Adsorption of CO, H₂, O₂, and CO₂ on clean and Cu-covered Re(0001): an XPS study

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The electronic and chemical properties of ultrathin films of Cu on Re(0001) have been investigated by means of X-ray photoelectron spectroscopy (XPS) and chemisorption of CO, H₂, O₂ and CO₂. A very similar Cu(2p½) binding energy is obtained for a monolayer of Cu on Re(0001) and the surface atoms of Cu(100). Measurements of the Cu(2p½) XPS peak position of Cu/Re(0001) as a function of film thickness show convergence to bulk properties for films with 4–5 layers of Cu atoms. Chemisorption of CO induces a large decrease in the electron density of the Cu adlayers. This is a consequence of: (1) charge transfer from the Cu overlayer to the Re(0001) substrate (induced by a repulsive interaction between the Cu σ charge and the electrons in the 5s orbital of CO) and (2) transfer of electrons from the Cu adatoms into the unoccupied 2p orbitals of the CO molecules (π back-bonding). The Cu–Re interaction enhances the electron donor capabilities of Cu atoms supported on Re(0001), making them more active for CO adsorption and CO₂ dissociation. Hydrogen adatoms shift the Cu(2p½) XPS peak position of Cu/Re(0001) surfaces toward higher binding energies. The present results indicate that spillover of hydrogen from Re to Cu can occur in mixed Cu/Re catalysts.

1. Introduction

Copper appears as a component in many bi-metallic catalysts used in important industrial processes [1,2]. Many fundamental studies have been focused on trying to understand the electronic and structural properties of these catalysts that are responsible for their superior activity and selectivity [1–5]. Work on ultrathin Cu films supported on well-defined transition metal surfaces (Cu/Ru(0001) [6–10], Cu/Rh(100) [11–14], Cu/W(110) [15,17], Cu/Pt(111) [18], Cu/Ni(111) [19] and Cu/Ni(100) [19]) has shown that a Cu atom in a matrix of a dissimilar metal can be significantly perturbed, and that this perturbation can dramatically alter its chemical and electronic properties. In this paper we investigate the chemisorption of CO, H₂, O₂ and CO₂ on clean and Cu-covered Re(0001) using X-ray photoelectron spectroscopy (XPS). This work is a continuation of a series of studies performed in our laboratory, in which the chemical and catalytic properties of Cu films on different metals have been examined by use of the modern techniques of surface science and high-pressure reaction kinetics [4,5,7,8,11–14,21].

The details of the Cu overlayer growth on Re(0001) (Cu and Re are virtually immiscible [20]) have been published elsewhere [21]. Cu was found to form stable, uniform layers at a Cu coverage of < 2 ML. For these films the Auger ratio of Cu to Re shows no change upon annealing from 115 to 1000 K [21]. At Cu coverages greater than 3 ML, the Cu/Re AES ratio shows a significant decrease upon annealing, consistent with the formation of three-dimensional islands (cluster crystallites) of Cu [21]. Thermal desorption spectra of Cu from Re(0001) show two discrete features [21], which
are related to Cu desorption from the multilayer (1000–1150 K) and monolayer (1150–1280 K) states. Both peaks appear to follow zero-order kinetics with activation energies of ~74 (multilayer) and ~93 kcal/mol (monolayer) [21].

2. Experimental section

The experiments were carried out in an ultra-high-vacuum surface analytical chamber (base pressure < 4 × 10^{-10} Torr) equipped with capabilities for low-energy diffraction (LEED), a hemispherical analyzer for XPS and Auger electron spectroscopy (AES), and a mass spectrometer for thermal desorption spectroscopy (TDS).

The Re(0001) crystal was cleaned following procedures reported in the literature [21]. The cleanliness and long-range order of the surface were verified by means of XPS, AES and LEED. The crystal was mounted on a manipulator capable of resistive heating to 1600 K, electron beam heating to 2600 K, and cooling to 150 K. A W–5% Re/W–26% Re thermocouple was spot-welded to the sample edge for temperature measurements.

