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New Look at the Mechanism for Alkali-Metal Promotion

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Angle-resolved photoelectron spectroscopy has been used to study the changes in the bonding of CO when coadsorbed with alkali-metal atoms. On metal surfaces [Cu(100) and Ru(0001)] various features in the photoemission spectra, including reduced site symmetry and a large shift of the 1π molecular orbital of CO, indicate a π-bonded configuration of the CO molecule. π bonding involves bonding through both the 1π and $2\pi^*$ molecular orbitals of CO. All of the data indicate a short-range interaction between the K and CO.

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In order to obtain a better understanding of the promoting effect of alkali metals in catalysis (e.g., the Fischer-Tropsch reaction), the coadsorption of CO plus an alkali metal has been studied on a variety of transition-metal surfaces.[1] Potassium is the most commonly used alkali metal and the changes in the CO adsorption properties are quite general, i.e., independent of the substrate. These include an increase in the metal-CO bond strength,[2] a large (~ 600 cm^{-1}) decrease in the C-O stretching frequency,[3,4] an increase in the vibrational overtone anharmonicities,[4] and in most cases an increase in the dissociation rate.[5-8] There is at present very little in the way of a first-principles understanding of these phenomena. Instead, most explanations have stemmed from the Blyholder model for CO adsorption,[9] and the Andersson model of alkali-metal adsorption. In Blyholder's picture, bonding occurs via 5σ donation to the metal and metal-d to CO-2π back bonding; the resulting partial occupancy of the antibonding level weakens the CO bond and is observed as a decrease in the C-O stretching frequency. Dry *et al.*[10] suggest that the alkali-metal adatoms enhance the substrate's ability to donate charge into the 2π orbital, thus further weakening the bond. Although this model may be correct for moderate changes in the C-O bond strength (e.g., for adsorption site-induced effects), we believe that it is inappropriate for addressing the extremely large C-O frequency shifts observed upon alkali-metal promotion since it requires an unreasonably large amount of 2π occupancy. This statement is easily substantiated by experimental data for the CO negative ion formed in resonant electron scattering. The vibrational frequency of CO$^-$ (with one electron in the 2π orbital) is reduced by[11] only ~ 300 cm^{-1} as compared to ~ 600 cm^{-1} in the cases at hand. Additionally the anharmonicity ($\omega_e x_e$) of CO$^-$ is found[11] to be 40 cm^{-1} compared to the 70-cm^{-1} value obtained for (CO + K)/Ru(0001).[4]

We will show using angle-resolved photoemission spectra from two quite different substrates that CO in the presence of K is π bonded in analogy with π bonded CO in cluster compounds,[12] bound at steps on metal surfaces,[13,14] or in deep hollow sites on Fe(111).[15] The two surfaces investigated in this study were the cubic (100) face of the noble metal Cu on which CO is only weakly chemisorbed (heat of adsorption ~ 0.6 eV) and the hexagonal (0001) face of the transition metal Ru where CO is strongly bound (~ 1.5 eV). We have chosen in this Letter to concentrate on an ordered overlayer of K with a subsequent saturation exposure of CO at $T = 100$ K. On Ru the ordered K layer is $\frac{1}{3}$ of a monolayer in a $(\sqrt{3}\times\sqrt{3})R\,30°$ structure,[16] while on Cu an incommensurate hexagonal overlayer is observed at a coverage of 0.3.[17]

Figure 1 shows the important symmetry features of the photoemission spectra of CO adsorbed onto a $(\sqrt{3}\times\sqrt{3})R\,30°$ overlayer on Ru (curves c and d), compared to CO adsorbed onto clear Ru (curves a and b) at 100 K. Curves a and d are measurements taken with s-polarized light and the detector in the plane of the polarization vector and the surface normal (the "allowed" geometry). Curves b and c are recorded in the "forbidden" geometry, where the projection of the detector direction onto the surface is perpendicular to the polarization vector. If the molecule is standing upright on a flat surface the 4σ intensity should be zero in the forbidden geometry because of simple selection rules; only the 1π level can be seen in this geometry (the residual 4σ intensity in curve b for CO

