# Adsorption states of carbon monoxide on oxygenated Cu(110) faces

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Oxygen preadsorption on Cu(110) surfaces strongly reduces the CO desorption peak at 220 K, typical for clean Cu(110) and induces the development of less tightly bound states, which probably correspond to sites on Cu(111) micro-facets, formed in the course of oxygen stimulated surface reconstruction. A smaller part of the CO molecules ( $\leqslant 20\%$) seems to interact with adsorbed oxygen to give adsorbed $CO_2^-$, which can be stabilized in the presence of $CO_2$ by formation of van der Waals complexes, e.g. $[CO_2 \cdot CO_2^-]$. At increasing temperature this complex decomposes or disproportionates to give desorbing CO and adsorbed $CO_3^-$. The interpretation is tentative, but some evidence is given to it by TDS from Cu(111), by XPS, STM and SIMS studies and by theoretical calculations.

**Keywords:** Thermal desorption; carbon monoxide; oxygenated Cu(110); surface reconstruction

## 1. Introduction

Several earlier studies report on a pronounced or even dramatic enhancement of hydrogenation activity due to small amounts of oxygen present on metal catalyst surfaces [1–4]. Up to now it is not clear whether structural effects (e.g., surface reconstruction) or chemical interaction or even both are responsible for this behaviour.

Copper is an essential component of catalysts for methanol synthesis from CO and hydrogen [5]. So it seemed worthwhile to study the influence of oxygen on the adsorption states of CO on well-defined copper surfaces, like Cu(110), which has a rather open structure. The investigation of a single crystal surface allows furthermore to monitor structural changes.

In a preceding investigation the influence of preadsorbed oxygen on the adsorption of carbon dioxide on Cu(110) was studied by thermal desorption spectroscopy (TDS) [6,7]. As $CO_2$ dissociates to a small extent even on oxygenated Cu(110) some features in the TD spectra might be due to the interac-

tion of CO with adsorbed oxygen. This was an additional motivation to study the CO/oxygen/copper system. Finally, it should be mentioned that in the course of catalytic CO hydrogenation, giving methanol over copper containing catalysts, adsorbed $CO_2$ (or $CO_2^-$) formed from CO and adsorbed oxygen is assumed to be a precursor of the formate intermediate ($HCOO^-$) [8,9].

## 2. Experimental

Copper single crystals were cleaned by repeated sputter/heating cycles and $CO(H_2)$ reduction. Structure and chemical composition of the surface were monitored by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). No contaminations could be detected by AES on Cu(110) single crystal faces after the cleaning procedure.

At background pressures of less than $10^{-8}$ Pa the sample could normally be cooled down to 85 K. By reducing the pressure over the liquid nitrogen reservoir of the sample holder a temperature of 70 K could be reached and held for about 30 min. Exposures of the sample to oxygen and carbon monoxide were performed at pressures between $10^{-4}$ and $10^{-6}$ Pa and at different temperatures. 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.

Adsorption of $CO_2$ was performed with $C^{18}O_2$ ($m = 48$) so that mass 30 was monitored during the subsequent desorption of $C^{18}O$. This measure was taken to eliminate the contribution of background $C^{16}O$.

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].

CO adsorption on Cu(110) also induces a p(2 × 1) pattern. The TDS peak area of the fully developed p(2 × 1) structure ($\Theta = 0.5$) was then used as coverage calibration for TDS.

While oxygen is known to occupy the long-bridge sites in the reconstructed p(2 × 1) structure [11], CO adsorbs into the four-fold coordinated sites between the rows [12].

## 3. Results

In order to test and calibrate the experimental set-up, adsorption of CO on clean Cu(110) was reinvestigated.