Cu deposition was performed by resistively heating a W filament wrapped with a high-purity Cu wire. The Cu doser was outgassed thoroughly prior to Cu deposition. Copper was vapor deposited at a sample temperature of ~350 K. After dosing Cu, the Re(0001) surface was annealed to 500 K and no impurities were detected by AES or XPS. Cu coverages were determined by TDS area analysis [21]. In this work, adsorbate coverages are reported with respect to the number of Re(0001) surface atoms (1.52 × 10^{15} atoms cm^{-2}). One Cu adatom per substrate surface atom corresponds to θ_{Cu} = 1.0.

The O(1s), Cu(2p) and Re(4f) XPS spectra of section 3 were recorded with Al Kα radiation. The variations in the binding energies of the O(1s) and Cu(2p) XPS regions were determined by referencing against the Re(4f_{7/2}) peak for Re(0001). Detection was normal to the surface in XPS and AES.

3. Results and discussion

3.1. Electronic properties of Cu films on Re(0001)

Fig. 1 displays representative spectra of the Cu(2p_{3/2}) XPS region for various coverages of Cu on Re(0001). The spectra were acquired after vapor depositing Cu on the clean Re(0001) surface at ~350 K and annealing the sample to 500 K. In fig. 1 the Cu(2p_{3/2}) peak shifts from 932.75 eV for the 0.46 and 0.92 ML coverages to a binding energy of 932.90 eV at 20 ML.

The effect of Cu coverage (film thickness) on the Cu(2p_{3/2}) peak position is illustrated in fig. 2A. Coverages of less than 1 ML show no shift in peak position from 932.75 eV. This phenomenon can be attributed to the formation of 2D islands of Cu on the Re(0001) surface. A similar behavior has been observed for submonolayer coverages of Cu on Ru(0001) [8,10,11] and Rh(100) [11,12]. For coverages larger than 1 ML, there is a monotonic increase in the Cu(2p_{3/2}) peak position up to a value of 932.90 eV. The total shift in Cu(2p_{3/2})
binding energy is 0.15 eV. This shift is considerably smaller than the shifts observed in previous studies for Cu/Rh(100) (0.6 eV [11]) and Cu/Ru(0001) (0.3 eV [11]). The electronic perturbation found for a film with two layers of Cu atoms (see fig. 2A) is much smaller than that seen for the first monolayer. An identical result was observed for the Cu/Rh(100) and Cu/Ru(0001) systems [11]. In general, supported Cu films with 4–5 ML show convergence to bulk properties [11], in good agreement with the results of theoretical calculations [22].

XPS data for Cu(100) show that the Cu(2p\textsubscript{3/2}) binding energy of the surface atoms is 0.22 eV lower than that of bulk Cu [23]. A similar difference (0.24 eV) has been reported for polycrystalline Cu [24]. These shifts in binding energy are a consequence of variations in the coordination number of the surface Cu atoms compared to the bulk atoms [25–27]. Recent work has shown that surface core-level shifts can provide useful information about the electronic properties of the surface atoms [25–27]. The data of fig. 2A show that the Cu(2p\textsubscript{3/2}) binding energy of a monolayer of Cu on Re(0001) is 0.15 eV smaller than that measured for the combined peak of bulk and surface atoms in 30 ML of Cu. If we reference the combined peak of bulk and surface atoms in 30 ML of Cu on Re(0001) to that of Cu(100) (see fig. 2B), a very similar binding energy is obtained for a monolayer of Cu on Re(0001) and the surface atoms of Cu(100). This result is consistent with a model in which both types of Cu atoms have similar electron densities. The Cu monolayer density on Re(0001) (1.52 \times 10^{15} \text{atoms/cm}^2) is almost identical to the surface atomic density of Cu(100) (1.53 \times 10^{15} \text{atoms/cm}^2). The changes in Cu(2p\textsubscript{3/2}) binding energy seen in fig. 2A can be simply attributed to an increase in the electronic coordination of the Cu atoms.

