Tilted CO on Clean and Potassium-Covered Ni(110): Adsorbate Orientation from Polar-Angle X-Ray-Photoelectron Diffraction

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Carbon monoxide adsorbed on clean and K-covered Ni(110) surfaces is studied by polar-angle x-ray-photoelectron diffraction to determine the C–O bond orientation relative to the surface normal. At 300 K CO adsorbs perpendicularly on clean Ni(110) with the C down, while at 120 K a high-coverage layer forms with CO tilted ±21° from normal in the [001] azimuth. The coadsorbed K/CO layer at 300 K is a mixture of tilted and perpendicular CO, the former having a tilt angle of 32° in the [001] azimuth. This tilted CO is due to the K interaction and is more strongly adsorbed than perpendicular CO.

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Marked changes in the surface chemistry of CO adsorbed on a transition metal accompany alkali-metal coadsorption.[1] While of fundamental interest, they are also important to an understanding of alkali-metal promotion in heterogeneous catalysts.[2,3] An obvious first step in our understanding of what happens to CO in the presence of an alkali metal is to know its orientation: Is it adsorbed in the usual perpendicular geometry with the C down? Some workers have interpreted their experiments in terms of alkali-metal-induced orientation changes,[4-8] but direct measurements have mostly found perpendicular CO.[9-12] One electron-stimulated-desorption ion-angular-distribution study found tilted CO in the presence of Na on Ru(001), but only at 80 K and for saturation CO coverage.[4] At other temperatures and coverages only perpendicularly adsorbed CO was found. It is unclear whether such orientation changes are more general, and how they relate to the alkali-metal–CO interaction and substrate structure.

A promising system for the study of this problem is CO + K on Ni(110). An fcc (110) surface is atomically rough, leading to more intrinsic variation in adsorption-site geometry than on, e.g., an fcc (111) surface. For the latter, the high symmetry of adsorption sites might mitigate the perturbation of a coadsorbed alkali metal.[9,10] For example, the adsorption sites for K on Ni(110) are the troughs between atomic rows in the [1$\bar{1}$0] direction,[13] while CO on the clean surface adsorbs in on-top and short-bridge sites atop the rows.[14,15] The (110) surface asymmetry does in fact lead to a tilted CO species even on the clean surface at low temperature and high coverage.

We studied this system using x-ray-photoelectron diffraction (XPD), which relies on the highly forward-peaked scattering of fast photoelectrons (kinetic energy >300 eV) by nearby atoms.[16] The method pinpoints the bond axis of CO by sensing the C-1s intensity increase due to scattering from the O. Typically, the forward-scattering peak is narrow enough (ca. 20°) to determine precisely the molecular-bond axis, and single-scattering calculations adequately describe the process.[9,17,18] We observed perpendicular and tilted CO on both clean and K-covered Ni(110). The results show for the first time that K-affected, strongly adsorbed CO on this surface can be definitely assigned to a species tilted 32° from normal along [001] directions.

The measurements were done under ultrahigh vacuum (UHV) on a well-characterized Ni(110) crystal. The x-ray source (1253.6-eV photon energy) and angle-resolving hemispherical analyzer are fixed; we vary the photoelectron polar angle ±60° from normal ($\theta=0°$) by sample rotation about an axis in the plane defined by incident photons and detected electrons. Zero of θ is defined by the symmetry of a substrate core or Auger level. Two azimuths 90° apart were measured corresponding to the electron parallel momentum in either the [001] or the [1$\bar{1}$0] direction. We improved the signal-to-noise ratio considerably relative to our earlier work[9,18] by multiple scanning of the 120° polar-angle range in 1° steps. At each angle the core-level intensity is taken as the net peak height above a linear background determined by measurement of either side of the peak. Potassium dosing is from an *in situ* source (SAES Getters, GmbH) with the relative coverage determined from K/Ni Auger-peak ratios, with the assumption of room-temperature saturation at $\theta_K=0.53$ (6.04×10^{14} K/cm^2).[13]

Results for K and CO adsorbed separately at 300 K are shown in Fig. 1. Here and in other figures we plot the net peak height times $\cos\theta$ to equalize the intensity increase with θ for a surface species,[19] and normalize the spectra to 1.0 at $-60°$ to facilitate comparison. Thus, for no forward-scattering enhancement, and neglecting large-angle scattering events from the substrate, we expect a constant adsorbate core-level intensity versus θ. The lines are computer-generated smoothings using an average window 8° wide. Error bars (statistical counting noise) are shown near 0°. In Fig. 1(a) for K 2p (both $\frac{3}{2}$

