Structure Determination of an Alkali Metal–CO Coadsorption Phase: Ni(111)-K/CO

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The structure of a Ni(111)-(2 × 2)–K/nCO ($n \approx 2$) coadsorption phase has been determined using K $2p$, C $1s$, and O $1s$ scanned energy mode photoelectron diffraction, and compared with results from pure CO and K adsorption phases having similar coverages. Coadsorbed K has little influence on the local hollow site geometry of the adsorbed CO molecules; the K remains in the atop site of the pure K layer, but the K-Ni bond length increases substantially (by 0.15 ± 0.05 Å), as does the Ni-Ni outer layer spacing. The results conflict with aspects of current interpretations of spectroscopic data from such systems.

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Much of the current interest in CO–alkali metal coadsorption on transition metal surfaces [1–3] stems from the known importance of alkali metal adsorbates in modifying the behavior of such surfaces, as witnessed by the role of alkali metals as promoters in catalytic reactions. Extensive spectroscopic studies have been conducted on several such systems, and a feature of special note is the very pronounced (20% or more) lowering of the C-O stretching frequency seen in vibrational spectroscopy due to the alkali coadsorbate; this change has been variously related to changes in electronic structure, in local adsorption site, and, thus, in the resultant C-O bond strength and chemical reactivity. There is, however, a dearth of quantitative structural information on such systems to support or refute such interpretation.

Here we present the results of a quantitative structural study of a K/CO coadsorption phase on Ni(111), using the technique of scanned energy mode photoelectron diffraction (PHD) [4], and compare these with the results of similar measurements on K [5] and CO [6,7] adsorbed individually on the same substrate at similar coverages. This adsorption system has been previously characterized using thermal desorption and vibrational spectroscopy by Uram and co-workers [8,9]; they find a marked increase in the desorption energy for both K and CO in the coadsorption system, and a systematic lowering of the C-O stretching frequency as described above. They interpret these results in terms of long-range electrostatic interactions as well as short-range interactions, possibly involving complex formation. By contrast, on the basis of a theoretical study Müller [10] has interpreted similar effects in the same K/CO coadsorbates on Pt(111) as due to a local site change of the CO induced by the alkali coadsorbate. Moreover, a very recent low energy electron diffraction (LEED) structure determination of the Cs/CO coadsorption system on Ru(0001) [11] shows that there is, indeed, such a site change in this system. By contrast, our results show that for Ni(111) there is no change in the adsorption site of either the CO or the K associated with the coadsorption. Indeed we find that the local CO adsorption geometry is almost identical with and without coadsorbed K, but the presence of the CO does lead to a significantly longer K-Ni nearest neighbor bond length and the coadsorbed phase does not show the substrate outer layer contraction of the Ni atoms nearest to the adsorbed K atoms which characterizes K adsorption on clean Ni(111) [5,12].

The experiments were conducted at the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H. (BESSY) synchrotron radiation facility using the Fritz Haber Institute's high-energy toroidal grating monochromator (HETGM) beam line [13] and a surface science spectrometer chamber equipped with a 152 mm mean radius spherical sector analyzer (VG Scientific) fitted with three-channel parallel detection. The Ni(111) sample was prepared and cleaned by the usual surface science methods, with the state of order and cleanness characterized *in situ* by LEED and soft x-ray photoelectron spectroscopy (SXPS). The method of preparation of the coadsorption phase was to deposit K from a well-outgassed SAES getter source with the sample at room temperature to produce a (2 × 2)-K phase. The sample was then cooled to approximately 100 K and exposed to 3–5 L (1 langmuir L = 10^{-6} torr sec) of CO to produce a saturated overlayer which retained a (2 × 2) ordered LEED pattern; comparison of the SXPS spectra with similar data taken from a $c(4 \times 2)$-CO phase on this surface indicated that the CO coverage is approximately 0.5 ML (monolayer), which would correspond to two CO molecules per (2 × 2) unit mesh. Because the (2 × 2) LEED pattern may result primarily from the preexisting K phase, we designate our coadsorption state Ni(111)-(2 × 2)–K/nCO, but with the knowledge that n is close to 2.

