The effects of CO, H, NH₃, CH₃OH, H₂O, and C₂H₄ on the electronic properties of ultrathin Cu films supported over Ru(0001): an XPS study

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The interaction of CO, H, NH₃, CH₃OH, H₂O, and C₂H₄ with ultrathin Cu films supported on Ru(0001) has been studied by means of XPS and TPD. For films with θₑ Cu < 1, adsorption of CO, C₂H₄, and H induced shifts of +0.5, +0.3, and +0.25 eV, respectively, in the Cu(2p₃/₂) peak position. Negligible shifts were observed upon adsorption of NH₃, CH₃OH, and H₂O. The XPS results are consistent with a model in which the electron density transferred from a Cu monolayer to the adsorbates follows the trend: CO > C₂H₄, H > NH₃, CH₃OH, H₂O.

1. Introduction

Study of the electronic properties of ultrathin Cu films supported on metal substrates is an area of active experimental research [1-6]. This interest originates from the fact that Cu appears as a component in many bimetallic catalysts used in important industrial processes [1]. Previous XPS studies for Cu/Ru(0001) [1] show that the Cu(2p₃/₂) binding energy increases with film thickness, reaching a constant bulk value at ~5 ML (monolayer). The atoms in a pseudomorphic monolayer of Cu on Ru(0001) are electronically perturbed with respect to the bulk atoms of pure Cu, appearing shifted ≈0.35 eV towards lower binding energy in the Cu(2p₃/₂) XPS spectra. This perturbation is a consequence of variations in the coordination number of the Cu atoms and the effects of the Cu–Ru interaction [1,2].

In the present work, we investigate the adsorption of CO, H, NH₃, CH₃OH, H₂O, and C₂H₄ on Cu/Ru(0001) by means of X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD). Chemisorption provides an interaction between adsorbate and surface atoms that can lead to electronic changes in the Cu film. These changes should induce surface core-level binding-energy shifts. Different shifts can be expected for electron-donor and electron-acceptor adsorbates. By monitoring variations in the binding energy of a core-level of the Cu overlayer after adsorption of a molecule, one can get information about changes in the electronic properties of the metal film and about the nature of the chemisorption bond.

2. Experimental

The experiments were performed in an ultrahigh vacuum system (base pressure ≤4×10⁻¹⁰ Torr) described previously [2]. The apparatus was equipped with capabilities for LEED, AES, XPS, and TPD. The XPS spectra were recorded with Al Kα radiation. Detection was normal to the surface in AES and XPS.

The Ru(0001) crystal was cleaned following procedures reported in the literature [3,8]. Cu was vapor deposited onto Ru(0001) at a surface temperature of ≈350 K by resistively heating a W filament wrapped with a high-purity Cu wire. After deposition, the crystal was annealed to 500 K to desorb any accumulated CO, and no impurities were detected by AES or XPS. The Cu coverages were determined by TPD area analysis and AES [8]. In this work, adsorbate coverages are reported with respect to the number of Ru(0001) surface atoms (1.64×10¹⁵ at-
oms/cm²). One admetal atom per substrate surface atom corresponds to \( \theta_{Cu} = 1 \).

3. Results and discussion

3.1. Adsorption of CO

CO adsorbs nondissociatively on Ru(0001), Cu/Ru(0001) and copper surfaces under UHV conditions [3,8,9]. Results of FT-IRAS for CO/Cu/Ru (0001) [9] show adsorption of the CO molecules on Ru and Cu a-top sites. The effect of CO adsorption on the Cu(2p_{3/2}) binding energy of Cu films supported on Ru(0001) is illustrated in fig. 1. The formation of Cu–CO bonds induces a shift towards higher binding energy in the Cu(2p_{3/2}) peak position. For \( \theta_{Cu} \ll 1 \), the CO-induced shift was always the same: 0.5 eV. This phenomenon is a consequence of the formation of two-dimensional islands of Cu on the Ru(0001) surface [1,8]. For \( \theta_{Cu} \gg 1 \), the magnitude of the CO-induced shift in Cu(2p_{3/2}) peak position decreased with increasing Cu coverage: 0.5 eV for 1 ML, 0.4 eV for 1.4 ML, 0.35 eV for 1.6 ML and 0.1 eV for 14 ML. In the last three cases, the Cu(2p_{3/2}) spectra represent a product of the combination of electrons emitted from subsurface and surface Cu atoms. The effects of CO on the Cu(2p_{3/2}) binding energy of surface Cu atoms are masked by contributions from subsurface Cu atoms. In all the cases examined, the effects of CO adsorption upon the Cu(2p_{3/2}) binding energy of the Cu films were reversible. The Cu(2p_{3/2}) peak position observed after desorption of CO was identical to that seen before adsorption of the molecule.