### 3.2. Adsorption of CO on Re(0001) and Cu/Re(0001)

CO adsorbs nondissociatively on clean Re(0001) at 100 and 300 K [28]. Heating a CO-covered Re(0001) surface to 400 K leads to dissociation of the CO [28]. Thermal desorption spectra of CO from Re(0001) [29] show four peaks located at 170 (weakly chemisorbed CO), 390 (strongly chemisorbed CO), 960 and 1120 K (recombination of C and O\textsubscript{2}). On copper surfaces, carbon monoxide is adsorbed molecularly, usually at atop sites [30], and desorbs without any dissociation in the temperature range between 190 and 230 K [31,32]. Results of TDS for CO/Cu/Re(0001) [29] show that at low Cu coverages (< 2 ML), a new desorption state is present (at ~ 270 K), with a corresponding binding energy higher than that of bulk Cu and lower than that for clean Re(0001). This state is interpreted [29] to correspond to CO adsorbed at Cu sites perturbed by the underlying Re. At higher Cu coverages (~ 5 ML), the CO TDS features are essentially the same as those found for bulk Cu [29]. In the present study we examine the interaction between CO and Cu/Re(0001) surfaces by monitoring the variations in the O(1s) XPS peak of adsorbed CO and in the Cu(2p\textsubscript{3/2}) XPS peak of the Cu adlayers.

A series of O(1s) XPS spectra for CO adsorbed on Re(0001) and on Cu/Re(0001) (θ\textsubscript{Cu} = 0.2, 0.6, 1.7) is shown in fig. 3. The spectra were taken...
Fig. 3. O(1s) XPS spectra for CO adsorbed on Cu/Re(0001) surfaces: (a) Re(0001), (b) 0.2 ML of Cu on Re(0001), (c) 0.6 ML of Cu on Re(0001), and (d) 1.7 ML of Cu on Re(0001). The relative peak intensities can be obtained by multiplying each spectrum by the corresponding scaling factor in the right side of the figure. The Cu films were vapor-deposited at a crystal temperature of ~350 K and annealed to 500 K before dosing CO. The spectra were taken after dosing 30 L of CO onto the surfaces at ~150 K.

After dosing 30 L of CO onto the surfaces at ~150 K. The Cu adlayers were vapor-deposited on the clean Re(0001) crystal at ~350 K and annealed to 500 K before dosing CO. For Re(0001) the large CO exposure used in our experiments is enough to saturate the surface [33]. The O(1s) spectrum for CO on Re(0001) appears ~2 eV at lower binding energy than that for adsorption of the molecule on a surface covered by 1.7 ML of Cu. A similar trend was observed for CO adsorbed on Cu/Rh(100) [11] and Cu/Ru(0001) [11] surfaces. In the case of CO on Cu$_{0.6}$/Re(0001), the O(1s) spectrum is characterized by the presence of two overlapping peaks. This spectrum is the product of a combination of electrons emitted from CO bonded to free regions of Re(0001) (peak at ~530 eV) and from CO adsorbed on two-dimensional islands of Cu (peak at ~532 eV). An identical behavior has been seen for adsorption of CO on Cu/Rh(100) and Cu/Ru(0001) surfaces with Cu coverages below 1 ML [11]. For adsorption of CO on Cu$_{1.7}$/Re(0001), the O(1s) spectrum is very broad showing unresolved satellites that extend to higher binding energy than the main peak. A very similar broadening has been seen in the O(1s) XPS spectra of CO adsorbed on polycrystalline Cu [34], Cu(110) [32], Cu$_{1.9}$/Rh(100) [11], and Cu$_{1.6}$/Ru(0001) [11]. In those cases the features toward high binding energy in the spectra have been attributed to strong shake-up transitions [11,32,35].

