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Article

Low temperature adsorption of CO on modified, vicinal Cu(100) surfaces: A comparative study

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ABSTRACT

The experimental results of the adsorption of CO on clean and potassium-modified vicinal Cu(100) surfaces at 125 K were presented. We studied three surfaces under identical experimental conditions. At 125 K, potassium forms disordered structure on vicinals and CO adsorbs only on sites not occupied by K. It was found that a small percent of the CO molecules dissociate on the stepped interfaces. The influence of steps dominates over pre-adsorbed alkali atoms at 125 K.

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1. Introduction

Investigation of the adsorption of molecules to vicinal surfaces is of considerable practical interest. Vicinal surfaces can be used as model systems to study the influence of steps and vacancies on surface reactions of adsorbing molecules [1,2]. Because of their lower coordination number, upper step atoms can be more reactive than other surface atoms. Modification of the interface by alkali metal adsorption gives models that are closer to real catalysts.

It is well known that CO molecules that adsorb on the Cu(100) surface are located on top of the substrate atoms with the C atom bonded to the metal [3–6]. Two ordered structures are observed at low temperature (80–130 K) saturation: the $(\sqrt{2} \times \sqrt{2})R45^\circ$ structure and the so-called “compressed phase” $c(7\sqrt{2} \times \sqrt{2})R45^\circ$, which correspond to coverages of 0.5 and $4/7 = 0.57$ substrate monolayers (SMLs) relative to the number of atoms of the substrate, respectively. The higher concentration in the compressed phase comes from antiphase domain walls, in which separation of CO on the top molecules is lower than in

the $(\sqrt{2} \times \sqrt{2})R45^\circ$ structure [3,7].

Adsorption of K on Cu at temperatures below 170 K (about half of the melting point of K) takes place without mixing of the atoms [8–10]. At close to full adsorbate monolayer (AML) coverage, where the adatom-adatom interaction dominates, the adlayer forms quasi-hexagonal or hexagonal structures. At low coverages, the adsorbate-substrate interaction dominates, resulting in the formation of a 2D gas (disordered arrangement) on the substrate. The stepped surfaces are similar because the size of the alkali atom is large enough not to “feel” the substrate irregularities [11]. The only difference is that K adatoms may be immobilized at the step edges, especially at the beginning of adsorption [12].

Here, we present the results of measurements of CO adsorption on Cu using a specially prepared sample with the presence of the three orientations (100), (119), and (115) [13]. The results of the measurements on these surfaces can be directly quantitatively compared with each other because the adsorption procedure is identical, thus avoiding the need to normalize the results of the separate experiments.

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2. Experimental

The experiments were performed in an ultrahigh vacuum chamber (base pressure $\leq 1.33 \times 10^{-8}$ Pa) of the beamline SX700 at the ASTRID storage ring, ISA, Aarhus, Denmark. Details of the equipment have already been published [14]. The Cu sample consisting of three vicinal surfaces to the (100) surface, namely, the (100), (119), and (115) surfaces, was mounted to the holder enabling cooling to around 120 K and heating above 1000 K. All of the procedures concerning degassing, cleaning, and annealing have been reported previously [13]. The observed low-energy electron diffraction (LEED) patterns of the clean surfaces are shown in Fig. 1.

K was deposited from a SAES Getters dispenser (SAES Group), which was mounted in front of the sample surfaces. The surface coverage of K (θ_K) was determined using the work function changes of the Cu(100) part of the substrate as a function of the K amount ($\Delta\Phi(\theta_K)$). The value at saturation corresponds to one atomic layer of potassium (i.e., $\theta_K = 1.0$ AML) [13]. The doses of CO were determined using indications of an ionization gauge (without sensitivity correction) and a typical dose of 1.0 Langmuir (L) was obtained with pressure $p = 1.33 \times 10^{-6}$ Pa after 100 s.

During K and CO adsorption, the sample was maintained at 125 K and we did not attempt to stabilize the interfaces to give good surface order. LEED images after adsorption of K and CO do not show qualitative changes. To achieve an ordered structure and well-defined diffraction pattern the sample should be

annealed at 200–250 K for several minutes.

Photoelectron spectra excited with synchrotron radiation (SR-PS) were measured with electron emission along the surface normal, and the photon beam incidence angle was 40° from the surface normal. Valence band (VB) spectra, containing the Cu 3d band, CO-derived features, and the K 3p peak, were registered using 40 eV photon energy and the binding energy (BE) was changed from 23 to -2 eV.

3. Results and discussion

Representative spectra of the more than 45 VB spectra obtained by photoelectron spectroscopy are shown in Fig. 2. The analysis mainly focused on the BE intervals of -1.5 to 6.5 eV (Cu 3d band) and 6.5 to 17.5 eV (CO-derived features). Figure 2 shows a typical spectrum synthesis of the CO-induced peaks for the Cu(115) surface after exposure of 1 L CO.