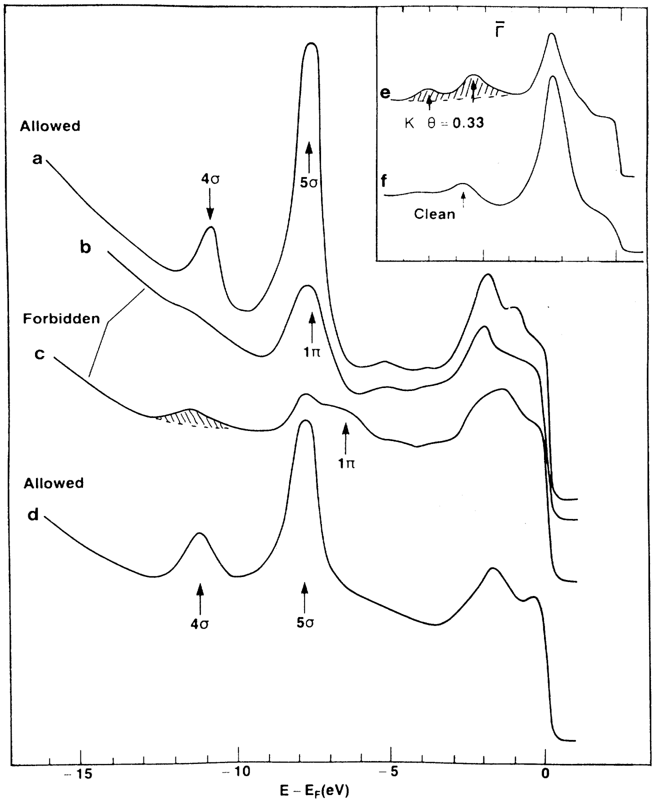

FIG. 1. Photoelectron spectra of (CO + K)/Ru(0001) system. Curve *a* (*d*) is the allowed geometry and *b* (*c*) the forbidden geometry measurement at 30 eV photon energy for CO (CO + K) adsorbed on Ru. The light is *s* polarized and the collection is 20° from the normal. Curves *f* and *e* are normal-emission spectra for *p*-polarized light for clean Ru and $\frac{1}{3}$ of a monolayer of K, respectively.

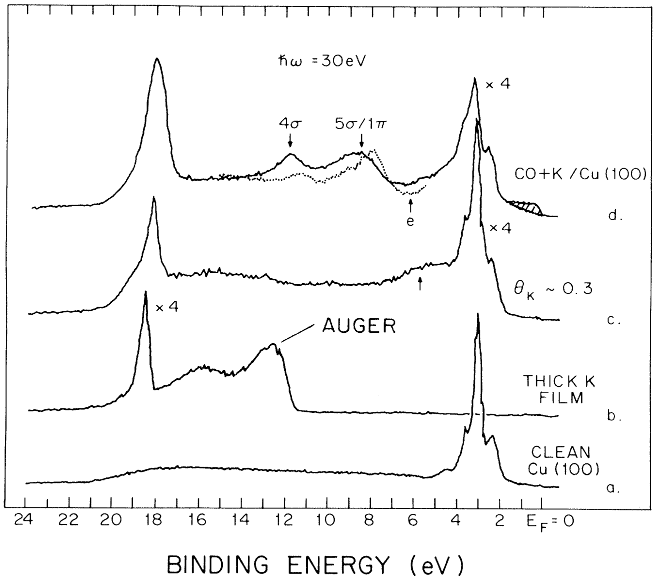

FIG. 2. Photoemission spectra of Cu(100), taken 15° off normal emission with *p*-polarized light. Curve *a*, clean Cu; *b*, a thick film of K; *c*, 0.3 of a monolayer of K in a hexagonal structure; and *d*, CO + K, 2-L CO at 110°K. Curve *e* is 20° off normal with *s*-polarized light.

on clean Ru is due to the imperfect polarization of the incident light). Similar results have been obtained for the (CO + K)/Cu system.[17]

There are three important observations from these data:

(1) The 1π-derived level is significantly shifted to lower binding energy.

(2) The symmetry of the CO molecule bound to the surface in the presence of K has been considerably lowered from the upright bonded CO found on clean surfaces. This is manifested in the increased signal from the 4σ level in the forbidden geometry (an increase of ~25% over the clean-Ru case) and by the upward shift of one component of the CO 1π level by 1 to 1.5 eV. Curves *d* and *e* of Fig. 2 show the equivalent π level for CO on Cu.

(3) A substantial increase in intensity near E_F was observed for (CO + K)/Cu, as illustrated in curve *d* of Fig. 2. This increase in intensity was observed for a wide range of collection angles and photon energies and its symmetry is compatible with π symmetry. We attribute this feature to emission from the CO 2π molecular orbital. On the other hand, we have been unsuccessful in identifying any contribution from the 2π level in the spectra for CO adsorbed onto clean Cu. This increased intensity near E_F may also occur on transition metals but because of the large substrate density of states near E_F it is difficult to identify. Broden, Gafner, and Bonzel[5] have reported an increase in emission near E_F for the (CO + K)/Fe(110) system, and Lee *et al.*[18] for the (CO + K)/Ni(111) system.