The mode of collection and analysis of the photoelectron diffraction data were generally as we have described elsewhere [4–7,14]. Specifically, PHD spectra were obtained by recording photoelectron energy distribution curves around the K $2p$, C $1s$, and O $1s$ core levels for a succession of photon energies in 2 eV steps to yield photoelectron kinetic energies in the range 80–400 eV. The individual core level peaks were separated from the background and integrated to yield PHD spectra which were then normalized by smooth average fits to yield modulation spectra. The problem previously experienced of separating the C $1s$ from the comparable intensity C *KVV* Auger peak in the energy range around 250–290 eV (e.g., [7]) was particularly acute for the coadsorption system due to the added presence of the intense K $2p$ and K *LVV* Auger peak, so in the data presented here this section of the C $1s$ PHD spectrum, and a shorter part of the K $2p$ spectrum, have been omitted to avoid confusion.

While full quantitative structure determination requires the use of proper multiple scattering simulations of the PHD data, some key qualitative features can be recognized from comparisons of spectra recorded under different conditions. In Fig. 1 we compare K $2p$ PHD spectra from the Ni(111)-(2 × 2)–K and (2 × 2)–K/nCO phases, and C and O $1s$ spectra from Ni(111)-c(4 × 2)–CO and the (2 × 2)–K/nCO phases. In each case an emission geometry which maximizes the sensitivity to the adsorbate-substrate layer spacing has been chosen. It is immediately clear that while the energetic locations of the main modulations in the C and O $1s$ spectra are similar in the two CO adsorption states, there is a pronounced difference in the K spectra depending on whether or not CO is coadsorbed. As there is now ample evidence that such PHD spectra are sensitive to the local adsorption site, we deduce that the local CO site is similar whether or not K is coadsorbed, whereas the local K geometry is significantly modified by the presence of coadsorbed CO. This qualitative conclusion is borne out by multiple scattering simulations using optimization of a normalized square-deviation reliability factor and a "linear" computational scheme to allow faster searches of the rich structural parameter space [15]. In particular, the CO molecules are found to occupy equally the same two inequivalent hollow sites ("hcp" above a second layer Ni atom, and "fcc" above a third layer Ni atom) which are involved in the c(4 × 2)-CO phase [7]. Figure 2 shows a schematic plan view of the resulting structure [assuming an ordered Ni(111)-(2 × 2)–K/2CO phase]. A complete summary of the structural parameters obtained in the present investigation of the coadsorption phase is compared in Table I with the equivalent parameters from the pure CO and K adsorption phases. In the coadsorption phase the C-Ni top layer spacings are 1.25 ± 0.05 Å for both sites [compared with 1.30 ± 0.05 Å for c(4 × 2)-CO], and the outermost Ni-Ni layer spacing is found to be 2.12 ± 0.10 Å [compared with 2.10 ± 0.15 Å in c(4 × 2)-CO]. The differences in the C-Ni layer spacing and indeed in the Ni-Ni top layer spacing relative to the bulk value (2.03 Å) are clearly of marginal significance. By contrast, although the K atom is found to retain the atop adsorption site of the (2 × 2)-K phase, there is a significant change in the local K-Ni bond length from 2.87 ± 0.03 Å in (2 × 2)-K [5] to 3.02 ± 0.05 Å in the coadsorption state, while the Ni-Ni top layer contraction of the pure (2 × 2)-K phase (to 1.86 ± 0.07 Å) is replaced in the coadsorbed state by a small expansion similar to that indicated for the c(4 × 2)-CO phase. Note that the results of a LEED study of the pure (2 × 2)-K phase [12] differ from our PHD in also revealing a significant "rumpling" of the outermost Ni layer; we find no evidence for any significant rumpling in either phase in our results, although we might expect LEED to be somewhat more sensitive to this effect. Figure 3 shows a comparison between theory and experiment for the K $2p$

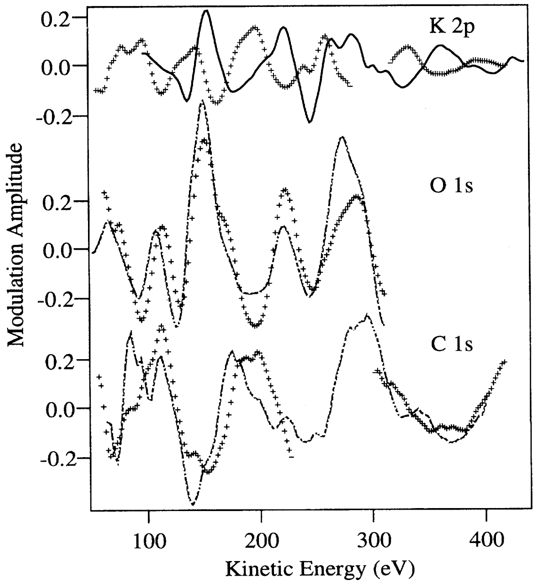

FIG. 1. Comparison of K $2p$, O $1s$, and C $1s$ PHD spectra from the Ni(111)-(2 × 2)–K/2CO phase (+ symbols) with similar measurements of K $2p$ from Ni(111)-(2 × 2)–K (full line), and O and C $1s$ from Ni(111)-c(4 × 2)–CO (dash-dotted lines). The K $2p$ and O $1s$ spectra were recorded at normal emission, the C $1s$ spectra at 40° in the [$1\bar{2}1$] azimuth.