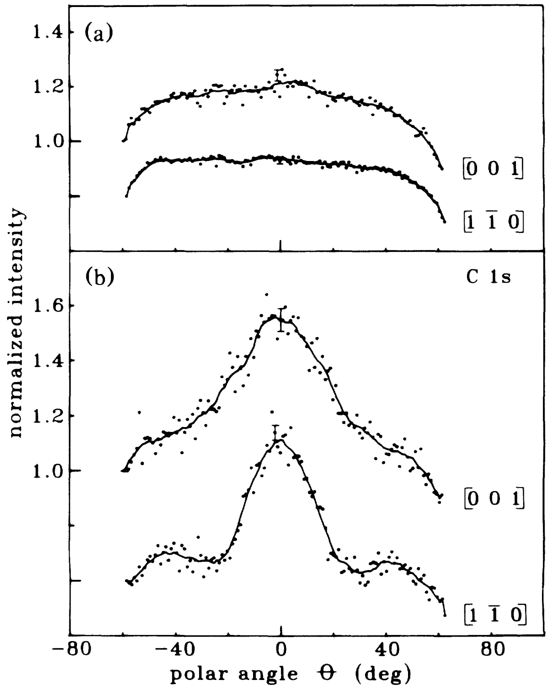

FIG. 1. (a) Scans of K 2p intensity for K adsorbed alone; both azimuths are shown. For [001], $\theta_K=0.53$; for [1$\bar{1}$0], 0.42. (b) Similar scans for the C 1s level of CO adsorbed alone. For both parts $T=300$ K.

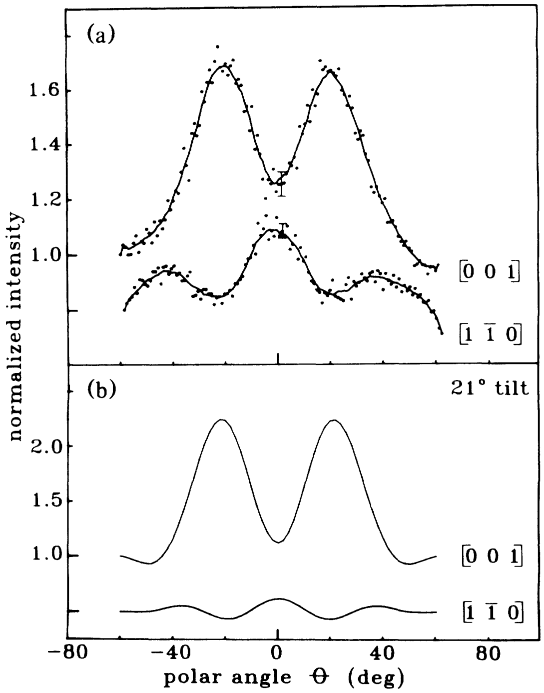

FIG. 2. Saturation CO adsorption at 120 K: (a) Carbon 1s scans in both azimuths are compared to (b) single-scattering calculations.

and $\frac{1}{2}$ levels show the same structure) the intensity is nearly constant up to ca. ±50°, where an intensity decrease due to the finite sample width sets in. No forward-scattering enhancement is seen, showing that the K is distributed in a single layer. The formation of a second layer would lead to structure due to the forward scattering of K 2p photoelectrons of the first layer by atoms in the second layer.

In contrast, the C 1s level from a saturation CO layer has a large (ca. 50%) enhancement at $\theta=0°$ in both azimuths, as well as smaller first-order diffraction peaks near ±40° for [1$\bar{1}$0] [Fig. 1(b)]. The O 1s level from such a layer shows no enhancment [i.e., a structure similar to Fig. 1(a)]. These spectra are characteristic of vertically adsorbed CO with the C end of the molecule bonded to the metal. The 27° width of the [1$\bar{1}$0] peak restricts the polar tilt to less than about 5°.[9,17] This width is affected by the Ni—CO bending vibration. From comparing the peak widths for [001] and [1$\bar{1}$0] we see that this bending mode is very asymmetric for the CO adsorption sites atop the rows.[20]

At 300 K the saturation CO coverage is ca. 70%, but below 160 K a complete monolayer can be adsorbed in a (2×1) structure having $p2mg$ symmetry. Several groups[21-26] have concluded that the CO tilts in [001] directions, with electron-stimulated-desorption ion-angular-distribution measurements setting the angle at 19°.[23,24] This tilt arises from repulsion between O ends of the molecules, adsorbed only 2.49 Å apart on the atomic row.[27] Figure 2(a) shows results for saturation CO at 120 K. Two well-resolved forward-scattering lobes appear at ±21° for [001]. Again, the enhancements are restricted to the C 1s core level. This agrees well with single-scattering calculations [Fig. 2(b)] for CO adsorbed with a 21° tilt in [001] directions and taking account of CO-metal bending vibrations (rms displacement 8°).[9,17] More enhancement is predicted than observed [note the scale change for the ordinate in Fig. 2(b)], partly an effect of the plane-wave assumption used in the calculation,[28] but the shapes of the curves agree. There is also good agreement with the earlier electron-stimulated-desorption ion-angular-distribution results[23,24] and with recent XPD experiments of Baskotte, Neumann, and Freund.[29] The [1$\bar{1}$0] scan shows a small peak at 0° which is not due to a remnant of vertically adsorbed CO, but rather to the tails of the forward-scattering cones (widths ca. 22°). These enter the analyzer parallel to the entrance slit, giving an effectively larger angular acceptance in this geometry, and leading to the worse agreement with theory for [1$\bar{1}$0]. Agreement for both azimuths is improved by our correcting for the "instrument function" [i.e., Fig. 1(a)], but this does not change the tilt angle. Further calculations showed that 1° changes in the mean tilt angle could be distinguished for these data [Fig. 2(a)].

