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Bonding and electronic structure of coadsorbed CO and K on Ru(001)

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The influence of coadsorbed potassium on the electronic structure of CO on Ru(001) was studied by the combined use of x-ray and polarized uv photoemission, as well as high-resolution Auger spectroscopy. The results from dense adlayers indicate that the strong electronic interaction of CO with neighboring K atoms occurs via the substrate leading to a rehybridization of the Ru–C–O bond of the perpendicularly adsorbed CO molecule and thus to some changes in the valence-band structure. The coverage-dependent binding-energy shifts are explained on the basis of a recent reinterpretation of the CO–Me bond.

Alkali-promoted adsorption of simple gases on transition metals has recently attracted great attention in surface science. The reason originates not only from the high technical importance of such systems for heterogeneous catalysis (e.g., Fischer-Tropsch reaction) or for low work-function photocathodes, but also from the fact that they are ideally suited to study surface bonding and strong interactions between different types of coadsorbates. Most studies on well-defined adsorbates have concentrated on the model system CO + K on different surfaces such as Fe(110),[1] Pt(111),[2,3] Ni(100)[4] and Ni(111),[5] Cu(100),[6] and Ru(001).[7,8] Unusual weakening of the intramolecular C-O bond and strengthening of the Me–C bond have been inferred from enhanced dissociation-probability,[1,3,4,6,9] higher desorption temperature,[1-7] strongly reduced C-O stretch frequencies,[2,7,8] and from vibrational overtone[8] and isotope-exchange experiments.[5,8] These studies have essentially dealt with the central question of how the electronic and geometric structure of the substrate-CO complex changes upon coadsorption of potassium.

The object of this Rapid Communication is to contribute to the clarification of this question by discussing selected data for high K coverages from an extensive study of the adsorption of CO and potassium on Ru(001).[10,11] By utilizing the results from a combined application of x-ray photoemission spectroscopy (XPS), angle- and polarization-dependent ultraviolet photoelectron spectroscopy (UPS), and high-resolution x-ray inducer Auger spectroscopy (XAES) studies, we can show that coadsorbed potassium induces a modified CO species which is vertically attached to the substrate close to neighboring K atoms and probably sp^2 rehybridized (similar to ketones). The shift of all core binding energies to lower values upon coadsorption of CO or K and the changes in the valence-band structure are discussed within the framework of a recent theoretical reinterpretation of the Me–CO bonding[12] and the suggested rehybridization.

The experiments were performed in a VG-ESCALAB MkI chamber equipped with twin anode (Mg, Al), uv lamp with polarizer, position-sensitive detector for high sensitivity,[13] LEED optics, mass spectrometer, and sample transfer mechanism. Potassium was evaporated from a commercial SAES getter source. Standard sample preparation techniques were used, and the cleanliness of the clean and the K-predosed surface was carefully checked with XPS. Experimental details will be given elsewhere.[10]

Some of the XPS results obtained after different exposures of K and CO are shown in Figs. 1 and 2. Figures 1(a) and 2(a) show that increasing coverages of K on a clean Ru(001) surface cause a *continuous decrease* of the K $2p$ binding energies from 294.4 and 297.1 eV ($\theta_K \sim 0.02$) to 293.7 and 296.4 eV ($\theta_K = 0.4$), respectively, and that the formation of a second layer is indicated by a second doublet

