Adsorption of Carbon Monoxide on Ni(110) Above Atmospheric Pressure Investigated with Surface X-Ray Diffraction

K. F. Peters,[1] C. J. Walker,[1,2] P. Steadman,[1] O. Robach,[1] H. Isern,[1] and S. Ferrer[1,*]
[1]*European Synchrotron Radiation Facility, BP 220, 38043 Grenoble cedex, France*
[2]*University of Leicester, Department of Physics and Astronomy, University Road, Leicester LE17RH, United Kingdom*

(Received 16 January 2001)

The crystallographic structure of CO adsorbed on Ni(110) has been investigated with x-ray diffraction at ambient pressures of CO ranging from 2.3 to 10^{-10} bars. At room temperature, the high pressure and vacuum structures are identical. Above room temperature (~130 °C), the high pressure of CO induces a restructuring of the Ni substrate that develops strained (111) microfacets.

DOI: 10.1103/PhysRevLett.86.5325 PACS numbers: 68.43.Mn, 61.10.Eq, 68.35.Bs, 68.35.Rh

Since the discovery in the 19th century that some gas molecules adsorbed onto a metal surface are readily converted into other molecules, *heterogeneous catalysis* has achieved tremendous technological, environmental, and commercial importance. Understanding the gas-metal interaction via the relevant adsorbate structures is a primary goal of modern surface science. The adsorbate geometry of gases on metal surfaces has thus been determined and cataloged for more than one thousand systems under the extreme vacuum conditions of 10^{-8}–10^{-14} bars where appropriate techniques were available. An essential question remains unanswered: *Are the known vacuum structures also the relevant structures present under real catalytic conditions near 1 bar?* Here, we now answer that question affirmatively (at room temperature) and negatively (at elevated temperature) for the archetypal case of CO over Ni(110). Based on x-ray diffraction measurements, the CO/Ni(110) structure is determined *in situ* from 10^{-10} to 2.3 bars CO at 25 °C. Interestingly, the vacuum structure persists unchanged over 10 orders of magnitude in pressure. A subsequent warming to ~130 °C at 2.3 bars then causes a massive restructuring of the Ni surface, consisting of the development of microfacets with (1 1 1) orientation and surface strain probably due to carbon dissolution. These results confirm the relevance of vacuum studies to catalysis and offer a glimpse at the complexity of elevated-pressure surface chemistry.

Nickel catalysts are used most frequently to produce methane from carbon monoxide and hydrogen [1]. The reaction is thermally activated (usually performed from 150 to 400 °C), carried at or above atmospheric pressure, and is thought to involve dissociation of CO adsorbed on the metal surface. In vacuum, adsorbed CO on Ni(110) forms a 2 × 1 structure consisting in an ordered zigzag arrangement of tilted molecules on short-bridge sites of the substrate as depicted in Fig. 1. The structural parameters obtained from the most recent LEED (low-energy electron diffraction) study [2] are given in Table I.

Several investigations on the adsorption of CO at pressures near the atmosphere have been recently performed on Ni or other metal surfaces of interest in catalysis, by means of suitable probing techniques unaffected by the atmosphere of gas around the samples. Nonlinear optical techniques involving the reflection of laser beams [3,4] measure the vibrations of the CO molecules bonded to the metal which provide information on the structure of the adlayer. Also, scanning tunneling microscopy (STM) investigations [5] can determine some structural characteristics of the chemisorbed layer such as symmetry elements and linear dimensions. However, to the best of our knowledge, no detailed study determining the relevant parameters of the structure such as bond lengths, bond angles, distortions on the substrate etc. has been published thus far.

The experiments reported in the following were performed at the surface diffraction beam line at the ESRF with x rays of wavelength 0.74 Å and a specially designed [6] ultrahigh vacuum. (UHV)/high pressure chamber mounted on a high precision diffractometer. In UHV (10^{-12} bars), the Ni(110) surface was prepared by standard methods (sputtering and annealing). High purity CO

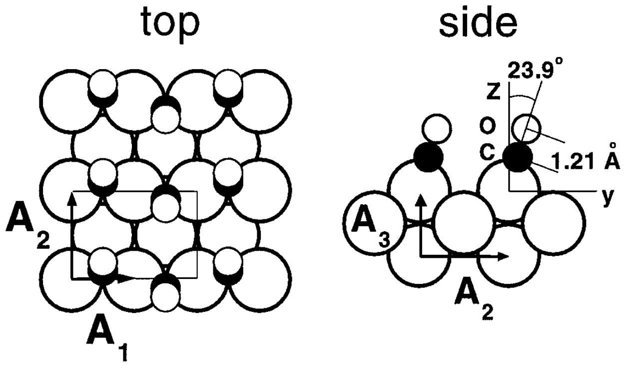

FIG. 1. Top and side views of the CO/Ni(110)-(2 × 1) structure. A_1, A_2, and A_3 are the lattice vectors used to describe the crystal lattice. $A_1 = A_3 = a_0\sqrt{2}$ ($a_0 = 3.524$ Å is the lattice constant on Ni) and $A_2 = a_0$. The rectangle shows the 2 × 1 unit cell. The tilt angle and bond lengths in the adsorbed CO molecules are those obtained from the fit of the data set at 2.3 bars of CO. In reciprocal space, H, K, and L are coordinates parallel to A_1, A_2, and A_3, respectively.