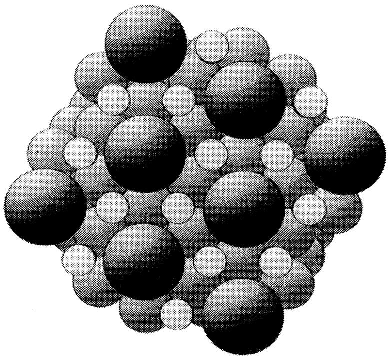

FIG. 2. Schematic plan view of a hard-sphere model of the Ni(111)-(2 × 2)–K/nCO structure (taking n = 2). The largest spheres are the K atoms drawn with an effective radius of 1.77 Å. The smallest spheres are the O atoms of the CO molecules perpendicular to the surface.

TABLE I. Layer spacing values (in Å) found in the present study of the Ni(111)-(2 × 2)–K/nCO surface phase, and in earlier studies of the c(4 × 2)-CO [6,7] and (2 × 2)-K [5] phases on Ni(111). Estimated errors are given in parentheses in hundredths of Å. z(Ni-Ni)nn is the layer spacing between the second Ni layer and the top layer Ni atoms directly below the K atoms. z(Ni-Ni)nnn is the equivalent parameter for the remaining top layer Ni atoms. The z(C-O) distance is deduced from the difference in z(C-Ni) and z(O-Ni) values.

Surface	c(4 × 2)-CO	(2 × 2)-K	(2 × 2)-K/nCO
z(K-Ni)	—	2.87(3)	3.02(5)
z(C-Ni)	1.30(5)	—	1.25(5)
z(O-Ni)	2.46(5)	—	2.46(5)
z(Ni-Ni)nn	2.10(10)	1.86(6)	2.15(10)
z(Ni-Ni)nnn	2.10(10)	1.87(6)	2.12(10)
z(C-O)	1.16(7)	—	1.21(7)

normal emission PHD spectra for the (2 × 2)-K and coadsorbed phases, showing that the pronounced changes seen in the experimental spectra (Fig. 1) are reproduced by the theory.

These structural conclusions need to be considered in the context of previous experimental spectroscopic and theoretical studies of Ni(111)-K/CO in particular, and alkali metal–CO coadsorption on metal surfaces in general. For Ni(111)-K/CO, Uram and co-workers [8,9] have shown that K coadsorption produces a pronounced reduction in the C-O stretching frequency, and coadsorption enhances the desorption energies of both species which are desorbed simultaneously in thermal desorption spectroscopy. Both of these results are characteristic of many alkali-CO coadsorption systems. The vibrational mode softening is commonly associated with increased occupation of the CO $2\pi^*$ antibonding level either due to direct charge transfer from the alkali or due to increased substrate backbonding in the presence of the alkali. On Ni(111) the rate of CO dissociation has been shown to be enhanced [16] by alkali coadsorption, consistent with a weakened C-O bond. Indeed in the case of Na/CO coadsorption on Pt(111), near edge x-ray absorption fine structure (NEXAFS) data [17] have been interpreted as indicating an expansion of the C-O bond length by 0.12 Å relative to the gas-phase value which could also accompany the increased antibonding character of the C-O interaction, although it has been suggested [18] that such interpretation may be ambiguous on the basis of similar results for the system Cu(100)-K/CO.

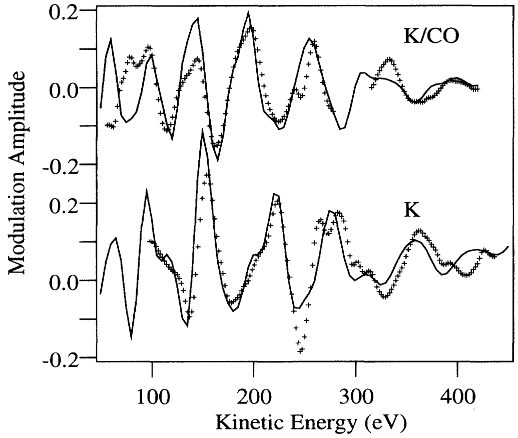

FIG. 3. Comparison of the K $2p$ experimental normal emission PHD spectra (+ symbols) from the (2 × 2)-K and (2 × 2)-K/nCO phases on Ni(111) with the results of multiple scattering calculations (full lines) for the best-fit structures.

