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Photoelectron spectroscopy for probing surface reactions at the CO/K/Cu(1 1 5) interface

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ABSTRACT

The adsorption of carbon monoxide on the potassium modified Cu(1 1 5) surface was investigated using photoelectron spectroscopy based on synchrotron radiation. From detailed analysis of the 1*s* core levels in combination with existing knowledge, the assignment of surface species is performed. It is demonstrated that in dependence of the alkali coverage, several adsorption states of CO are present on the interface at 135 K. From the temperature dependence of the C 1*s* and O 1*s* profiles it is established that surface reactions based on CO dissociation start from 223 K over an interface with a potassium coverage close to half a complete K overlayer. The role of potassium as a reordering environment of adsorbed CO, leading to molecule dissociation and disproportionation is proposed. It is observed that a higher density of potassium on the substrate surface blocks adsorption sites for incoming CO molecules and no dissociation takes place.

1. Introduction

Adsorption and dissociation of carbon monoxide over metal surfaces are interesting phenomena which are directly related to catalysis. On copper surfaces (even stepped) CO adsorbs molecularly with its C towards the surface and desorbs without dissociation in the temperature range of 200–300 K. It appears, that the capability of forming the stable metal carbide is the condition for CO dissociation over the metal surface (e.g. [1]). In principle, copper does not form carbide at the surface but instead maintains the stable graphitic surface carbon. That is why the principal condition for dissociation could be fulfilled and it is interesting to find whether the process is induced in the presence of alkali metal. It was found that the interaction of CO with pre-adsorbed alkali is very local, i.e. confined to nearest or next-nearest neighbor sites and is largely chemical rather than electrostatic with formation of surface complexes. For example at the CO/K/Cu(1 1 0) interface it was proposed that upright CO is directly bonded to K via the 1π orbital of CO [2]. On a potassium dosed Cu(0 0 1) surface complex interactions were observed but without dissociation of carbon monoxide (e.g. [3]). The study of adsorption properties of potassium modified stepped surfaces is the next step relative to the investigations on modified flat surfaces.

The clean Cu(1 1 5) surface up to around 570 K is characterized by straight and equally spaced steps without reconstruction. The elementary surface cell is found to be 255.3 pm × 663.2 pm and its geometrical structure was discussed in detail in the past [4–9]. Thermal roughening of Cu(1 1 5) was recorded at temperatures lower than usually observed in the case of close-packed faces, i.e. just over 570 K (about $0.42 \times T_m$, where T_m is the melting point) [4,10]. Adsorbed potassium on the Cu(1 1 5) surface at 340 K causes the double step reconstruction which is parallel to observed faceting, i.e. formation of large (1 1 4) facets at higher K coverages [11].

In the present work the adsorption of CO on an alkali-modified vicinal copper surface is studied. As an example the Cu(1 1 5) surface is chosen with its considerable step density and it is modified with K in the coverage regime from zero up to a complete alkali overlayer. The adsorption properties of the CO/K/Cu(1 1 5) interface was investigated with the help of synchrotron radiation induced photoelectron spectroscopy. The influence of the modifications of the surface on the adsorption phenomena is presented in the light of detailed knowledge of simple, elemental systems including K/Cu and CO/Cu for low-index and stepped substrates.

2. Experimental

The experiments were carried out at the Super ESCA beamline [12,13] at the Elettra storage ring, Trieste, Italy. The source is a 5.6 cm, 80 period undulator, which at a ring energy of 2 GeV gives a

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tunable energy from 180 eV to 1200 eV. The optics is a modified version of the SX700 monochromator with prefocussing mirror, entrance slit and refocussing optics. The experimental chamber is a stainless steel ultrahigh vacuum (UHV) chamber equipped with a VSW CLASS 150 multichannel electron energy analyser, a LEED facility, a mass spectrometer, an Ne^+ ion sputter gun, alkali metal evaporating facilities and a gas inlet system. The instruments are driven by a computer program which allows simultaneous control of all devices involved in a specific experiment. Work function changes were determined from the change of the cutoff energy of the photoemission spectrum ($h\nu = 380$ eV) with the sample biased at −9.0 V relative to the ground potential. During experiments the working pressure in the apparatus was below 1.00×10^{-10} Torr.

The temperature of the sample was measured by a chromel-alumel (type K; nickel–chromium and nickel–aluminium alloys) thermocouple fixed to the top of the specimen. The manipulator had the facilities of liquid nitrogen cooling and the sample could be cooled down to c.a. 130 K. A heating procedure, up to 900 K, was accomplished by passing a DC current through the sample holder. The Cu(1 1 5) crystal was cleaned by series of Ne^+ bombardment (1.2 kV, 2.5 μA, 5 min) and heating to 900 K (1–2 min). This relative active copper surface needed prolonged treatment with such series in order to reduce contamination to the noise level as controlled by photoemission.

Potassium was dosed to the front of the sample surface from a degassed chromate dispenser (SAES Getters) similarly as described previously [14]. Doses of CO of high purity were determined by an ionization gauge without taking into consideration the sensitivity of the gas. A saturated layer of gas on each potassium modified copper was achieved after CO exposure of 1.5 L.