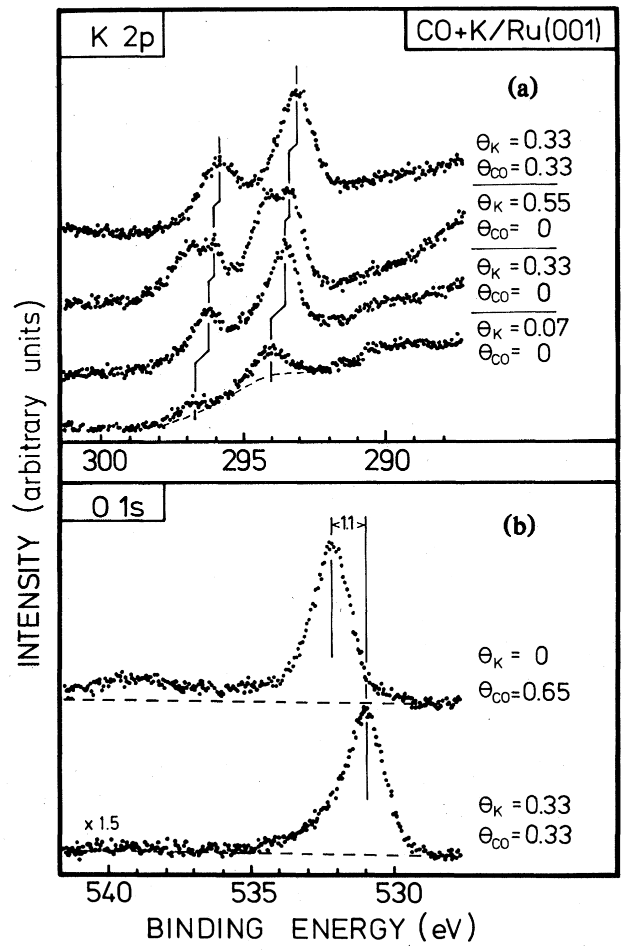

FIG. 1. XPS spectra of (a) the K $2p$, and (b) the O $1s$ level are shown for different coverages of K and CO on Ru(001). K and CO coverages are referred to the substrate and have been calibrated using TDS and XPS peak areas (Ref. 10). The background of the clean Ru surface is indicated by dashed lines. Binding energies were accurately calibrated (Ref. 14) and are referred to the Fermi level.

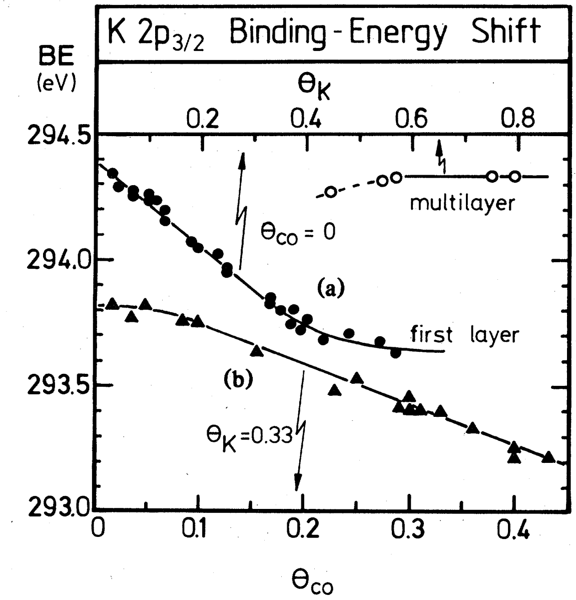

FIG. 2. Binding-energy shift of the K $2p_{3/2}$ level as a function of (a) K coverage on a clean Ru surface, and (b) CO coverage on a K predosed surface ($\theta_K = 0.33$).

at higher binding energies. This binding-energy (BE) decrease for the growing first layer can be easily understood as initial-state effect caused by charge repulsion. Adsorbed alkali-metal atoms donate charge into the metal valence band which leads to an enhancement of electron density near the surface.[15] Thus, a strong dipole is formed causing a considerable reduction of the local potential and the work function. Although most of the additional charge in the substrate is localized close to the adsorbed alkali-metal atom,[9,15] some polarization of substrate density of states (DOS) away from the adsorbate site occurs due to electronic repulsion. Increasing K coverage then leads to enhanced repulsion and thus to a *reduction* of the charge donation from neighboring alkali-metal atoms.[15] This charge "backdonation" explains the observed, continuous decrease of the K $2p$ binding energies [Figs. 1(a) and 2(a)], and the reduction of the dipole moment per K atom as indicated by the behavior of the work function.[10,15]

The O $1s$ BE shift for CO coadsorbed with potassium as compared to CO on the clean surface has most likely the same origin, in that the enhanced substrate DOS gives rise to enhanced Me–C bonding causing additional filling of the CO-π^* orbital and also rehybridization of the Me–C–O complex. This charge donation to the CO molecule and/or the rehybridization cause the observed O $1s$ BE decrease [Fig. 1(b)], an increase of the work function at most coverages,[10] a strengthening of the Me–CO bond, as evidenced by higher CO desorption temperatures[1,2,4–8,10] and a decrease of the C-O bond strength indicated by an enormous reduction of the C-O stretch frequency of up to 600 cm^{-1}.[2,5,7,8,10] Final-state (i.e., screening) effects can be excluded as a noticeable source for the observed BE shifts, because in the present example all observed main peaks belong to well-screened final states, i.e., enough charge has been transferred to fully screen the core hole.[10,11,16]