Due to differential pumping of the mass spectrometer the background level was markedly reduced compared to the former investigation [13] and also the

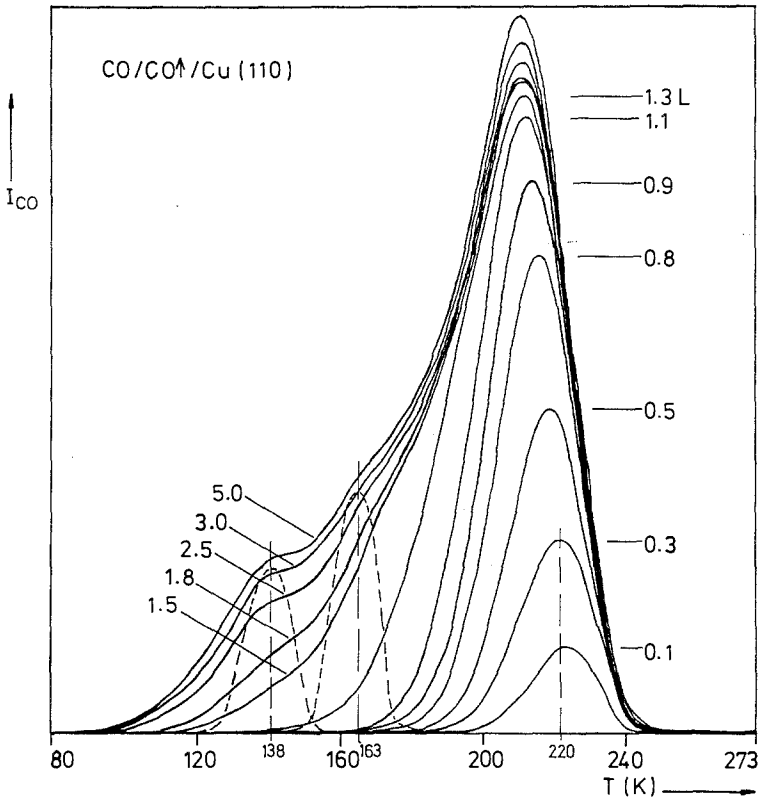


Fig. 1. Coverage dependence of CO desorption from clean Cu(110). Thermal desorption of CO from clean Cu(110) after different CO exposures (0.1–5.0 L) at 85 K.

exposure temperature that could be reached was appreciably lower (85 versus 110 K). Owing to these improvements a structure consisting of at least two overlapping peaks could be made visible in the broad low temperature tail of the TD spectra as shown in fig. 1.

In addition to the two states at about 138 and 163 K the broadening of the main peak at the low temperature edge is seen, indicating the compression of the CO molecules at the surface at higher coverages. Evidence to the latter process is also given by the coverage dependent desorption energy which decreases from 53 to 42 kJ/mol with increasing CO coverage above $\Theta_{CO} = 0.35$.

In the following series of spectra the influence of preadsorbed oxygen on the adsorption of CO was studied. While oxygen was preadsorbed in increasing amounts (0–10 L) at 300 K, the subsequent CO exposure was constant (5 L in all runs) and performed at 85 K.

Fig. 2 reveals the almost total suppression of the "normal" clean-surface CO state at 220 K. No $CO_2$ desorption could be observed. At oxygen exposures greater than 2 L the 160 K peak is also reduced while the 135 K peak seems to be shifted to 120 K and slightly enlarged. The total CO coverage diminishes

