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Poisoning and non-poisoning oxygen on Cu(410)

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Abstract

We have investigated ethene and oxygen co-adsorption on Cu(410) by high resolution electron energy loss spectroscopy. We find that these two species compete for the adsorption sites and that pre-exposure to oxygen affects ethene adsorption more or less strongly depending on oxygen coverage and the kind of occupied sites. The $c(2 \times 2)$ O overlayer is inert with respect to ethene adsorption, while when some oxygen is removed by thermally induced subsurface incorporation, ethene chemisorption is restored. The latter species also adsorbs on the disordered oxygen phase formed when O₂ is dosed at low crystal temperature. Contrary to the bare surface case, most of the ethene ends up in a π -bonded configuration. Dehydrogenation occurs, too, albeit as a minority channel. The so-produced carbon reacts already at low temperature with adsorbed oxygen to yield carbon monoxide, which desorbs around 190 K.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The importance of surface defects for the understanding of catalytic properties of metals has become more and more evident [1]. Recent studies show that in their presence both CO adsorption [2] and decomposition [3] occur, even on gold. Similarly, ethene was demonstrated to be stabilized at the open step edges of Ag(410) [4], its adsorption energy being three times larger than at (100) terraces [5]. The interest in ethene adsorption on metals is motivated by its importance for hydrocarbon chemistry and for related technological applications. It is known from previous work that π -bonded ethene adsorbs reversibly at low Miller index Cu surfaces [6–8]. However, recent studies have shown [9–11] that on Cu(410) not only di- σ bonding, but also complete dehydrogenation occurs at low crystal temperature (T). The carbon resulting from dissociation decorates the step edges and deactivates them. After saturation of such sites, only π -bonded ethene is observed and the probability of dehydrogenating

further C₂H₄ molecules decreases significantly. Interestingly the crystal reactivity can be restored by annealing to $T = 900$ K, at which temperature most of the carbon moves subsurface. Terraces must be involved in these processes since neither di- σ bonding nor dehydrogenation take place on Cu(210) [12], characterized by the same step geometry but by narrower (100) terraces.

The adsorption of ethene on different oxygen pre-covered surfaces is interesting because of the long-standing question of what determines the unique selectivity for the ethene epoxidation reaction of Ag. It is known from previous work that π -bonded ethene is present on oxygen-covered Pt(111) [13], Pd(100) [14], Ag(110) [15], Ag(100) [15] and Cu(110) [8]. This apparent simplicity hides, however, a more complex scenario. In fact, on Ag oxygen favors ethene adsorption increasing the attained coverage and the sticking probability, while on Pt and Pd it prevents adsorption in the more strongly bound di- σ state [16] because of the oxygen-induced withdrawal of the electrons from the metal substrate. On Cu(110) the situation is more complex. In the absence of oxygen a π -bonded species is present for exposures lower than 0.2 l and a tilted moiety (desorbing below 160 K) at higher exposure, while on (2×1) -O/Cu(110) only a π -bonded species

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is present, characterized by a dominant wag mode and with a heat of adsorption of 32 kJ mol^{-1} [8].

Oxygen adsorption on copper was intensively studied by different surface science techniques [17–34] due to the importance of this material for catalysis [35] and for the prospective applications in microelectronics.

On Cu(100), oxygen adatoms vibrate with an energy of 42 meV on the unreconstructed surface, on which they occupy the fourfold hollows, and at 36 meV when the substrate undergoes a missing row reconstruction, corresponding to an atomic O coverage $\Theta = 0.5 \text{ ML}$ [36, 37]. On Cu(110), O forms added rows and vibrates at 47.5 meV for $\Theta = 0.25 \text{ ML}$ and at 48.9 meV for $\Theta = 0.5 \text{ ML}$ [38]. Disordered adatoms were reported to vibrate at 55 meV [39].

On Cu(111) the $\nu(\text{Cu-O})$ mode was observed between 45 and 48 meV in the temperature range $100 \text{ K} < T < 230 \text{ K}$ [40] while it decreases to 30 meV when the exposure is performed at $300 \text{ K} < T < 450 \text{ K}$ [41, 42]. Dubois [41] suggested that this weak peak is associated with oxygen atoms sitting at threefold hollow sites with a small adsorption height. The higher frequencies recorded at low T for (110) and (111) disordered phases indicate that the oxygen adatoms are in lower coordination sites such as the bridge sites.