The K coverage is expressed in terms of adsorbate monolayer (AML), i.e. one monolayer corresponds to the saturated potassium layer on Cu(1 1 5). At low temperature adsorption ($T < 340$ K), a first complete potassium layer on Cu(1 1 5) has a density of 3.63×10^{18} at/m^2 [15]. For the interfaces under investigations, the K coverage was determined with the help of the work function changes. In accordance with the elaborated calibration curve, the work function minimum corresponds to 0.60(1) AML [15]. It is worth to mention that the alkali adatoms usually form structures having high adsorbate-substrate coordination. Additionally, at lower coverages, due to repulsive interaction induced by the ionic character of the alkali, they are able to form long-range ordered structures on metal surfaces (e.g. [16]).

Experimental photoelectron spectra were carefully analyzed taking into account procedures for elimination of uncertainties [17]. The secondary continuous spectrum and the peaks were fitted with the help of a Shirley-type background line and the asymmetric Gaussian–Lorenzian sum function. It is assumed that the area under the total feature corresponds to the intensity of the photoelectron transition. After registration of the core line, the region of the Fermi edge obtained with the same photon energy was recorded as well. With the help of position of the Fermi edge, each binding energy value was determined with high accuracy.

3. Results

It is known that from careful studies of the core level line shape and its temperature dependence, information about the surface species resulting from the surface reactions could be obtained. In this work, identification of the interface species was made with the help of the well known literature findings concerning the photoemission peak positions of known compounds. In the case of the same molecule but at different adsorption site, the binding energy could be characteristic of the site and all values could create the specific sequence. For example, the sequence of the binding energy of BE(ontop) > BE(bridge) > BE(hollow) was proposed for adsorbed CO [18]. In addition, a prediction of the possible (most probable) reaction products was made according to the simple chemical rules. Combining a data base of photoemission assignments with the experimental strategy of annealing interface, the recognition of the surface species is presented in the following subsections. The results of assignment of different CO states are listed in Section 3.3 in Tables 1 and 2 based on the C 1*s* and O 1*s* regions, respectively.

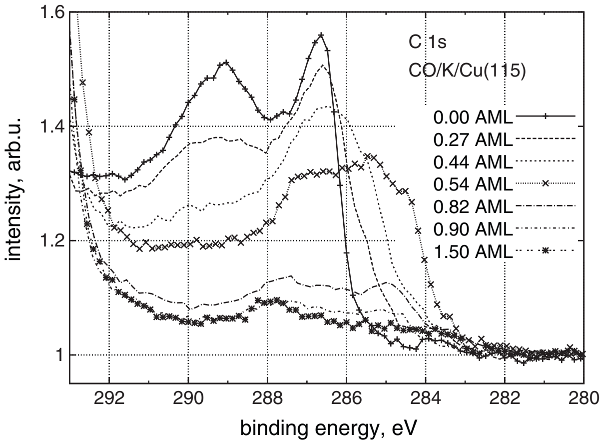

Fig. 1. Photoemission spectra in the energy range of the C 1*s* level for a saturated CO layer on the K/Cu(1 1 5) interface at 135 K. The parameter of the curves is the surface coverage of potassium. The photon energy was $h\nu = 415$ eV and the electrons were recorded in normal emission.

3.1. Low temperature (135 K) adsorption

Spectra of the C 1*s* and O 1*s* regions of the K/Cu(1 1 5) interface saturated with CO for different amounts of pre-adsorbed potassium are collected in Figs. 1 and 2, respectively. Carbon monoxide adsorbed on a bare copper surface gives 1*s* spectra of C (and analogue 1*s* spectra of O) containing a main peak and two satellites [19,15]. For the BE range showed in Fig. 1, the low binding energy tail of the second satellite is visible only. With potassium introduced to the surface, the carbon peaks slightly interfere with the strong intensity K 2*p* line on its high binding energy side, Fig. 1. For a potassium coverage of 0.27 AML, the addition of a saturated CO layer increases the work function by +0.66 eV relative to the K-predosed surface. In the photoemission spectrum the simple

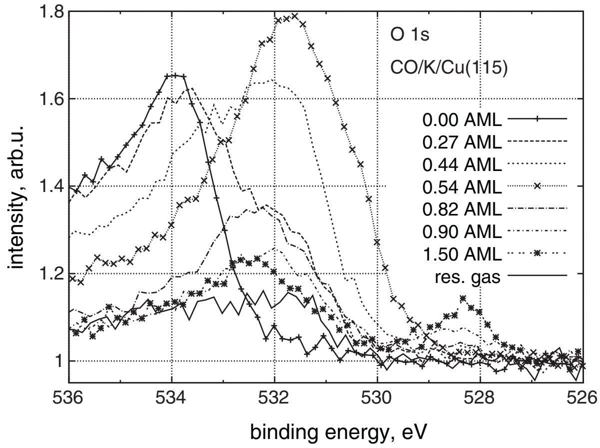

Fig. 2. Photoemission spectra in the energy range of the O 1*s* level for a saturated CO layer on the K/Cu(1 1 5) interface at 135 K. The parameter of the curves is the surface coverage of potassium. The photon energy was $h\nu = 660$ eV and the electrons were recorded in normal emission.