The data of fig. 1 agree well with XPS [2,4] and UPS [3,4] studies for supported Cu films that show an increase in the binding energy of the core and valence levels of Cu upon CO chemisorption. The shifts in fig. 1 are comparable to the corresponding shift found for the surface atoms of Cu(100): 0.5 eV [10].

The observed direction for the CO-induced shift in the Cu(2p_{3/2}) level is consistent with a reduction in the electron density of the Cu adlayers upon CO adsorption. According to a microscopic model [11–13], the core-level shift induced by an adsorbate (\( \Delta_{CL} \)) can be related to changes in the coordination number of the surface atoms (\( \Delta_c \)), charge redistributions produced by the chemisorption process (\( \Delta_{CRB} \)) and differences in final state effects arising from modifications of the screening of the core hole (\( \Delta_{FS} \))

\[
\Delta_{CL} = \Delta_c + \Delta_{CRB} + \Delta_{FS}
\]

For late transition metals, an increase in the coordination number of the surface atoms leads to a core-level shift towards high binding energy [11–13]. Charge flow between adsorbate and surface tends to cancel the shift in the case of electronegative adsorbates, and reinforce it in the case of electron-withdrawing adsorbates [113]. The CO-induced shifts in fig. 1 (\( \approx 0.5 \) eV) exceed the differences in Cu(2p_{3/2}) binding energy between bulk Cu and the surface atoms of Cu(100) (0.22 eV [10]), polycrystalline Cu (0.24 eV [10]) and Cu\(_{<1.0}/Ru(0001)\) (\( \approx 0.35 \) eV [11]). This fact suggests that the shifts of fig. 1 are not simply due to an increase in the coordination number of the Cu atoms, but also a consequence of transfer of electrons from the Cu film into the unoccupied 2π* orbitals of the CO molecule.
(2\pi backbonding). Recent quantum-chemical calculations \cite{14,15} indicate that 2\pi back donation is the driving force for the chemisorption of CO on copper surfaces.

3.2. Adsorption of atomic hydrogen

H\(_2\) dissociates upon adsorption on clean Ru(0001) at 100 K \cite{16}. In contrast, H\(_2\) does not dissociatively adsorb on Cu surfaces at low temperature and under UHV conditions because of a high-energy barrier to dissociation \cite{16}. H\(_2\) thermal desorption spectra from Ru(0001) surfaces partially covered by Cu \cite{16} reveal hydrogen chemisorbed on the Cu adatoms. Since H\(_2\) does not dissociate on Cu, the hydrogen must first dissociate on free Ru sites and then “spillover” onto the Cu overlayer \cite{16}.

Fig. 2 displays Cu(2p\(_{3/2}\)) XPS spectra acquired before and after dosing 50 langmuir (L) of H\(_2\) onto Cu/Ru(0001) surfaces. The following H-induced shifts in Cu(2p\(_{3/2}\)) peak position were measured: 0.25 eV for \(\theta_{\text{Cu}}=0.12\), 0.25 eV for \(\theta_{\text{Cu}}=0.23\), 0.20 eV for \(\theta_{\text{Cu}}=0.41\), 0.15 eV for \(\theta_{\text{Cu}}=0.54\), 0.10 eV for \(\theta_{\text{Cu}}=0.76\), 0.05 eV for \(\theta_{\text{Cu}}=1.06\) and 0.00 eV for \(\theta_{\text{Cu}}=1.4\). At low Cu coverages, an appreciable fraction of the Ru surface is free, producing a large reservoir of hydrogen adatoms that can migrate and saturate the Cu islands. An increase in the Cu coverage diminishes the size of the free regions of Ru that are necessary for H\(_2\) dissociation, reducing the amount of atomic hydrogen that spills over onto the Cu islands. This results in only a small shift in the Cu(2p\(_{3/2}\)) binding energy. At \(\theta_{\text{Cu}}=1.06\), a negligible H-induced shift is found. For this case, it appears that some H\(_2\) still dissociates on the edges of the crystal or defect sites not blocked by Cu.

The shifts seen in fig. 2 could be merely due to an increase in the coordination number of the Cu atoms. For Ru(0001) surfaces with \(\theta_{\text{Cu}}<0.25\), the H-induced shift (0.25 eV) is very similar to the difference in the Cu(2p\(_{3/2}\)) peak position between bulk Cu and the surface layer of Cu(100) (0.22 eV \cite{10}).