Cu(410)-O displays different vibrational frequencies at different surface temperatures as well [17]. At high coverage and low T the energy loss is at 46 meV, indicating the occupation of bridge sites at the step edge and most probably also at the terraces. Upon annealing, the oxygen frequency moves irreversibly to 34 meV, close to the value observed for the missing row reconstructed Cu(100)-O surface. Thus this site corresponds most probably to the occupation of the long bridge (LB) site at the step. Finally, when dosing O_2 at high temperature, an ordered $c(2 \times 2)$ phase forms at $\Theta = 0.5 \text{ ML}$, corresponding to the appearance of Cu-O chains at the step edge and to the occupation of fourfold hollow sites at the terraces. A single O-Cu loss is then observed at 38 meV and ascribed to the unresolved stretch modes of the O adatoms at the two non-equivalent adsorption sites. In the absence of promoters no further losses corresponding to subsurface or oxide phases form, contrary to the case of low T oxidation of Ag [43–45]. On K-pre-dosed Cu(111) a loss at 57–61 meV was also observed and assigned to subsurface oxygen [46].

In this paper we investigate the adsorption of ethene on different oxygen phases forming on Cu(410) at low temperature by high resolution electron energy loss spectroscopy (HREELS), with the aim of determining the effect of oxygen pre-adsorption on ethene chemisorption.

2. Experimental details

The experimental UHV system (base pressure $\sim 5 \times 10^{11} \text{ mbar}$) is equipped with a home-built HREEL spectrometer, a low-energy electron diffractometer (LEED), a cylindrical-mirror analyzer for Auger spectroscopy, an ion gun for *in situ* sample preparation and a four-degrees-of-freedom manipulator. In the present set-up the sample can be heated to 900 K by electron bombardment and cooled down to the minimum temperature of 145 K by liquid N_2 . HREEL spectra were recorded using

specular detection at an incident angle of $\sim 67^\circ$ and low incident electron energy ($E_0 = 2.9 \text{ eV}$). Different ethene coverages were produced upon exposure at $T = 145 \text{ K}$. The HREEL spectra were recorded after heating the sample to the indicated temperature and cooling it back to $T \sim 145 \text{ K}$.

The Cu(410) single crystal is a 10 mm diameter disc, oriented with an accuracy of 0.1° . The sample surface geometry consists of three-atom-row wide (100) terraces alternated with monatomic steps running in the $\langle 001 \rangle$ direction and thus showing an open geometry. The surface was prepared by cycles of sputtering with Ne^+ ions followed by annealing for 3 min at 900 K, until spectra indicative of the clean surface were observed in HREELS. Ethene and oxygen exposure were performed by backfilling the vacuum chamber. The exposure, expressed in monolayers of Cu(410) ($1 \text{ ML} = 1.58 \times 10^{15} \text{ atoms cm}^{-2}$), is obtained as a product of the pressure increase and the duration of the dose.

3. Results

3.1. C_2H_4 on bridge-bonded oxygen

Figure 1 shows the HREEL spectrum measured after an ethene exposure of 0.36 ML on O/Cu(410). This oxygen phase was obtained with an O_2 exposure of 1.8 ML at 150 K. The corresponding spectrum is reported in figure 1(b): the broad energy loss peaked at $\sim 42 \text{ meV}$ indicates dissociative O_2 adsorption with the formation of a disordered oxygen adlayer in which adatoms occupy both the fourfold hollows of the (100) terraces [36, 37] and bridge sites at the step [17, 39]. When dosing O_2 at normal incidence at a translational energy of 90 meV the initial sticking probability is ~ 0.2 and depends little on the angle of incidence [47]. Due to the rapid decrease of sticking probability with coverage and temperature, we can estimate that, after an exposure of 1.8 ML by backfilling, the O coverage should not exceed 0.1 ML. The spectrum recorded after exposing a bare Cu(410) surface (i.e. not pre-covered with oxygen) to 0.36 ML of ethene is also shown in figure 1(a). For ethene the sticking probability is nearly independent of coverage [11] and is of the order of ~ 0.5 for backfilling conditions, from which coverage is estimated to be about $\sim 0.2 \text{ ML}$. From comparison with the reference spectra mentioned above (figures 1(a) and (b)) it is evident that, on an oxygen pre-covered surface, all the peaks due to ethene are relatively more intense and redshifted with respect to the bare surface case, with the only exception of the wag mode (117 meV, figures 1(a) and (c)). The O-Cu loss at 42 meV, on the contrary, decreases in intensity and becomes a shoulder of the 48 meV peak. Figures 1(d) and (e) report the evolution of the HREEL spectra with temperature.