Figure 3 shows CO + K coadsorption results for θ_K

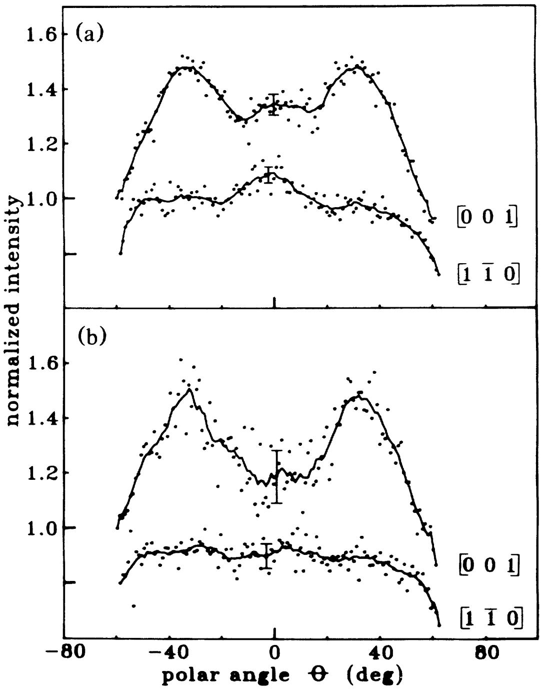

FIG. 3. Coadsorption (CO + K) at 300 K: C 1*s* XPD scans (a) before and (b) after heating to 485 K. Potassium coverages are $\theta_K = 0.16$ for [001] and 0.19 for $[1\bar{1}0]$.

$= 0.16$ ([001]) and 0.19 ($[1\bar{1}0]$) at 300 K. Whitman and Ho[30] studied coadsorption near this θ_K range with thermal-desorption and high-resolution electron-energy-loss spectroscopy. They find a strongly affected CO species with a lowered C—O stretch frequency (1660 cm^{-1}) and an increased desorption temperature, mixed with a less-affected species. The latter is selectively desorbed by a brief heating to 485 K. The scans in Fig. 3(a) are much different from those for the clean surface [Fig. 1(b)] and show tilted (±32°) and vertical CO. Vertical CO is especially clear in the $[1\bar{1}0]$ scan; the 32° tilt angle is apparently large enough to make tilted CO invisible in this azimuth. This absence of any nonvertical enhancement in the $[1\bar{1}0]$ scan suggests that the tilt is limited to [001] directions. Scans in Fig. 3(b) taken after heating of the coadsorbed layer to 485 K show that the heating desorbs all vertical CO. Tilted CO is thus the K-stabilized species observed in high-resolution electron-energy-loss spectroscopy and thermal-desorption spectroscopy, having a weakened C—O bond and an increased adsorption energy. As on the clean surface, the O 1*s* level shows no forward-scattering enhancement: The C end of the molecule remains bonded down. Similarly, K 2*p* levels show no change from Fig. 1(a) after CO adsorption, making adsorption atop K unlikely. Mixtures of perpendicularly adsorbed and vertical CO were also observed at other K coverages, with the largest amount of perpendicular CO occurring for small θ_K.

While these measurements cannot determine the adsorption site, they do suggest some possibilities. For strongly affected CO, Whitman and Ho[30] thought a short-bridge site was likely, next to a K in a fourfold hollow. One can then imagine the CO tilt arising through electrostatic attraction between the (negative) O end of the molecule and a partially ionic K^+. Recent reports[31] of a K-induced "missing-row" reconstruction of Ni(110) for $\theta_K < 0.31$ suggest an alternative. This reconstruction exposes (111) "microfacets" at 35.3° to (110) (with the assumption of no relaxation). If the reconstruction is not lifted by CO adsorption, an attraction between K in the troughs and CO might move the molecule from the short-bridge site to the microfacet. Here its bonding geometry would be similar to that on a (111) surface,[9,10] i.e., perpendicular to the microfacet, yielding nearly our observed tilt angle.

In summary, we have observed tilted CO induced by K coadsorption and for the first time associated the tilted species with alkali-metal–induced thermal stability. This contrasts with previous reports of alkali-metal–induced CO orientation changes[4–6] in which the effect was very sensitive to CO or K coverage. The tilt, 32° in [001] directions, is reminiscent of the (2×1) *p*2*mg* CO structure, from which, however, the coadsorbed species can be clearly distinguished. Since CO adsorbs vertically in other coadsorbed systems,[9–12] the special geometry of the substrate plays an important role. These results illustrate the capabilities of XPD in highly accurate determinations of the adsorbate structure.

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