3.3. Adsorption of H\(_2\)O, NH\(_3\) and CH\(_3\)OH

In this section, we examine the effects of water, ammonia and methanol on the Cu(2p\(_{3/2}\)) level of Cu/Ru(0001). All these adsorbates are characterized by the fact that they bond to metals through their oxygen or nitrogen lone-pair orbitals. Quantumchemical calculations indicate that NH\(_3\) and H\(_2\)O act as moderate electron donors when adsorbed on several sites of Cu(100), Cu(110) and Cu(111) \cite{17-19}.

No evidence for dissociation of NH\(_3\) on Cu/Ru(0001) surfaces was observed, in agreement with published results for NH\(_3\)/Ru(0001) \cite{20} and NH\(_3\)/Cu(110) \cite{21}. NH\(_3\) thermal desorption spectra taken after dosing 20 L of ammonia onto Cu/Ru(0001) at \(\approx 110\) K showed the presence of three different adsorbed states at temperatures of about 140, 200 and 275 K. The NH\(_3\)-TPD peak at \(\approx 140\) K can be assigned to multilayers physisorbed on top of the first adsorbed layer of ammonia \cite{20,22}. The states at 200 and 275 K correspond to desorption of molecularly chemisorbed NH\(_3\) and have estimated heats of adsorption of about 50 and 68 kJ/mol. On Cu/Ru(0001), the chemisorbed states appeared \(\approx 15\) K higher in temperature than those on multilayers of Cu or on Cu(100) \cite{22}. This suggests that the supported monolayer of Cu is electronically perturbed and that this perturbation manifests itself in the bonding of NH\(_3\).

Interestingly, although there is a relatively strong bond between Cu and NH\(_3\), this adsorbate does not induce any significant shift in the Cu(2p\(_{3/2}\)) peak.
position of the Cu monolayer (≈0.05 eV, see fig. 3). A similar phenomenon was observed when the Cu\textsubscript{1.0}/Ru(0001) surface was saturated with water or methanol at ≈110 K (see fig. 3). At these low-temperature conditions, neither water nor methanol decomposes upon adsorption [23]. TPD experiments showed a sharp peak at 190 K for desorption of the first layer of water bound to Cu\textsubscript{1.0}/Ru(0001) (heat of adsorption ≈46 kJ/mol). This desorption temperature is somewhat higher than the value of 175 K reported for water chemisorbed on Cu(111) and Cu(110) [24,25]. Previous studies [23] report a higher desorption temperature for methanol bound to Cu\textsubscript{1.0}/Ru(0001) (desorption peak at ≈160 K) than for chemisorption of the molecule on Cu multilayers (desorption peak at ≈135 K).

The data of fig. 3 indicate that adsorption of NH\textsubscript{3}, H\textsubscript{2}O and CH\textsubscript{3}OH does not produce any appreciable shift (≤0.05 eV) in the Cu(2p\textsubscript{3/2}) binding energy of Cu\textsubscript{1.0}/Ru(0001) and suggest that the electron density of the supported Cu monolayer may be very similar before and after chemisorption of the electron-donor species. The results of fig. 3 are in full agreement with the general observation that shifts induced by electropositive adsorbates are usually very small, and can be towards higher or lower binding energies, never exceeding the bulk binding energy [13]. The negligible shifts induced by NH\textsubscript{3}, H\textsubscript{2}O, and CH\textsubscript{3}OH in the Cu(2p\textsubscript{3/2}) peak position of Cu\textsubscript{1.0}/Ru(0001) are due to a cancellation of two effects (increase in coordination number versus transfer of charge from the adsorbate toward the surface), and not to the non-ionic nature of the chemisorption bonds. If these bonds were totally covalent, an appreciable shift should be observed towards the Cu(2p\textsubscript{3/2}) binding energy of bulk Cu [13].

3.4. Adsorption of C\textsubscript{2}H\textsubscript{4}

At 130 K, ethylene adsorbs molecularly on clean and Cu-covered Ru(0001) surfaces [26]. Results of HREELS indicate that on Cu\textsubscript{1.0}/Ru(0001), ethylene is π-bonded to the Cu atoms, but di-σ-bonded to the Ru sites [26]. The ethylene attached to Ru dissociates upon heating to 230 K, whereas no decomposition and desorption is observed for the Cu-bonded C\textsubscript{2}H\textsubscript{4} [26].

Fig. 4 shows Cu(2p\textsubscript{3/2}) spectra taken before and after saturating the surface with ethylene.

