onto the long-bridge sites on (110). So, not only structural changes but

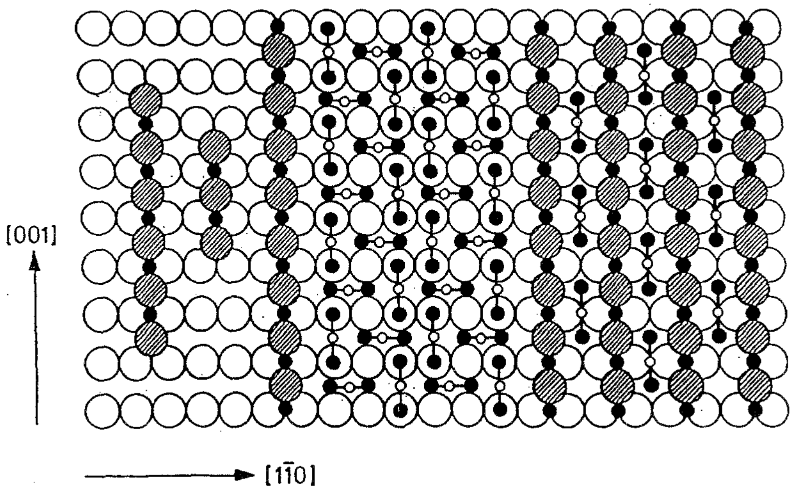

Fig. 5. Model of partially oxygen reconstructed Cu(110) with p(2×1)O domains and adsorbed CO_2. (Relative length of CO_2 molecule is slightly higher than in reality.) (•—○—•) CO_2; (▨, ○) Cu (first, second layer); (•) adsorbed oxygen.

also chemical interaction (and possibly partial charge transfer between adsorbed O^-/O^{2-} and CO_2) enhances molecular CO_2 adsorption. An attempt of modelling the transition from the clean Cu(110) surface to an added-row p(2 × 1)O structure with simultaneous CO_2 adsorption is shown in fig. 5. In this model the arrangement of adsorbed CO_2 molecules as suggested by Freund et al. [16] for a Ni(110) surface is used, while another arrangement is tentatively proposed for the p(2 × 1)O surface. In the latter case CO_2 saturation is reached when the ratio of adsorbed CO_2 molecules to all accessible Cu surface atoms not taken by oxygen is 0.125.

Taking these two facts into account the experimentally determined CO_2 coverage resulting from 5 L exposure corresponds to about 0.65, i.e. 65% of the *uncovered* Cu atoms are occupied by CO_2.

The different behavior of room temperature and low temperature (85 K) oxygen treated surfaces can then qualitatively be explained in the following way: Adsorption of oxygen at 300 K effects the formation of p(2 × 1)O *domains* [15], with (1 × 1) regions inbetween. On the (1 × 1) surface areas marked dissociation of CO_2 takes place, while molecular adsorption occurs on the p(2 × 1)O regions. With increasing p(2 × 1)O area molecular adsorption increases up to a limiting coverage of 0.125. Low temperature/low dose oxygen exposure yields statistical distributed oxygen (possibly mobile) on the surface, which reduces dissociation of CO_2 remarkably, but does not diminish the number of adsorption sites for CO_2 to an appreciable extent. But every heating of the sample in order to effect thermal desorption, and subsequent adsorption of oxygen at 85 K incudes the formation and enlargement of p(2 × 1)O domains leading finally – after passing a maximum – to the same constant coverage value of about 0.08–0.09. Complete coverage by CO_2 was not reached as the highest CO_2 dose applied in these experiments was 5 L which is obviously not sufficient to achieve saturation.

Our findings are in good qualitative agreement with the results reported by Hadden et al. [9] obtained on polycrystalline copper at higher pressures and temperatures. Campbell et al. [17] reported that they did not observe adsorption and dissociation of CO_2 on Cu(110) between 110 and 250 K for exposures up to 350 L. This discrepancy can easily be understood in view of our observation that the CO_2 desorption peak maximum appears at 100 K (figs. 1–3).

In conclusion, submonolayer coverages of oxygen on copper stimulate molecular CO_2 adsorption and possibly give rise to the formation of activated species like CO_2^- and CO_3^- [8,18,19] which could be a precursor of formate ($HCOO^-$), known to be an important intermediate in methanol synthesis.

We hope for more experimental evidence from HREELS studies of this system planned for the near future.

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