The involvement of the 1π and 2π molecular orbitals of CO in the bonding, and the anomalously large CO bond weakening (frequency shift), argue for a π-bonding configuration of the molecule as observed in at least one transition metal complex $[(\eta^5\text{-}C_2H_5)_3Nb_3(CO)_7]^{12}$ where one CO, with its C atom threefold coordinated to three Nb atoms, is tilted 50° such that the oxygen is coordinated to two of the metal atoms. The CO stretching frequency in this configuration is 1330 cm^{-1}. The tremendously large shift in the CO stretch is a result of π bonding, where in a simple molecular orbital picture this involves both metal donation to the CO 2π level and direct 1π interaction with the metal. This simple picture can easily be adopted to explain the 1412- and 1557-cm^{-1} CO stretching frequencies reported for CO bound to a kink site of a stepped Pt surface,[14] the 1520-cm^{-1} frequency observed for CO at a step site on a Ni surface,[13] or the 1530-cm^{-1} C-O stretch for CO bound in a deep hollow site on Fe(111).[15] What remains to be determined is the role of the K atom in creating the π-bonded configuration on a single-crystal surface.

Details of the geometry of this π-bonding configuration are more difficult to assess than its symmetry. The 1π interaction and the reduction of symmetry can either result from the CO binding to the surface in a bent configuration[19] because of an *indirect through metal K-CO interaction, or a long-range interaction* (see discussion in Norskov, Holloway, and Lang[20]); or there could be a *direct interaction between K and CO involving overlap of the molecular orbitals* as suggested by Sachtler.[21] Though we cannot answer this question unambiguously at this time, we have considerable evidence that the K-CO interaction is short range:

(1) Thermal desorption spectra demonstrate autocatalytic desorption behavior.[16] The K and CO stabilize each other at the coverages used in this work.[16]

(2) The K $3p$ core level at ~ 18 eV binding energy undergoes dramatic changes in line shape and intensity when CO is adsorbed. High-resolution spectra from thick K films (like curve *b* of Fig. 2) show $3p$ core levels that can be resolved into two spin-orbit peaks (~ 0.3 eV splitting) with a surface and bulk contribution to each. K adsorbed on the surface in an ordered submonolayer array exhibits a $3p$ core level that is much more asymmetric [Fig. 2(c)] than seen for bulk K. When CO is adsorbed onto this ordered K structure there is a ~ 0.3-eV shift to lower binding energy of the K $3p$ peak, a ~ 2.5 increase in its intensity, and a threefold broadening. This line-shape change of the K $3p$ when CO is adsorbed has also been observed on Fe,[5] Pt,[6] and Ni.[22] All of the experimental evidence indicates that the change in the $3p$ line shape is due to an initial-state change, indicating a direct CO-K interaction.

(3) There is a conspicuous change in the Auger spectra from the K $3p$ core hole. In Fig. 2 the photon energy was chosen at 30 eV so that the Auger spectra resulting from the decay of the K $3p$ core hole appears above the K $3p$ photoionization peak. Curve *b* for the thick K film contains peaks at 12.5 eV ($M_{23}VV$ Auger transition) and 15.8 eV (plasmon loss).[23] The spectrum shown in curve *c* for $\theta_K = 0.3$ has an appreciably reduced Auger signal strength compared to the thick film, presumably because of the changes in the valence charge density induced by the bonding of K to Cu. When CO is adsorbed (curve *d*) we cannot find any peaks in the spectra associated with the Auger decay of the K $3p$ hole. A possible explanation is that there is a crossed Auger process between the K and the CO due to their direct interaction that dominates the decay.[24]

(4) The adsorption of K induces new electronic states below the substrate *d* bands, which are shifted or attenuated by adsorbed CO. Figure 2, curve *c*, shows that the presence of an ordered hexagonal K overlayer on Cu creates a broad peak positioned below the Cu *d* bands at 5–5.5 eV binding energy. Similarly on Ru(0001)/$\theta_K = 0.3$, a new peak is observed ~ 7 eV below E_F. Additionally, an existing surface resonance is shifted from ~ 5.8 to 5.5 eV. Both of these levels show dispersion changing $k_{\parallel}$. The observation of alkali-metal–induced peaks below the *d* bands of the substrate is not uncommon [Na/Ag(110),[25] K/Ni(100),[22] and K/Fe(110)[6]]. These data, along with the theoretical calculation for Cs on W(100) by Wimmer *et al.*,[26] indicate that there is a "polarized-metallic" bond between the metal and the alkali-metal atom. Both Figs. 1 and 2 show that coadsorption of CO removes, shifts, or attenuates these K-induced resonances. This observation suggests that the alkali-metal–induced surface resonances are directly involved in the bond of the CO to the surface.

We believe that the above observations can best be interpreted as supporting a direct K-CO interaction. It is hoped that they will stimulate additional theoretical and experimental studies designed to further elucidate the details of alkali-metal interactions with metal surfaces and coadsorbed molecules.

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