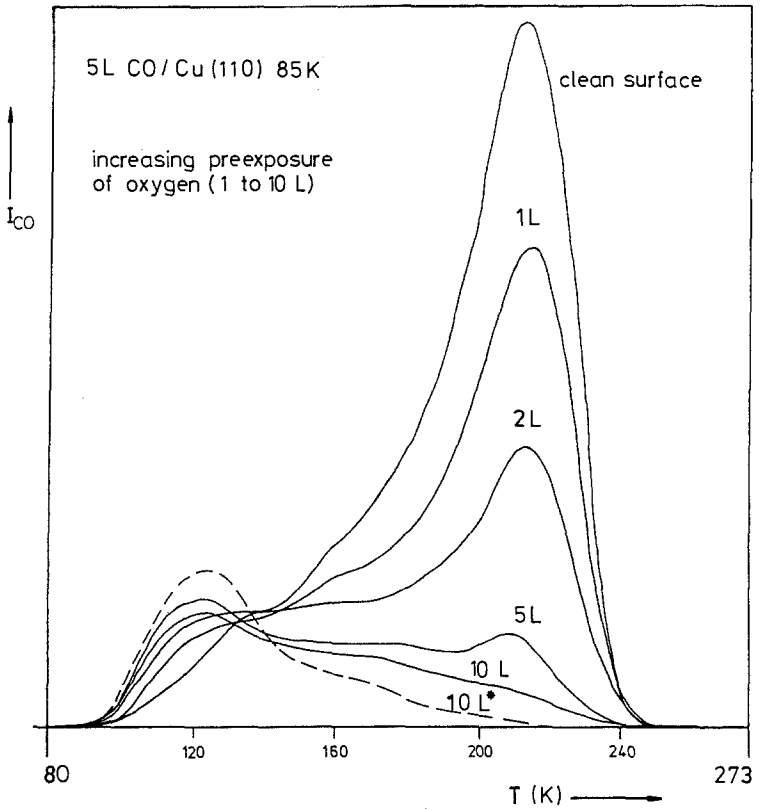


Fig. 2. Thermal desorption of CO from Cu(110) in dependence on oxygen preadsorption. 5 L CO at 85 K for all curves; preadsorption of 1–10 L oxygen at 300 K, except for curve 10 L* which was exposed to 10 L oxygen at 600 K.

from 0.7 to 0.2 and the sticking coefficient from 0.45 to almost 0.01 at $\Theta_{CO} = 0.2$. By selecting an intermediate oxygen coverage of $\Theta_O \approx 0.35$ and increasing the CO dose step-wise it was possible to fill and develop successively the different adsorption states as demonstrated by fig. 3. Before the peak at about 160 K (here with maximum at 155 K) completely develops it starts overlapping with the 120 K peak. Most probably an interaction between CO and oxygen takes place on the surface as the low temperature states develop in the presence of oxygen. But nevertheless, still CO is released in the TD runs and not $CO_2$.

As $CO_2$ is known to partly dissociate even on oxygenated copper surfaces [6,7] exposure and adsorption of $CO_2$ might yield analogous states as CO exposure on this surface. Therefore $CO_2$ was exposed at 85 K to a Cu(110)-p(2 × 1)O surface and subsequently CO desorption from this surface was followed. The result for increasing $CO_2$ exposures is shown in fig. 4. For comparison CO desorption from a CO exposed (5 L) Cu(110)-p(2 × 1)O surface is also shown in fig. 4 (dashed curve), revealing a close similarity to the $CO_2$ induced CO states,