0031-9007/01/86(23)/5325(4)$15.00

TABLE I. Structural parameters of CO/Ni(110)-(1 × 2).

	Ref. [2]	This work	
		10^{-10} bars	2.3 bars
Ni-C tilt angle (deg)	20(4)	21.7(5)	21.3(5)
C-O tilt angle (deg)	20(4)	23.5(9)	23.9(7)
Ni-C bond length (Å)	1.85(4)	1.84(2)	1.83(2)
C-O bond length (Å)	1.15(7)	1.19(3)	1.21(3)
Ni-Ni expansion (Å)	···	0.052(3)	0.058(2)

gas was further purified, by means of a distillation process, for introduction into the chamber. The chamber had a cylindrical, x-ray transparent, Be window which allowed the incoming and diffracted beams to reach the sample surface and the detector, respectively.

We collected two independent sets of crystallographic data *in situ* after exposing a well-prepared Ni surface to 10^{-10} and 2.3 bars of CO. (The gas was kept in the chamber during the measurements.) At crystallographic positions (H, K, L) in reciprocal space, the structure factor was obtained by measuring the integrated intensity of the diffracted beam as the crystal was rocked around the surface normal and by applying the appropriate corrections [7].

Figure 2 shows the results. The top panel gives the structure factors of six diffraction rods. Four have integer-valued H and K corresponding to the periodicity of the substrate lattice, and two rods have fractional index arising from the CO 2 × 1 periodicity. The bottom panel displays the structure factors of the fractional reflections at $L \cong 0$. Inspection of the figure shows immediately that the vacuum and high pressure data sets are virtually identical and thus demonstrates that both structures are the same. Crystallographic analysis of the high pressure data through a least square minimization routine results in the continuous red curve in the figure. Referring to Fig. 1, our *a priori* model had five parameters to describe the atomic coordinates plus a scale, roughness, and Debye-Waller factors. The adjusted coordinates were (y, z) for both the C and O atoms plus the z coordinate of the topmost Ni atoms. The best fit model resulted in the structural parameters shown in Table I. The agreement with the results of Ref. [2] is excellent. In addition, our analysis reveals a slight expansion of the Ni planes that was not detected in Ref. [2]. The table also shows the results of the analysis of the low pressure data which coincide with these at high pressure.

From the previous experiments, we can conclude unambiguously that the equilibrium structure at room temperature of CO on Ni(110) at 2.3 bars of CO ambient pressure is the same as that obtained under UHV conditions by dosing the Ni(110) surface at saturation with 10^{-10} bars of CO.

To our knowledge, this is the first chemisorbed structure determined in detail near the atmospheric pressure.

The effect of temperature on both cases is, however, drastically different. Annealing the Ni crystal to ~130 °C in 10^{-10} bars of CO causes disordering and desorption of the chemisorbed layer while the Ni substrate remains intact. This is seen via the fractional order reflections (from the CO adlayer), whose intensities drop to zero while the