CO is adsorbed on metal surfaces by the Blyholder mechanism [36], which involves $\sigma$ donation of electron density from CO into the unoccupied metal orbitals and $\pi$ back-donation of electron density from occupied metal orbitals into the lowest unoccupied molecular orbitals ($2\pi$) of the CO molecule. Recent theoretical [37] and experimental [38] results indicate that $2\pi$ back-donation is energetically more important in determining the character of the bond than is $\sigma$ donation. Experimental evidence indicates a higher CO desorption temperature (~200 K) from Re(0001) [29] than from Cu surfaces [31,32], suggesting that $2\pi$ back-donation is much larger for CO adsorption on Re(0001). On the basis of this result, we can tentatively attribute the shift in binding energy observed in fig. 3 for the O(1s) spectrum of CO adsorbed on increasing coverages of Cu to a simple initial-state stabilization of the O(1s) level caused by a decrease of electron density in the admolecule.

Fig. 4 illustrates the effect of CO adsorption on the Cu(2p$_{3/2}$) binding energy of Cu layers ($\theta_{\text{Cu}} = 0.2$ and 1) on Re(0001). The formation of Cu–CO bonds induces a shift toward higher binding energy in the Cu(2p$_{3/2}$) peak position. For Cu coverages of less than 1 ML the CO-induced shift in binding energy was always the same: 0.4 eV. This phenomenon is a consequence of the formation of 2D islands of Cu on the Re(0001) surface. For Cu coverages larger than 1 ML, the magnitude of the CO-induced shift in Cu(2p$_{3/2}$) peak position decreased with increasing Cu coverage: 0.4 eV for 1 ML, 0.3 eV for 1.7 ML, and 0.1 eV for 15 ML. In the last two cases the Cu(2p) spectra represent a product of the combination of electrons emitted...
from subsurface and surface Cu atoms. The effects of adsorbed CO on the Cu(2p$_{3/2}$) binding energy of the surface Cu atoms are masked by the contributions from the subsurface Cu atoms.

The direction of the CO-induced shift in fig. 4 is consistent with a reduction in the electron density of the Cu adatoms upon CO adsorption. The decrease in Cu electron density is probably a consequence of: (1) charge transfer from the Cu adlayer to the Re(0001) substrate (induced by a repulsive interaction between the Cu $\sigma$ charge and the electrons in the 5$s$ orbital of CO [37c]); and/or (2) transfer of electrons from the Cu adatoms into the unoccupied $2\pi$ orbitals of the CO molecule ($2\pi$ back-bonding). The data of fig. 4 agree well with results of XPS [11,15,18] and UPS [9] studies for supported Cu films that show an increase in the binding energy of the core and valence levels of Cu upon CO chemisorption.

Studies of CO adsorption onto a monolayer of Cu supported over Re(0001) [29], show a CO TDS maximum increased by approximately 80 K with respect to the peak maximum on Cu(100). In a previous study of Cu/Rh(100) and Cu/Ru(0001) we found [39] that an increase in CO desorption temperature is accompanied by a reduction in the Cu(2p$_{3/2}$) binding energy of the supported monolayer relative to the corresponding value for the surface atoms of Cu(100). This type of correlation is not observed for Cu/Re(0001). The results of fig. 2 indicate that the atoms in a monolayer of Cu on Re(0001) and the surface atoms of Cu(100) have almost identical binding energies suggesting that both types of Cu atoms have similar electron densities. Changes in the valence levels of an atom may not lead to variations in the binding energy of the core levels if they do not produce a net charge transfer. The Cu–Re interaction can affect the relative position and symmetry of the valence levels of Cu (without changing the core-level binding energies), favoring $2\pi$ back-donation and giving a stronger Cu–CO bond for CO/Cu$_{10}$/Re(0001) than for CO/Cu(100).