All the observed losses can be associated with modes of π -bonded ethene (see table 1 for a detailed assignment), except for the Cu-O vibration at $\sim 42 \text{ meV}$ and for the Cu-C stretch at 48 meV (figure 1(a)) [10]. In agreement with this assignment the latter peak is still present after annealing the surface to 204 K.

After C_2H_4 exposure on the O-covered surface the ethene-related peaks vibrate at 117 meV, 155 meV, 190 meV, 370 meV and 379 meV, respectively. Their intensity decreases

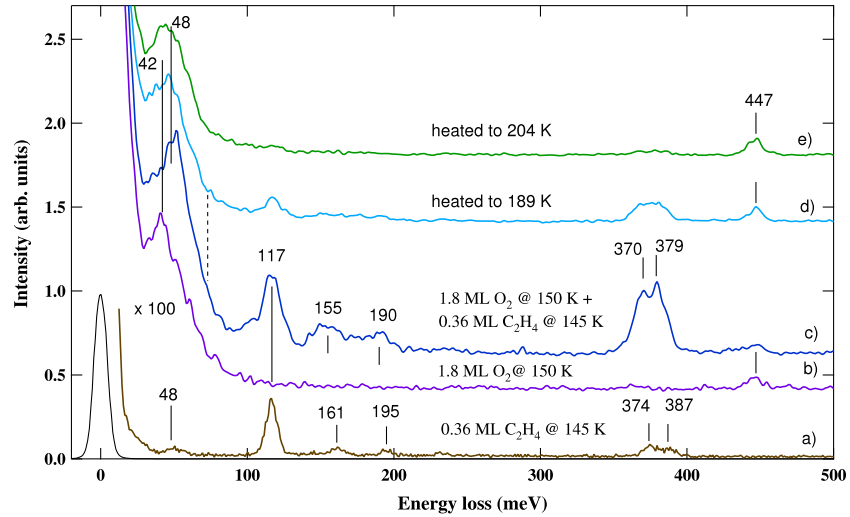


Figure 1. Normalized HREEL spectra measured in-specular under different conditions: (a) after exposure of the bare Cu(410) surface to 0.36 ML of ethene, (b) after dosing 1.8 ML O₂ at 145 K, (c) after adding 0.36 ML of ethene, (d) and (e) are recorded after annealing the sample to 189 and 204 K. The spectrum recorded after exposure of the bare surface to 0.36 ML of ethene is also shown in (a).

Table 1. Ethene vibrational modes measured on bare and oxygen-pre-covered Cu(410) in comparison to previous investigations on the low Miller index Cu surfaces. Gas-phase values are also reported [52]. (Note: * and ** denote the frequencies reported for two different C₂H₄ adsorption states on Cu(110). Such states correspond in both cases to tilted configurations reached for exposures smaller (*) and larger (***) than 0.1 L, respectively.)

Vibration mode loss energy (meV)	Bare Cu(410)	Cu(410)/O ₂ in bridge sites	Cu(410)/O ₂ subsurface	Cu(100) [7]	Cu(110) [8]	Cu(110)/(2 × 1)-O [8]	Cu(111) [6]	Gas [52]
Cu-C	48	50	48					—
CH ₂ rock, ν ₁₀							102	102
CH ₂ out-of-plane wagging, ν ₇	117	117	116	112	112*	119	112	118
CH ₂ scissors, ν ₃	161	155	160	160	158*	156**	156	166
CH ₂ scissors, ν ₁₂							179	179
C=C stretch, ν ₂	195	190	193	193	189**		201	201
First overtone of the CH ₂ wagging mode, 2ν ₇	230		227	226				—
CH ₂ symmetric stretching, ν ₁	374	370	370	371			370	375
CH ₂ asymmetric stretching, ν ₉	387	379	383				382	385

upon annealing to 189 K and vanishes at 204 K, where only the 48 meV peak remains in accord with our previous investigations [9]. The weak loss at 447 meV present on the O-covered surface is due to OH resulting from dissociative water adsorption from the background during O₂ exposure.

Since no additional features form as a result of heating, we can conclude that either no reaction has occurred between oxygen and ethene or that the reaction products have desorbed. At variance with the results for bare Cu(410) [9] there is no evidence of the presence of di-σ-bonded ethene.