A key result from our present experiments is that CO is found to adsorb in hollow sites in both the pure CO layer and the coadsorption phase. We should note in this context that for many years vibrational spectroscopic data from the Ni(111)-c(4 × 2)–CO phase were thought to indicate bridging CO molecules, but there is now ample evidence from both PHD [6,7] and surface extended EXAFS [19] that this is not correct. As mentioned above, theoretical calculations for the Pt(111)-K/CO phase identified a CO site change (from atop to hollow) as the key factor in the pronounced softening of the C-O stretching vibration [10]; moreover, there is experimental evidence for just such a site change for Cs/CO coadsorption of Ru(0001) [11]. In both cases, CO is proposed to move to a higher coordination site in the presence of the coadsorbed alkali. Our results show that this site change clearly does not occur on Ni(111) where the CO already occupies hollow sites in the absence of coadsorbate. By contrast, more recent density functional calculations for Pd(100)-K/CO [20] indicate that both the reduction in the C-O stretching frequency and the synergistic increase in K and CO desorption energies can be understood in terms of a change in the electron distribution by the adsorbed alkali ions which results in a partial filling of the CO π^* orbital; they suggest this mechanism should apply generally to alkali-CO coadsorption systems, and also note that the effect is short range due to the screening effect of the metallic electrons. Evidently the close spacing of CO and K in our structure (Fig. 2) is consistent with a short range interaction of this kind. The one surprising feature of our results, however, is that the increased desorption energy of the K is accompanied by an *increase* in the K-Ni nearest neighbor spacing. This runs contrary to simple views of bonding of increased strength, but may be less crucial for the polarization mechanism of this recent theoretical study. Interestingly, the recent Ru(0001)-Cs/CO structural study [11] shows no apparent change in the Cs-Ru distance due to the presence of the CO; by contrast, a very recent study of K/CO coadsorption on Co($10\bar{1}0$) finds a substantial increase in the K-Co layer spacing on coadsorption, although the K remains in the hollow adsorption sites [21].

There remains the question of whether there is any evidence for an extension of the C-O bond length in our measurements. Unfortunately, the precision in our structure determination is not really adequate to answer this question in a convincing way. The C-O bond length is deduced in our measurements from the difference in the location of the O and C atoms (for which the most sensitive data are the O 1*s* and C 1*s* PHD spectra, respectively), and the estimated precision in each of these locations perpendicular to the surface is ±0.05 Å, leading to a precision in the C-O bond length of ±0.07 Å, and a precision in the *difference* in the C-O bond lengths for the $c(4 \times 2)$-CO and (2×2)-K/2CO phases of ±0.10 Å. Our results do indicate that the C atoms in the coadsorption phase are 0.05 Å closer to the top Ni layer than in the pure CO phase, and that the O atom locations relative to this layer are identical. We thus deduce a coadsorption-induced lengthening of the C-O bond of 0.05 ± 0.10 Å, consistent with the NEXAFS result for Pt(111)-Na/CO, but also consistent with the possibility of no change in this bond length.

In summary, this complete quantitative analysis of an alkali-CO coadsorption phase, Ni(111)-(2×2)–K/*n*CO, shows that there is a significant lengthening of the K-Ni nearest neighbor bond length associated with CO coadsorption, and that the substrate relaxation is essentially the same as that found for a pure CO layer and distinctly different both qualitatively (an expansion rather than a contraction) and quantitatively from that produced by a pure K layer. The CO hollow adsorption sites are unchanged by the presence of coadsorbed K, and, while a very small C-O bond length expansion is indicated, this lies within the estimated precision of the measurements.

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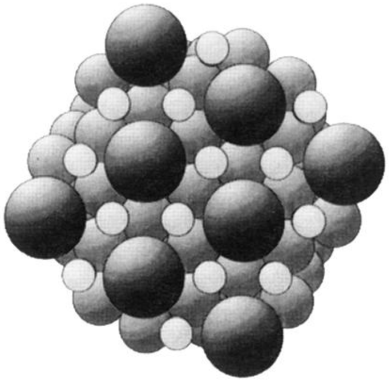

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