3.3. Adsorption of H$_2$ on Re(0001) and Cu/Re(0001)

H$_2$ dissociates upon adsorption on clean Re(0001) [29,40,41]. H$_2$ thermal desorption spectra from Re(0001) show only a single peak [29,40,41]. The peak maximum varies from $\sim$ 575 K for a 0.05 L H$_2$ exposure to $\sim$ 490 K for a 2.0 L H$_2$ exposure [29]. The 2.0 L exposure results in saturation of the spectra [29]. H$_2$ does not dissociatively adsorb on Cu surfaces at low temperature and under ultrahigh vacuum conditions because of a high energy barrier to dissociation [42]. The thermal desorption spectra of H$_2$ from Re(0001) surfaces partially covered by Cu [29] reveal a new hydrogen desorption state (at $\sim$ 390 K) with a higher binding energy than that from pure Cu. This peak is believed to be associated with atomic hydrogen adsorbed on Cu overlayers perturbed by the Re substrate [29]. Since H$_2$ does not dissociate on Cu, the hydrogen in the new state must first dissociate on free Re sites and then "spillover" onto the Cu overlay. Similar behavior has been observed for H$_2$ adsorption on Cu/Ru(0001) [43].

Fig. 5 shows Cu(2p$_{3/2}$) spectra taken before and after dosing 30 L of H$_2$ onto Cu/Re(0001) surfaces ($\theta_{\text{Cu}} = 0.08$, 0.2, 0.63 and 1.02). Adsorp-
3.4. Adsorption of \( \text{H}_2 \) on \( \text{Cu} \) films supported on Re(0001)

Previous studies indicate that the interaction of \( \text{H}_2 \) with Re(0001) [41,49] and Cu [50] surfaces is rather complex in that several different oxygen species are formed depending upon the \( \text{O}_2 \) dose and the temperature. At temperatures above 300 K, \( \text{O}_2 \) is adsorbed dissociatively. Fig. 6 displays \( \text{O}(1s) \) spectra taken after dosing 30 L of \( \text{O}_2 \) onto clean Re(0001) and Cu/Re(0001) surfaces at \( \sim 350 \) K. The spectra probably correspond to atomic oxygen bonded to Cu and/or Re atoms. The \( \text{O}(1s) \) peak shifts \( \sim 0.4 \) eV toward lower binding energy in going from Re(0001) to Cu_{1.85}/Re(0001).

The effects of \( \text{O} \) chemisorption upon the Cu(2p) spectra of Cu films supported on Re(0001) are illustrated in fig. 7. Oxygen induces a shift of \( \sim 0.1 \) eV toward higher binding energy in the Cu(2p_{3/2}) peak. A similar result has been reported for the \( \text{O}/\text{Cu}/\text{W}(110) \) system (15). The Cu(2p) region shows no change in the line shape or in the separation between the Cu(2p_{3/2}) and Cu(2p_{1/2}) peaks upon \( \text{O}_2 \) adsorption. In particular, the XPS spectra of the O/Cu/Re(0001) surfaces do not show the strong Cu(2p) satellites that are characteristic of CuO [51]. We did not observe any extra features in the Re(4f) XPS spectra (not shown) after \( \text{O}_2 \) exposure nor was there change in

The data of fig. 5 indicate net transfer of charge from the Cu overlayers when hydrogen is adsorbed. The large electron affinity of atomic hydrogen in gas phase (17.4 kcal/mol [47]) suggests that this species will be an electron acceptor upon adsorption on metals. Quantum-chemical calculations for \( \text{H} \) on Cu clusters [48] show transfer of electron density from the metal toward the adatom. For Re(0001) surfaces with coverages below 0.25 ML the \( \text{H} \) induced shift in Cu(2p_{3/2}) binding energy (\( \sim 0.35 \) eV) is much larger than the difference in Cu(2p_{3/2}) peak position between bulk Cu and the surface layer of Cu(100) (0.22 eV [23]). This fact indicates that the shift in Cu(2p_{3/2}) binding energy seen in fig. 5 is not simply due to an increase in the coordination number of the Cu atoms, but also a consequence of additional electronic interactions between the hydrogen adatoms and the Cu films.
Fig. 6. O(1s) XPS spectra for oxygen on Re(0001) and Cu/Re(0001) surfaces. The Cu films were deposited at a crystal temperature of \(-350\) K and annealed to 500 K before dosing \(O_2\). The spectra were taken after dosing 30 L of \(O_2\) onto the surfaces at \(-350\) K.