One observation, which has led to some confusion in the past, remains to be explained. Figures 1(a) and 2(b) show that the K $2p$ level also shifts continuously to lower binding energies with increasing CO coverages. This seems to be in contradiction to the model of an electronegative CO molecule, because it should lead to a reduced repulsion in the valence band. However, the explanation for this effect can be derived from a recent reinterpretation of the CO bonding. Bagus, Nelin, and Bauschlicher[12] have shown, theoretically, that the main contribution to the usual Me–CO bond is provided by π backbonding rather than by 5σ donation which was generally accepted as major contributor. In fact, the 5σ overlap (or the $4a_1$ and $1b_2$ overlap, see below) with the metal causes considerable repulsion which leads to a negative contribution to the M–CO bond strength and to a polarization of substrate DOS away from the CO molecule.[12] This repulsion apparently overcompensates the charge transfer towards the CO molecule (π bonding) and leads to some reduction of alkali charge in the substrate, thus causing a K $2p$ BE *decrease*.

More information about the bonding can be derived from the UPS results (see Fig. 3). The comparison of UPS spectra from a saturated CO/Ru(001) layer with those from a saturated CO+K monolayer clearly indicates that adsorbed CO has a somewhat changed electronic structure upon K coadsorption. In the He II spectra the two-level structure is essentially maintained but both peaks are slightly shifted by about 0.3 eV to higher BE, and their intensities are reduced according to the respective CO coverage [Fig. 3(a)]. In the

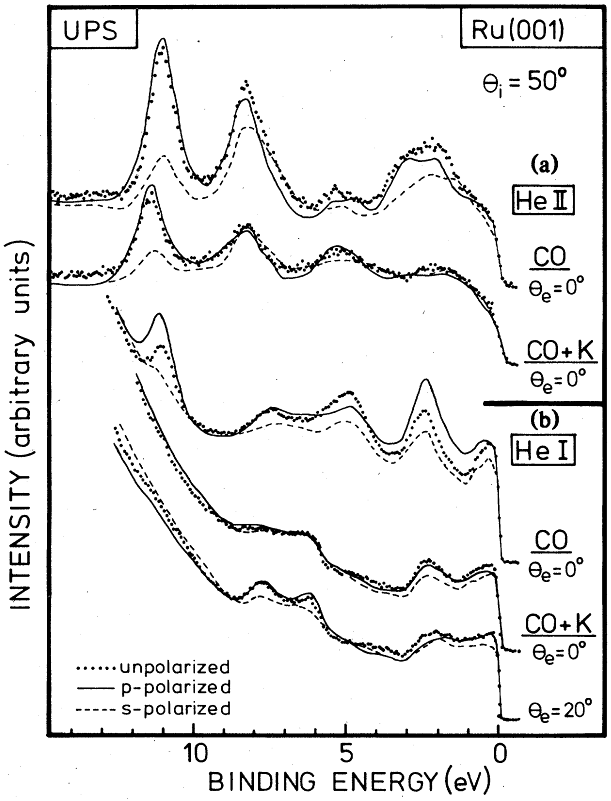

FIG. 3. UPS He II (a) and He I (b) spectra for saturated CO on a clean and on a $(\sqrt{3}\times\sqrt{3})R30$ K-predosed Ru(001) surface, respectively. Angles are referred to the surface normal (angle of light incidence: 50°; emission angles θ_e are given in the figure). Different polarizations of the uv light have been used: dots (unpolarized), continuous lines (p polarized), and dashed lines (s polarized).

He I spectra of the CO + K layer, the "4σ" peak at about 11 eV is drastically reduced at all emission and polarization angles, and an additional peak at about 6.3 eV is clearly discernible [Fig. 3(b)].

The assignment of the observed UPS peaks and our picture of the bonding of CO coadsorbed to potassium can be derived from a variation of both the polarization of the incident uv light and the angle of emission and, in particular, from angle-resolved, x-ray–induced Auger spectra.[11,17] These XAES spectra unambiguously show that the CO molecule is vertically (+/−5°) adsorbed in the saturated CO + K layer.[11] This finding is corroborated by the He II UPS data [Fig. 3(a)] which show an equivalent polarization-dependent behavior of the "4σ" peak (11 eV) for the pure CO as compared to the CO + K layer. According to symmetry selection rules, normal emission from σ (a_1) orbitals is forbidden for pure *s* polarization and a perpendicularly adsorbed molecule.[18] The polarization-dependent He I spectra of Fig. 3(b) clearly show that this is the case for CO/Ru, and also the He II spectra reflect this selection rule if one takes into account that the degree of He II polarization is only about 60%. Unfortunately, for CO + K/Ru, only the He II spectra clearly show an identical polarization dependence of the "4σ" peak, since the He I excited emission from this orbital is strongly reduced probably because of cross-section effects.