The total intensity of the CO-derived peaks increases with sample exposure. In the case of the Cu(100) surface, quantitative analysis of the $5\sigma/1\pi$ feature is difficult because of the presence of a satellite peak at a BE position of 8.35 eV. Starting from small exposures (< 1.0 L CO) and ending with 5 L CO, the intensity ratio of 4σ sat (satellite) to 4σ slightly changes. The value used here refers to the spectrum obtained for a saturated layer of CO. The adsorbate intensity is represented by only the area of the CO 4σ peak.

The intensity of the Cu 3d band almost uniformly decreases with sample exposure except in the 0–1.5 and 4–5 eV regions.

Fig. 1. LEED images of the clean surfaces under investigation.

Fig. 2. Series of valence band spectra obtained during adsorption of CO in the range 0–5 L on the Cu substrate and examples of peak synthesis of CO-derived features after exposure of 1 L CO. (1) Clean surface; (2) 0.1 L CO; (3) 0.2 L CO; (4) 0.5 L CO; (5) 1.0 L CO; (6) 5.0 L CO.

This behavior indicates redistribution in the Cu 3d band during CO adsorption. The area under the 3d band in the interval –1.5 to 6.5 eV was chosen as a good representation of the substrate intensity. The changes in intensity of the Cu 3d band and CO 4σ peak with CO exposure are shown in Fig. 3.

3.1. CO adsorption on the clean Cu surfaces

The photoemission results show that the adsorption of CO takes place with the same sticking coefficient for all three surfaces under investigation. After saturation of the interface by CO, the intensity of the Cu 3d band reached an average intensity of 0.76(2) with respect to the initial intensity. Assuming that the coverage of CO molecules at saturation is 0.57 SML, the electron escape depth of 36.9(1) eV photoelectrons through the CO adlayer is $0.57/\ln(1.0/0.76) = 2.08$ SMLs. In the course of the analysis, the Cu 3d band was divided into several contributions and the average value of the kinetic energy of the photoelectrons was calculated from the energy of its fragments with their intensity as the weighting factors. Because the electron escape depth will be used to determine the surface coverage from the ratio of the substrate peak intensity, in this case the SML units are more practical.

For the three substrates, the signals coming from CO molecules up to 1.0 L steadily increase and then become constant (saturate). The value of the intensity at saturation is different to the substrate and the relative (with respect to the Cu 3d intensity) values obtained were 0.264, 0.195, and 0.122 for the (100), (119), and (115) surfaces, respectively. The 4σ satellite to 4σ intensity ratio is practically the same for the three sub-

strates and equals to 0.58.

3.2. CO adsorbed on the K/Cu surfaces ($\theta_K = 0.40_{100}$ AML)

For the interface with pre-adsorbed K (0.40 AML), the area under the Cu 3d band decreases with exposure and at the saturated layer of CO molecules is 0.78(2) of the initial value (signal corresponding to the interface with K). This shows that free sites on the Cu substrates accept a smaller number of CO molecules compared with surfaces without K. Adsorption of CO also results in an increase of the K 3p signal by 1.53, 1.25, and 1.18 for the (100), (119), and (115) surfaces, respectively [11,15]. The behavior of the signal of the CO 4σ is similar to that of the surface without K. The relative (with respect to Cu 3d) intensity signals are 0.195, 0.137, and 0.092 for the (100), (119), and (115) surfaces, respectively. The 4σ satellite to 4σ intensity ratio is practically the same for the three substrates and equals to 0.34.

3.3. CO adsorbed to the K/Cu surfaces ($\theta_K = 0.65_{100}$ AML)

After saturation of the interfaces with CO, the intensity of the Cu 3d band is 0.85(2) of its initial value. Adsorption of CO also results in an increase of the K 3p signal by 1.63, 1.34, and 1.28 for the (100), (119), and (115) surfaces, respectively. The relative CO 4σ signal intensity (with respect to Cu 3d) are 0.168, 0.110, and 0.075 for the (100), (119), and (115) surfaces, respectively. The 4σ satellite to 4σ intensity ratio is practically the same for the three substrates and equals to 0.23. All of these analysis results are listed in Table 1.

Fig. 3. Relationship between normalized intensity and exposure of the Cu 3d band and CO 4σ feature obtained during adsorption of CO on clean and modified surfaces. (1) Cu(100); (2) Cu(119); (3) Cu(115).

Table 1

Results of analysis of the photoelectron spectra for the three interfaces under investigation.