Fig. 7. Effect of \(O_2\) adsorption on the Cu(2p,\(1/2\)) spectra of Cu/Re(0001) surfaces. The Cu adlayers were deposited at \(-350\) K, and annealed to 500 K before dosing \(O_2\) at \(-350\) K.

the separation between the Re(4f\(_{5/2}\)) and Re(4f\(_{7/2}\)) peaks. However, oxygen caused a widening of the peaks and a reduction in the depth of the valley between them.

Previous studies indicate that adsorbed atomic oxygen induces an appreciable shift (\(-0.5\) eV) toward higher binding energy in the surface core levels of the metal substrate [45b,46]. This type of phenomenon is not seen for the Cu core levels of O/Cu/Re(0001). The data of fig. 7 show almost identical binding energies before and after dosing \(O_2\), suggesting that for both systems the Cu atoms have similar electron densities. The exact morphology of the O/Cu/Re(0001) surfaces is unknown. The Gibbs (free) energies of formation for rhenium oxides (ReO\(_3\), \(\Delta G^\circ = -88\) kcal/mol; ReO\(_2\), \(-127\) kcal/mol; Re\(_2\)O\(_5\), \(-254.8\) kcal/mol [52]) are considerably more negative than those of copper oxides (CuO, \(\Delta G^\circ = -31\) kcal/mol; Cu\(_2\)O, \(-34.9\) kcal/mol [52]). From a thermochromatic viewpoint, atomic oxygen should prefer to bond to Re atoms. AES, LEED, UPS, TDS and work function measurements indicate that adsorbed atomic oxygen induces segregation of Cu on W(110) [16], leaving islands of O and Cu (three-dimensional cluster crystallites) on the surface. At 90 K, O adsorption occurs on atop of Cu\(_{1.0}/W(110)\) or Cu\(_{2.0}/W(110)\), with O diffusing to the W surface without desorption on heating to 300 K, at which point incipient Cu segregation occurs [16].

3.5. Adsorption of CO\(_2\) on Re(0001) and Cu/Re(0001)

On clean Re(0001), CO\(_2\) adsorbs as an undistorted linear molecule with its axis parallel to the surface up to a crystal temperature of 120 \(\pm 5\) K [53]. In the temperature range of 120–135 K a fraction of the adsorbed molecules desorb and the rest transform to an intermediate tentatively identified (by HRFS) as a bent CO\(_2^-\) species, which dissociates to CO and O\(_2\) at 135 K and above [53]. Carbon dioxide is thought to be adsorbed on polycrystalline Cu both in a physisorbed form (\(\Delta H_{\text{ads}} = 4.3\) kcal/mol [54]) and in an anionic (CO\(_2^-\) [55,56]) chemisorbed state (\(\Delta H_{\text{ads}} < 14.3\) kcal/mol [55]). Previous studies [32,57,58] indicate
that there is no measurable adsorption or dissociation of CO₂ on Cu(110) and Cu(111) under ultrahigh vacuum conditions. Experiments with CO₂ pressures of 65 to 650 Torr and surface temperatures in the range between 400 and 600 K show a very small probability for dissociation of the molecule (CO₂ → CO + O₂) on Cu(110): less than one reaction per 10⁸ collisions of CO₂ molecules with the surface [58]. In the present work we investigate the activity of Cu films supported on Re(0001) for CO₂ dissociation.

Fig. 8A displays an O(1s) spectrum acquired after dosing 50 L of CO₂ onto a Cu₁₅/Re(0001) surface at ~ 180 K. The spectrum can be attributed to atomic oxygen and carbon monoxide adsorbed on the Cu overlayer. Annealing the surface to 320 K desorbs CO (which is evolved between 210 and 270 K), leaving an O(1s) spectrum similar to those observed for adsorption of atomic oxygen on Cu multilayers. Fig. 8B illustrates the effects of CO₂ adsorption on the Cu(2p₃/₂) spectrum of Cu₁₅/Re(0001). At ~ 180 K, the dissociative chemisorption of CO₂ induces a shift of 0.35 eV toward higher binding energy in the Cu(2p₃/₂) peak position. The direction of the shift is identical to those observed for adsorption of CO and O on Cu overlayers. An increase of the surface temperature to 320 K leads to desorption of CO, shifting the Cu(2p₃/₂) spectrum by ~ 0.2 eV toward lower binding energy.