![Fig. 3. Effects of NH\textsubscript{3}, H\textsubscript{2}O, and CH\textsubscript{3}OH on the Cu(2p\textsubscript{3/2}) XPS spectra of Cu\textsubscript{1.0}/Ru(0001). The spectra were taken at 110 K before and after saturating the surface with NH\textsubscript{3}, H\textsubscript{2}O, or CH\textsubscript{3}OH.](image)

![Fig. 4. Effect of ethylene adsorption on the Cu(2p\textsubscript{3/2}) spectra of Cu/Ru(0001) surfaces. The relative peak intensities can be obtained by multiplying each spectrum by the corresponding scaling factor shown in the right side of the figure. The spectra were taken at 110 K before and after saturating the surfaces with ethylene.](image)
after dosing ethylene onto Cu/Ru(0001) surfaces at 110 K. Adsorption of C\textsubscript{2}H\textsubscript{4} on Cu films with \(\theta_{\text{Cu}} < 1\) produced a shift of 0.3 eV towards higher binding energy in the Cu(2p\textsubscript{3/2}) peak position. The C\textsubscript{2}H\textsubscript{4}-induced shift was somewhat smaller than that induced by CO adsorption (0.5 eV, see above). For Ru(0001) surfaces with \(\theta_{\text{Cu}} > 1\), the magnitude of the C\textsubscript{2}H\textsubscript{4}-induced shift decreased with increasing Cu coverage: 0.3 eV for \(\theta_{\text{Cu}} = 1\), 0.25 eV for \(\theta_{\text{Cu}} = 1.1\), 0.2 eV for \(\theta_{\text{Cu}} = 1.8\), and 0.05 for \(\theta_{\text{Cu}} = 5\). The same phenomenon was observed above for the CO/Cu/Ru(0001) system. A possible explanation is that the CO-Cu and C\textsubscript{2}H\textsubscript{4}-Cu interactions are of short-range nature affecting only the top layer of Cu atoms and not disturbing subsurface atoms which have a large contribution to the Cu(2p\textsubscript{3/2}) XPS spectra of thick Cu films. Annealing the C\textsubscript{2}H\textsubscript{4}/Cu/Ru(0001) surfaces to 220 K led to desorption of the ethylene bonded to Cu, shifting the Cu(2p\textsubscript{3/2}) spectra to the positions seen before adsorption of the molecule.

The shifts in fig. 4 are probably a consequence of an increase in the coordination number of the Cu atoms. The magnitude of the shifts is very close to the difference in Cu(2p\textsubscript{3/2}) binding energy between bulk Cu and the surface atoms of polycrystalline Cu (0.24 eV [10]), implying that the C\textsubscript{2}H\textsubscript{4}-Cu bond is mostly covalent. The bonding mechanism of ethylene to metals involves transfer of electron density from the highest occupied \(\pi\)-orbital of the molecule into the metal, and electron backdonation from the metal into the lowest unoccupied \(\pi^*\)-orbital of ethylene [27]. If these charge transfers cancel each other, the adsorption bond of the molecule on the Cu overlayer can be predominantly covalent.

A comparison of the adsorbate-induced shifts in figs. 1 and 4 indicates that the degree of ionicity is larger in the Cu–CO bond than in the C\textsubscript{2}H\textsubscript{4}–Cu bond. The \(\pi^*\)-acceptor orbitals of CO and ethylene are at the same energy: 1.8 eV above the vacuum level [28]. Therefore, the electron-acceptor ability of both molecules should be very similar. On the other hand, the HOMO of ethylene is 3.3 eV less stable than that of CO [28], making the olefin a much better electron donor. The result is a C\textsubscript{2}H\textsubscript{4} admolecule that has a lower negative charge and a more covalent chemisorption bond than adsorbed CO.

4. Conclusions

For Cu/Ru(0001) surfaces with \(\theta_{\text{Cu}} < 1\), adsorption of CO, C\textsubscript{2}H\textsubscript{4}, and H-induced shifts of +0.5, +0.3, and +0.25 eV, respectively, in the Cu(2p\textsubscript{3/2}) peak position. Negligible shifts were observed upon adsorption of NH\textsubscript{3}, CH\textsubscript{3}OH, and H\textsubscript{2}O. The XPS data suggest that the electron density transferred from a Cu monolayer to the adsorbates follows the trend: CO > C\textsubscript{2}H\textsubscript{4}, H > NH\textsubscript{3}, CH\textsubscript{3}OH, H\textsubscript{2}O. The present results illustrate the utility of surface core-level shifts for studying the nature of the chemisorption bond of electron-donor and electron-acceptor species on metal overlayers.

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