K coverage	CO amount	Intensity of photoemission features	
		Cu 3d	CO (VB)
0	0.57 SML; saturation value for (100)	similar band attenuation, in av. 76(2)%	4σ intensity at saturation: $I(100) > I(119) > I(115)$; the same relative 4 satellite intensity, ~58%
0.40 ₁₀₀ AML	$\sim 0.60 \times 0.57$ SML = 0.34 SML	similar band attenuation, by CO in av. 78(2)%	4σ intensity at saturation: $I(100) > I(119) > I(115)$; the same relative 4 satellite intensity, ~34%
0.65 ₁₀₀ AML	$\sim 0.35 \times 0.57$ SML = 0.20 SML	similar band attenuation, by CO in av. 85(2)%	4σ intensity at saturation: $I(100) > I(119) > I(115)$; the same relative 4 satellite intensity, ~23%

3.4. Discussion

The photoemission intensity graph shows that the amount of adsorbed CO decreases with the presence of K on the surface. This is because the K ions block adsorption sites and CO cannot adsorb to K. Blocking of the surface sites occurs at both low and high K concentration, and where K has less ionic character. Most likely, at low temperatures potassium geometrically hinders the substrate and the interaction between the adsorbates has short-range character, mainly repulsive [16].

Because of this interaction, other adsorption sites for CO that are different to the “on-top” sites could be expected. For example, in the C 1s spectrum of the K/Cu(115) interface, peaks with lower BE were found, which represent the bridge and hollow sites [12]. While the adsorbate interaction on the Cu(100) surface at saturation ($\theta_{\text{CO}} = 0.57$ SML) leads only to tilting of the molecules adsorbed on top of the surface, the repulsive interaction between K and CO results in displacement of the molecules to other positions relative to the substrate atoms, similar to the Ru(001) [17] and Cu(111) surfaces [18]. Unfortunately, the CO orbitals in the valence band are not sensitive to the position of ad-molecules, and only the change in the line width of 4σ and $5\sigma/1\pi$ indicates these modifications.

It was also observed that the number of CO molecules at saturation decreases with increasing step density. The total densities of Cu atoms on the (100), (119), and (115) surface are 15.31×10^{18} , 16.81×10^{18} , and 17.67×10^{18} atom/m², respectively. If the Cu atoms lying directly under the step atoms are not taken into account, the ratio of (100):(119):(115) will be 15.31:13.44:11.78. The bottom step atoms are highly coordinated and hence are much less attractive sites for the adsorption of CO. Two explanations have been proposed for this effect: CO molecules are adsorbed mainly on the terraces and/or a small portion of CO is dissociated on the step atoms and does not contribute to the 4σ peak intensity [19–21].

The same order of the number of adsorbed CO molecules was also observed for the modified surfaces. The smaller attenuated signal of the substrate, which is normalized to unity at the beginning of gas adsorption, means that fewer CO molecules adsorbed at regions not covered by K. On the surfaces with pre-adsorbed K, the CO molecules tend to be sparsely adsorbed and there is no tilting of the CO molecules. Instead, a

decrease in the 4σ satellite intensity is observed compared with the pure surfaces. Owing to the fact that the photoemission signal is averaged over the region of analysis, the 4σ satellite signal is averaged over CO molecules from different adsorption sites. CO molecules that are weakly bound to the substrate have a 4σ satellite of relatively high intensity (50%–60% of the main peak) while those interacting with Cu have a relatively low 4σ satellite intensity ($\leq 30\%$). The number of CO molecules that strongly interact with the substrate increases with K present on the surface. The interaction of CO with K seems to be repulsive. The indirect substrate-mediated effects cannot be excluded, creating new adsorption sites as a consequence.

The 4σ – $5\sigma/1\pi$ peak separation, which is indicative of the substrate-CO bonding with a smaller separation indicating stronger bonding, suggested by the CO desorption temperature was not observed. The average 4σ – $5\sigma/1\pi$ peak separation is at the same level (3.35(10) eV) for all vicinal and K-modified surfaces.

4. Conclusions

Quantitatively, the Cu(100), Cu(119), and Cu(115) surfaces exhibit differences in the uptake of CO, both on the clean surfaces and on the K-modified surfaces, as observed in the photoemission spectra of Cu 3d and CO(4σ). K atoms block the on-top sites of the Cu surfaces that are available for the adsorption of CO on the clean surfaces. With new CO sites, there is a stronger interaction with the substrate. Only in the case of high K-coverage (0.65 AML) the effect of the different steps on the Cu 3d intensity at CO saturated layer is strongly reduced. At CO saturation, the 4σ intensity (I) follow the order: $I(100) > I(119) > I(115)$ for both the clean and K-modified surfaces. On the stepped surfaces, a small percent of CO molecules dissociate immediately after adsorption at 125 K.

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Low temperature adsorption of CO on stepped and K-modified Cu surfaces was studied. At CO saturation, the 4σ intensity (I) follow the order: $I(100) > I(119) > I(115)$ for both the clean and K-modified surfaces.

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