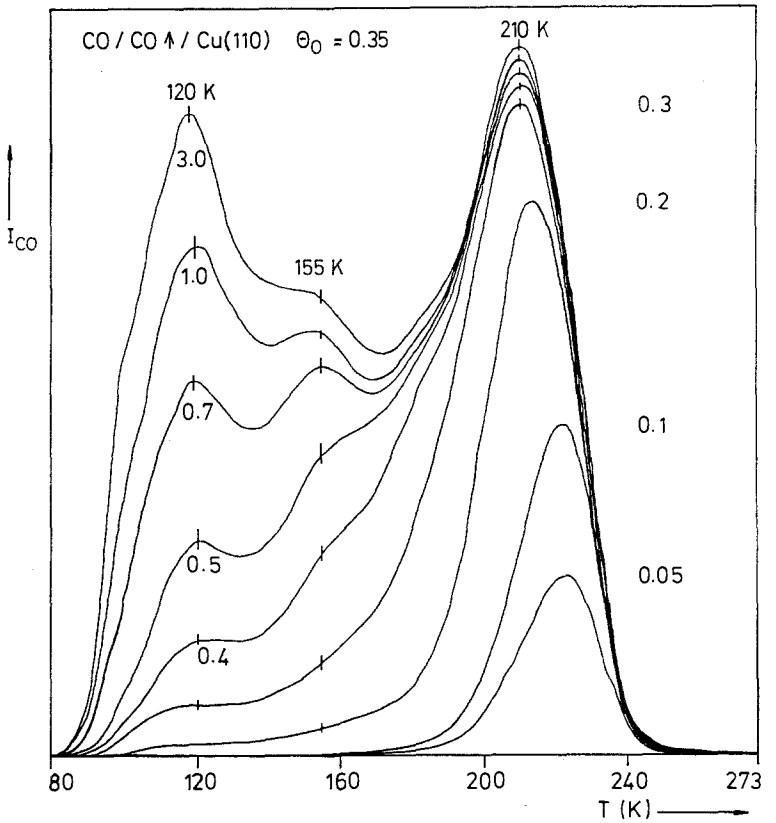


Fig. 3. Coverage dependence of CO desorption from oxygenated Cu(110). Thermal desorption of CO from oxygenated Cu(110) ($\Theta_O = 0.35$) in dependence on CO dose (0.05–3.0 L).

but with a much higher population of CO releasing sites (reduction factor 0.3 !), as a much higher amount of CO was admitted (5 L) compared to pure $CO_2$, with only a small degree of dissociation on the oxygenated surface [6,7]. Noteworthy is the total congruence of the 120 K peak for either CO or $CO_2$ exposure and the shift of the 160 K peak to 170/176 K in the presence of $CO_2$.

## 4. Discussion

The results presented above reveal a marked reduction of CO adsorbed in fourfold sites [12] on Cu(110) ($T_p = 220$ K) by preadsorbed oxygen and a slight reduction of binding energy ($T_p \approx 195$–$210$ K), but they also demonstrate the development of oxygen induced sites with markedly lower binding energy and density for adsorbed CO. The experimentally observed TD-peak temperatures for CO desorption from differently pretreated Cu(110) surfaces are summarized in table 1.