3.2. C₂H₄ in presence of an ordered oxygen overlayer

As already explained in the introduction, it is known from our previous investigations that the loss at 38 meV is the signature of an ordered oxygen overlayer consisting of Cu-O chains at the step edge and of additional oxygen adatoms at the terraces [17]. In our experiments this layer was obtained

when a sample pre-exposed to 260 ML of oxygen at room temperature was annealed to $T = 900$ K. A typical HREEL spectrum recorded at $T = 145$ K after this treatment is shown in figure 2(b). When this surface was exposed to 0.36 ML ethene at 145 K no significant changes are observed in the spectrum (figure 2(c)), indicating a total passivation of the surface. The spectrum recorded after an identical C₂H₄ dose on bare Cu(410) is also shown in figure 2(a) for comparison.

3.3. C₂H₄ in presence of subsurface oxygen

If the oxygen layer obtained after dosing 260 ML of O₂ is held at 900 K for 8 min the layer evolves into a phase exhibiting only a weak loss at 37 meV (figure 3(b)). Since, in agreement with the literature [31], no recombinative desorption of O₂ is observed, most of the O atoms must have penetrated into the subsurface region [17], although we did not observe any loss in the energy range expected for subsurface oxygen (57–61 meV)

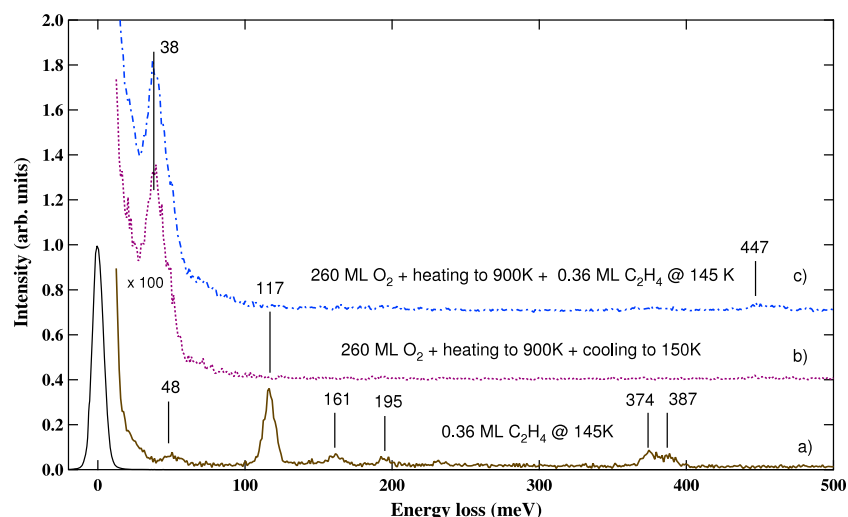


Figure 2. Normalized HREEL spectra recorded in-specular after: (a) exposure of the bare Cu(410) surface to 0.36 ML ethene at 145 K, (b) exposure of the bare surface to 260 ML O₂ followed by a flash to 900 K and cooling back to 150 K and (c) exposure of the surface in (b) to 0.36 ML ethene.

that was observed in the presence of alkali promoters [46]. Figure 3(c) shows normalized HREEL spectra measured after dosing 0.36 ML of ethene on the so-prepared surface. Ethene adsorption occurs, but the intensity of the ethene modes is lower compared to the one observed for the same dose on the bare surface (figure 3(a)) while all modes are slightly redshifted. The peak at 37 meV is obscured by a more intense loss at 48 meV. When the layer is annealed to 189 K (figure 3(d)) the intensity of the ethene modes and that of the 48 meV peak decreases while the 37 meV loss reappears. A weak loss at around 260 meV is now present, indicating CO formation. Further annealing to 204 and 300 K (figures 3(e) and (f)) causes the total disappearance of the ethene peaks and a further intensity reduction of the low frequency features.

4. Discussion

Based on a previous HREELS investigation of oxygen adsorption on Cu(410) the assignment of the losses due to oxygen is as follows: the peak at 42 meV is due to O adatoms at terraces [36] while the peak at 38 meV is the signature of the formation of the $c(2 \times 2)$ O structure. Annealing this layer to $T = 900$ K for a sufficiently long time (8 min in the present study) the intensity of the mode decreases and slightly redshifts to 37 meV. Since no O₂ desorption is observed we conclude that the decrease of the oxygen peak intensity is due to subsurface incorporation of the oxygen atoms.

The assignments of the HREELS peaks due to ethene are summarized in table 1 together with selected results from the literature. Redshifts of all peaks (except the wag mode) are observed when dosing ethene on oxygen-pre-covered Cu(410), whose magnitude depends on the oxygen bonding sites.