The assignment of the peak at 7–8 eV in the UPS spectra is, at least, partly clear. For CO/Ru, it is composed of two contributions from the 5σ and the 1π orbital, respectively. For CO + K/Ru, it can be unambiguously stated that the 7–8 eV peak must also represent a $\pi(b)$ orbital because both the angle-resolved XAES[11] and the polarization- and angle-dependent UPS results are only compatible with this assignment. The question of whether a "5σ" orbital also contributes to the 7–8 eV peak must be discussed together with the new peak at 6 eV which is not observed for pure CO or K layers. Three different models appear to be possible. (1) The 5σ orbital of CO + K/Ru remains nearly unchanged compared to CO/Ru and is also contained in the 7–8 eV peak; the peak at 6 eV must then be due to a Me–CO π bond probably derived from the CO-2π orbital;[19] (2) The 5σ plays again the same role as usual and is represented by the 6 eV peak; and (3) the Me–CO bond is rehybridized (sp^2) and new σ and π bonds (i.e., a_1 and b_1,b_2 orbitals of a C_{2v} point group) are formed similar to those of ketones. Model (1) appears unlikely because our angle-resolved XAES results[11] as well as results from metastable quenching experiments[5] clearly indicate the position of a 2π-derived orbital close to the Fermi level as expected. Moreover, the additional repulsion induced by charge donation from the coadsorbed K atoms would be expected to push the 5σ level to lower binding energies. Model (2) can be excluded because the polarization dependence of the peak at 6 eV [Fig. 3(b)] is *not* compatible with an orbital which is totally symmetric with respect to the C-O axis. Therefore, we come to the conclusion that model (3) gives a reasonable explanation, in that the peak at 7–8 eV reflects emission from the usual "1π" orbital ($1b_1$), while the peak at 6 eV is due to emission from a rehybridized $1b_2$ orbital which is partly responsible for the Me–C bonds. Then 4σ becomes $4a_1$ in C_{2v} which may also partly contribute to the Me–C bond.[20] the question of whether the $5a_1$ orbital is contained in the 7–8 eV or in the 6 eV peak cannot be solved by the present results and must be left to synchrotron studies.

In addition, the electron-energy loss spectroscopy (EELS) and thermal desorption (TDS) results of coadsorbed CO + K[2,5,7,8,10] can be easily explained by sp^2 rehybridization (and thus the loss of one π bond) as well as by additional π backbonding involving the C-O antibonding π^* level ($2b_1$). We note that our XAES results[11] clearly show considerably increased intensity at high kinetic energies which is equivalent to the metastable quenching spectra for CO + K/Ni(111).[5] These experimental findings are compatible with increased π^* density as well as with a nonbonding $2b_2$ orbital localized at the oxygen atom.[20]

We finally note that direct interaction between CO and potassium (e.g., formation of a K–CO bond[6,7]) can be excluded on the basis of the present results as evidenced by the *gradual* decrease of the K 2*p* BE and by the constant line shape[10] upon CO uptake (see Figs. 1 and 2). Rather, indirect interaction via the substrate is the most probable reason for the observed results. However, because of the rather localized nature of the additional VB charge donated by the K atoms, the strong indirect interaction between K and CO is limited to a few Å around a K atom. Therefore, photoemission results from dilute K adlayers ($\theta_K \sim 0.1$) clearly show two CO species, one forming at low CO coverages, which apparently is the same CO + K species as discussed above, and one subsequently filling in at higher CO coverages, which is very similar to CO on a clean Ru(001) surface.[10]

In conclusion, the present results clearly show that CO is perpendicularly adsorbed on a K-predosed Ru(001) surface. For high K coverages only one CO species forms whose electronic structure is different from usual CO. The Me–C–O bond is likely to be sp^2 rehybridized, having increased π^* bonding and new "σ" (a_1) and "π" (b_1,b_2) bonds, some of which are responsible for the additional VB peak at lower binding energy. All peak shifts and work function changes can be understood in detail partly by applying the Bagus model for the Me–CO bond. The results clearly indicate that the interaction between CO and potassium occurs indirectly via the substrate.

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