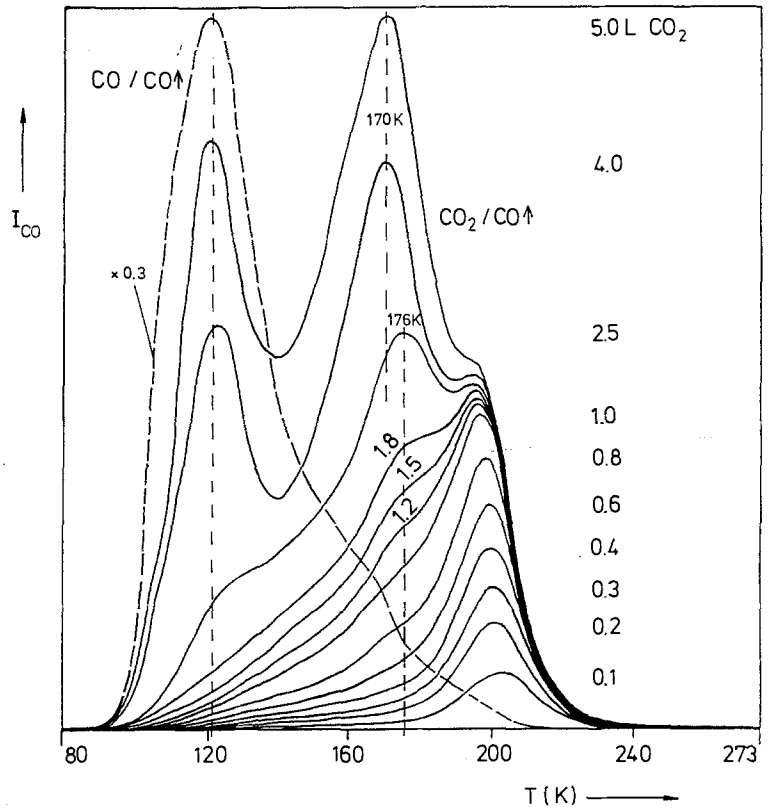


Fig. 4. Comparison of CO desorption following either CO or $CO_2$ exposure. Full lines: thermal desorption of CO from Cu(110)–p(2×1)O in dependence on $CO_2$ exposure (0.1–5.0 L $CO_2$). Dashed line: thermal desorption of CO from Cu(110)–p(2×1)O after exposure to 5 L CO (diminished by a factor of 0.3 compared to full lines). Note the shift of the 160 K peak to higher temperature (170 to 176 K) in the presence of $CO_2$.

Table 1
Peak temperatures (K) of CO desorption from different Cu(110) substrates after CO or $CO_2$ exposure

| System | $T_p(1)$ | $T_p(2)$ | $T_p(3)$ | $T_p(4)$ |
|---|---|---|---|---|
| CO/CO; Cu(110), clean | 220 | 163 | 138 | |
| CO/CO; Cu(110)–oxygenated, $\Theta_O = 0.35$ | 210 | 155 | 120 | |
| CO/CO; Cu(110)–p(2×1)O, $\Theta_O = 0.5$ | ≈196 | ≈160 | ≈120 | |
| $CO_2$/CO; Cu(110)–p(2×1)O, $\Theta_O = 0.5$ | ≈196 | 170–176 | 123 | |
| $CO_2/CO_2$; Cu(110)–p(2×1)O, $\Theta_O = 0.5$ [a] | – | – | ≈134 low, broad | 100 main peak |

[a] $CO_2$ desorption (from ref. [6]).

A straightforward interpretation of the type of adsorbed species is not yet possible. Further investigations by other methods than TDS are necessary.

Making use of XPS [14], LEED [10], STM [15], EELS/ARUPS [11] results from the literature and a SIMS result obtained in this study and by speculating a bit, one might attribute the different adsorption states tentatively as follows: oxygen adsorbs on Cu(110) into the long-bridge sites [11] up to $\Theta_O = 0.5$ forming a $p(2 \times 1)$ overlayer structure [10] composed of added rows [15] which give rise to the formation of Cu(111) micro-facets. Fourfold coordinated sites of the second copper layer, which are the preferred sites for CO adsorption will thereby be partly or completely removed, depending on the oxygen coverage. This process is responsible for the decrease of the "normal" 220 K CO desorption peak from clean Cu(110). The 220 K peak not only diminishes in area but also shifts to lower temperatures, finally down to 196 K (see table 1). This may be due to a collective electronic influence of chemisorbed oxygen ($O^-$) or just to an enhanced compression of CO molecules in the remaining unreconstructed Cu(110)–$(1 \times 1)$ islands.

As oxygen preadsorption induces the formation of Cu(111)-facets and as Kirstein et al. [16] observed a broad multiple peak between 150 and 170 K and a double peak between 120 and 130 K when desorbing CO from Cu(111) surfaces, the peaks at 120 and 155 to 160 K (figs. 2–4) might primarily be attributed to CO desorption from these facets. Probably, this interpretation holds for the larger part of desorbing CO molecules after CO exposure.

CO desorption after $CO_2$ exposure yields very similar patterns compared to those following CO exposure (see comparison in fig. 4) but with markedly reduced intensity (about one fifth). Furthermore the CO induced peak at 160 K is shifted to higher temperatures (170–176 K) in the $CO_2$ induced spectrum. Copperthwaite et al. [14] reported XPS spectra, which were obtained after $CO_2$ interaction with Cu(211). Up to at least 130 K they did not observe any indication of CO in the spectra. The situation on Cu(211) will be different, but the formation of $CO_2^-$ from CO and $O^-$ adsorbed on Cu(110) might also occur if CO adsorbs into the fourfold coordinated sites of the third layer with adjacent oxygen in the long bridges.