We tentatively explain the missing redshift for the wag mode as follows. For π -bonded molecules at flat surface areas this mode has a much higher dipole activity than for the other modes. The latter are, on the contrary, more easily observed in the presence of defects such as steps and co-adsorbates. For a low coverage disordered oxygen overlayer (conditions

of figure 1(b)) ethene molecules can be adsorbed both close to and further away from the oxygen adatoms. The former are expected to behave as on the bare Cu(410) surface and thus to give rise to an intense wag mode with a modest contribution of non-dipole active modes. Molecules close to O adatoms give rise, on the contrary, to intense modes at higher energies, redshifted with respect to adsorption on the pristine surface because of the interaction with oxygen. Since the O coverage is low most ethene molecules are at pristine surface sites and their wag mode dominates the HREELS signal at 117 meV. In accord with this interpretation this loss is clearly broader than for the pristine surface due to redshifted contributions of molecules close to O. The intensity observed for the high frequency modes arises, on the contrary, mostly from ethene molecules located close to oxygen adatoms.

This effect may arise either because such molecules are tilted with respect to the surface plane, thus causing the higher frequency modes to become dipole-active [8], or by reducing the O-induced disorder reduction of the specular intensity which makes impact scattering relatively more important [48]. In accord with an oxygen-induced redshift of all losses we observe reduced frequencies for all modes, including the wag mode, when the surface is loaded with subsurface oxygen by high temperature oxygen treatment (see figure 3). In this case, however, the surface is well ordered and the specular reflectivity is high. The wag mode of the ad molecules therefore dominates because of its dipolar activity showing the redshift induced by oxygen which affects all molecules due to its large (subsurface) coverage.

The data indicate that, when the oxygen layer is disordered, reactive sites remain available for ethene adsorption (figure 1). Since dipole coupling should cause a blueshift (contrary to experimental evidence) of the modes and possibly also a decrease of their intensity due to depolarization, we ascribe the changes in relative intensity of the ethene modes to the different adsorption configurations. Because of the dipole-scattering selection rule for metal surfaces [49] the large

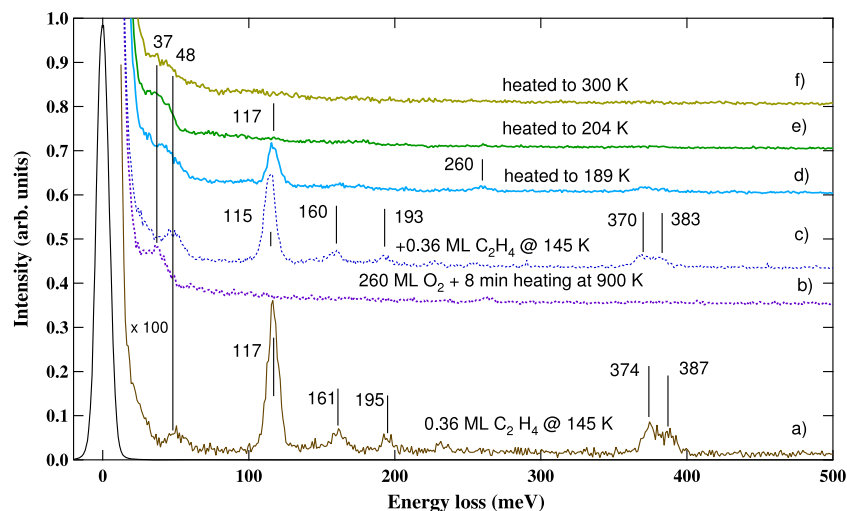


Figure 3. Normalized HREEL spectra recorded in-specular after: (a) 0.36 ML ethene uptake on the bare surface at 145 K, (b) 260 ML of O_2 at 300 K followed by annealing at 900 K for 8 min (thus resulting in the population of subsurface sites), (c) additional exposure to 0.36 ML of ethene at 145 K and (d)–(f) annealing to increasing temperatures.

difference in the relative intensities of the scissor and of the CC stretch modes between the O-covered and the bare surface indicates a tilted configuration of the ethene molecule. This assignment is supported by the anomalously high intensity of the CH stretch modes with respect to the bare surface.

The peak at 48 meV indicates ethene dehydrogenation and carbon formation. We mention that, after prolonged ethene exposure on the bare Cu(410) surface at low T , a weak loss at 73 meV was detected in HREEL spectra ([10] not shown). Such a feature, which disappeared during subsequent annealing, was assigned to atomic hydrogen resulting from ethene dehydrogenation. The data indicate therefore that some C_2H_4 dissociation takes place already at 145 K even if the incoming ethene molecules impinge with thermal energies.