A series of O(1s) spectra taken after dosing 50 L of CO₂ onto Re(O001) and Cu/Re(O001) surfaces at ~ 350 K is shown in fig. 9. For clean Re(0001) the broad O(1s) spectrum corresponds to CO₂ and O₂ [53]. Under the experimental conditions of fig. 9 CO does not adsorb on Cu [29,31]. Decomposition of CO₂ on Cu₁₅/Re(0001) surfaces yields adsorbed atomic oxygen and CO evolution. For Cu₁₅/Re(0001), the dissociation of CO₂ induced an increase of ~ 0.15 eV in the binding energy of the Cu(2p₃/₂) XPS peak (not shown). The results of fig. 9 show clearly that a Re(0001) surface covered with 1.5 ML of Cu is much more active for CO₂ dissociation than a film with a coverage equivalent to 20 layers of Cu atoms.

A comparison of our results for Cu₁₅/Re(0001) surfaces in figs. 8 and 9 with data previously reported for the interaction of CO₂ with Cu(110) [32,58] and Cu(111) [57] under ultrahigh vacuum conditions, indicates that the supported
Cu layers on Re(0001) have a larger activity for CO dissociation. It appears that the copper-rhenium interaction makes the Cu atoms more active for breaking C-O bonds. Recent studies for CO/Cu \textsubscript{1-x} Re(0001) [29] indicate a Cu-CO bond much stronger than those of CO adsorbed on Cu(100), Cu(110) and Cu(111). This behavior can be explained by assuming that the Cu atoms supported on Re(0001) are better electron donors (i.e., more active for \sigma back-bonding) than the surface atoms of pure Cu. A similar argument can be used to explain the strong interaction found between CO\textsubscript{2} and Cu overlayers on Re(0001). The chemisorption bond of CO\textsubscript{2} on Cu surfaces is dominated by transfer of electrons from the metal substrates into the LUMO of the adsorbate [56]. An enhancement in the transfer of electron charge from the metal to CO\textsubscript{2} should increase [56] the heat of adsorption of the molecule and the strength of the Cu-CO\textsubscript{2} bond. In addition, the C-O bond strength should decrease [56] since the population of the LUMO of CO\textsubscript{2} is increasing and the orbital is strongly antibonding with respect to the C-O bonds. This facilitates the dissociation of CO\textsubscript{2}.

4. Summary

(1) Cu adlayers formed by vapor-deposition at a sample temperature of \sim 350 K, with subsequent annealing to 500 K, form two-dimensional islands on the Re(0001) surface. These islands are characterized by a constant Cu(2p\textsubscript{3/2}) binding energy. A very similar Cu(2p\textsubscript{3/2}) peak position is obtained for a monolayer of Cu on Re(0001) and the surface atoms of Cu(100). The electronic perturbation found for a film with two layers of Cu atoms is much smaller than that seen for the first Cu monolayer on Re(0001). Measurements of the Cu(2p\textsubscript{3/2}) XPS peak position of Cu/Re(0001) as a function of film thickness show convergence to bulk properties for films with 4–5 layers of Cu atoms.

(2) The XPS results suggest that CO and H induce an appreciable decrease in the electron density of the Cu overlay upon adsorption.

(3) The Cu-Re interaction enhances the electrons donor capabilities of Cu atoms supported on Re(0001), making them more active for CO adsorption and CO\textsubscript{2} dissociation than the atoms in pure Cu.

(4) The present data indicate that “spillover” of hydrogen from Re to Cu can occur in mixed Cu/Re catalysts.

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