$CO_2^-$ is a labile species from which CO might desorb by decomposition at 120 K leaving $O_{ad}^-$ at the surface (figs. 2–4). $CO_2^-$ can be stabilized in the presence of abundant adsorbed $CO_2$ by forming solvated clusters according to theoretical calculations [17]. The smallest cluster would be $[CO_2 \cdot CO_2]^-$ from which CO and $CO_2$ could desorb at 170–176 K by dissociation leaving again $O^-$ at the surface (fig. 4, full line). But one might also consider the intermediate formation of $CO_3^-$ by disproportionation of the cluster as suggested by Copperthwaite et al. [14],

$$[CO_2 \cdot CO_2]^- \xrightarrow{160\ K} CO_3^- + CO\uparrow$$

and the subsequent decomposition of $CO_3^-$ at somewhat higher temperature

$$CO_3^- \xrightarrow{176\ K} O_{ad}^- + CO\uparrow .$$

This sequence would explain the broad peak around 170–176 K (fig. 4) under which the smaller 160 K peak is buried and would also be in agreement with the XPS data [14] if compared with values for carbonate [18].

In a preliminary SIMS experiment ions with the mass 135 and 137 were detected (with the ratio $I_{135}/I_{137}$ corresponding to the natural isotope ratio of $^{63}Cu/^{65}Cu$) after interaction of $CO_2$ with Cu(110)–p(2 × 1)O. These masses correspond to a cluster $[^{63/65}Cu \cdot CO \cdot CO_2]$, which might well be generated from the $[Cu \cdot CO_2 \cdot CO_2^-]$ cluster by ion impact dissociation due to the low stability of $CO_2^-$. On Ni(110) Freund and co-workers [19] observed the transition from stretched $CO_2$ to bent $CO_2^-$ with increasing temperature (above 100 K). So this bent $CO_2^-$ might be the precursor for dissociation on Cu(110).

The results presented here for Cu(110) are in agreement with results of the XPS study by Copperthwaite et al. [14] of $CO_2$ interaction with Mg(0001), where $CO_{ad}$ and $CO_{3(ad)}$ are observed, resulting from disproportionation of the $[CO_2 \cdot CO_2^-]$ cluster. But the pathway for subsequent $CO_3^-$-dissociation yielding $CO\uparrow$ and $O_{ad}^-$ on Cu(110) is obviously another one than that observed for polycrystalline copper, Cu(211) and Mg(0001), for which carbon ($C_{ad}^0$) and surface oxide are observed, according to [14]

$$CO_3 \rightarrow C_{ad}^0 + \text{“oxide”}.$$

The small peaks at 138 and 163 K which develop on “clean” Cu(110) after higher exposures (fig. 1) were not mentioned yet. They might be due to residual oxygen on the surface, following the same arguments as above. But with respect to the deviation of the 138 K peak from the oxygen induced peak (120 K) and the rather large amount of oxygen, which would be necessary to explain these peaks (we were unable to detect this amount of oxygen by RF-Auger) it seems more likely, that CO molecules – after having filled the grooves on the (110) surface – adsorb on short-bridge sites and on on-top positions on this surface, giving rise to these two additional peaks.

In conclusion, CO adsorption into fourfold sites of the second Cu layer of Cu(110) is markedly reduced in number and slightly in binding energy by preadsorbed oxygen. New sites at Cu(111) micro-facets are formed by oxygen induced surface reconstruction. Furthermore interaction of CO with $O_{ad}^-$ and/or $CO_2$ may give rise to further adsorption states.

We are well aware that our interpretations are highly speculative and need more substantiation by other methods.

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