Upon annealing the C produced by ethene dehydrogenation reacts with adsorbed oxygen atoms leading to CO formation. Such CO is stable on the surface up to 189 K. The latter is slightly larger than the one reported for the low Miller index Cu surfaces [39] due to the stabilization of CO occurring at the steps of the Cu(410) surface. Direct reaction of ethene with oxygen can be excluded since additional losses would be expected after its occurrence, contrary to experimental evidence. Indeed on Ag surfaces [50, 51] ethene oxide (EtO) is slightly more strongly bound than ethene and, since after annealing to 189 K some ethene is still present, the same should be true for EtO as well. Even the much more likely total oxidation can be excluded since in this case water and CO_2 should be produced. CO_2 would readily desorb due to its lower heat of adsorption; water should, however, either remain on the surface or react with oxygen to produce OH. In the former case additional losses should be present at around 100 and 200 meV while in the latter the intensity of the OH stretch mode at 447 meV should increase (see figure 1), contrary to experimental evidence.

In the presence of an ordered oxygen overlayer (figure 2) the situation is quite different: no losses at the vibrational frequencies of ethene are detected after exposure. The reactive

sites are now passivated by oxygen and the surface is inert with respect to ethene.

If the so-prepared oxygen layer is annealed for a prolonged time (before exposing it to ethene) most oxygen atoms penetrate into the subsurface region and only a faint loss at 37 meV survives (figure 3). Dosing ethene on such a surface leads to an intermediate situation. The intensity of the ethene modes is low compared to the bare surface, no enhancement of the scissor and CC stretch is observed and the redshift of the peaks is small, indicating possibly that the molecule is not tilted as was the case for figure 1. A careful inspection of the behavior of the spectrum in the low frequency region hints at what may have happened. The disappearance of the oxygen-related loss at 37 meV after ethene adsorption and its reappearance with a lower intensity after the desorption of the latter indicates that this mode is shielded by ethene adsorbing close to O.

The appearance of the mode at 48 meV after ethene dosing indicates the production of carbon arising from ethene dissociation. The intensity of the latter peak decreases and it merges with the oxygen peak upon annealing to 189 K. This behavior is similar to what was observed in the presence of the disordered oxygen phase and indicates the reaction of C with O to produce CO. This explanation is supported by the observation of a small loss at 260 meV after annealing at 189 K.

Finally, it is worth briefly commenting on the mutual role of steps and terraces. While for the bare Cu(410) surface the step enables di- σ -bonding configuration, this species is absent for the O-pre-covered surface, independent of the nature of chemisorbed oxygen. The inhibition of di- σ -bonding by pre-covered oxygen was reported previously also for the surfaces of other metals [13–15]. The (110)-like step is, on the contrary, essential for the occurrence of dehydrogenation, independently of the presence of co-adsorbed oxygen: no dehydrogenation was indeed ever reported for low Miller index Cu surfaces [9].

For the π -bonded state the presence of the step induces an increase in its desorption temperature compared to low

Miller index Cu surfaces [6–11]. However, due to the higher reactivity of Cu with respect to Ag surfaces [1], the change in the reactivity of the former, due to the presence of the step, is less dramatic than for the latter.

5. Summary

Adsorption of ethene was investigated on Cu(410) pre-covered by oxygen in three different bonding configurations: disordered adlayer, $c(2 \times 2)$ structure and subsurface site occupation. We find that:

- (1) Oxygen inhibits di- σ -bonding of ethene, but does not prevent C_2H_4 dehydrogenation. The so-produced carbon can react with the oxygen adatoms to form CO, which desorbs around 190 K.
- (2) For adsorption on disordered O layers the intensity of the losses due to π -bonded ethene is larger than for adsorption at the bare surface. This effect indicates a tilted adsorption configuration of the molecules adsorbed close to the O adatoms. Such molecules undergo a redshift of their modes.
- (3) The most stable bonding configuration of oxygen, the $c(2 \times 2)$ overlayer, completely inhibits ethene adsorption.
- (4) In the presence of subsurface oxygen ethene can adsorb and partially dehydrogenate. The carbon reacts with the residual O adatoms producing CO, which desorbs at 190 K. π -bonded ethene molecules are still present in a configuration similar to that of the bare surface, but with slightly redshifted frequencies.

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