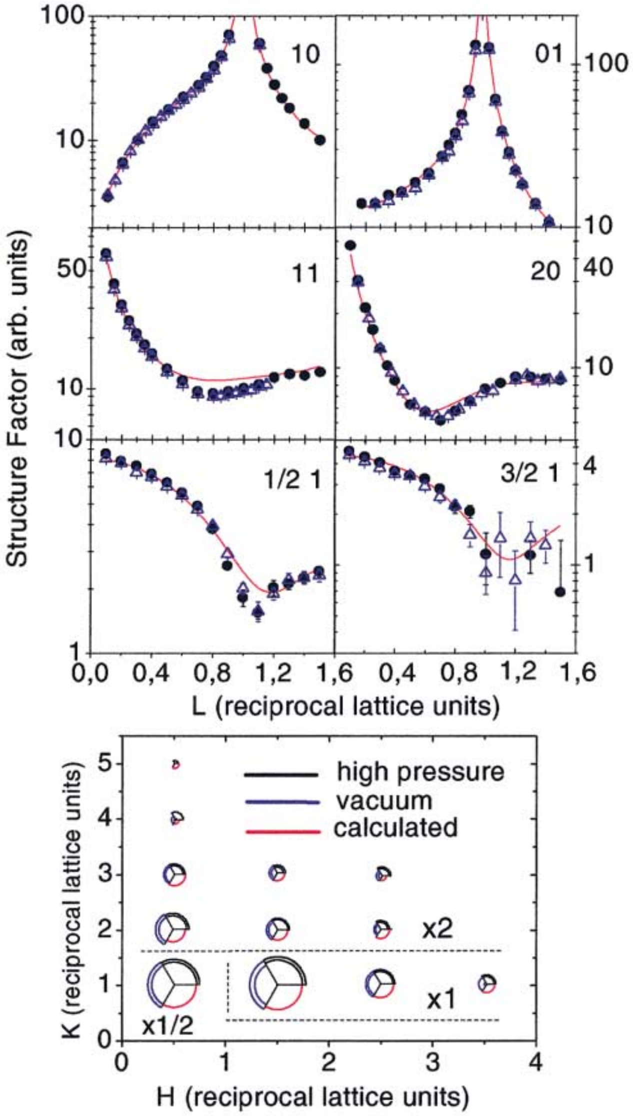

FIG. 2 (color). Crystallographic structure factors of CO/Ni(110)-(1 × 2) at room temperature. Upper panel: black circles: measured structure factors from four integer rods $[(H, K) = (1,0), (0,1), (1,1), \text{and } (2,0)]$ and two fractional order rods $[(H, K) = (\frac{1}{2}, 1), (\frac{3}{2}, 1)]$ in 2.3 bars of CO; blue open triangles: structure factors measured in 10^{-10} bars of CO; red solid lines are calculated structure factors from our best fit to the high pressure data. In the integer rods, the diverging values of the structure factors at some integer values of L correspond to the bulk Bragg reflections of the Ni crystal. Bottom panel: In-plane fractional order structure factors measured at $L = 0.1$. The radius of the black 120° sectors are proportional to the structure factors of the reflections from the structure in 2.3 bars of CO. The error bars are indicated by the two radii. The blue sectors represent the structure factors for the vacuum structure and the red ones are calculated from the fit to the high pressure data.

integer order reflections (which derive principally from the Ni surface) are unaltered. The same thermal treatment in 2.3 bars of CO also causes the vanishing of the CO reflections but, in strong contrast with the vacuum annealing, it induces a major restructuring of the Ni substrate. The intensities of the integer order reflections are greatly diminished (depending on the duration of the annealing they can drop to zero) and new, intense reflections appear. They are marked with gray triangles in Fig. 3 that show a series of scans along the K axis for different values of L.

As can be seen, the K coordinates of the maxima shift when L is varied. This shows the existence of directions in reciprocal space which make an angle different from 90° with the $(1\,1\,0)$ substrate plane. A plot in an L vs K diagram of the positions of these new reflections results in two very well-defined straight lines with slopes 0.994(2) and $-1.007(8)$. In conventional cubic coordinates, the above lines coincide precisely with the $[1\,1\,1]$ and $[1\,1\,-1]$ directions. As a cubic crystal terminated in a surface plane with orientation (H, K, L) has diffraction streaks along the $[H, K, L]$ direction, the above results indicate that the original Ni(110) surfaces develops faceting in $\{1\,1\,1\}$ planes due the reaction with CO.

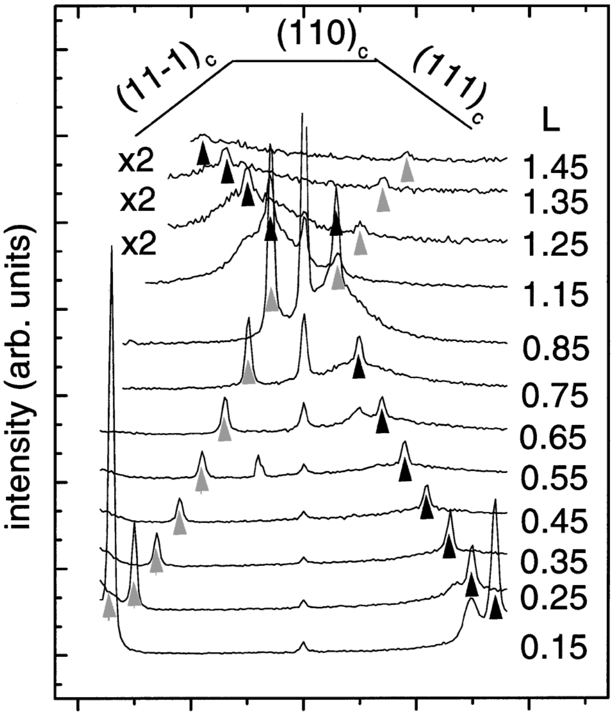

FIG. 3. Scans along the K direction in reciprocal space for different values of L (H was kept constant at 0), obtained after annealing the Ni crystal a few minutes in a high pressure of CO. The peaks marked with light and dark gray triangles arise from microfaceting of the Ni crystal surface.

Some insight on the nature of the microfacets can be obtained by analyzing the intensities of the facet reflections since as it has been previously shown [8], for a given value of L, they are different if an inhomogeneous strain exists in the surface region. Inspection of Fig. 3 reveals that this is the case since the peaks at $K < 1$ are more intense that those at $K > 1$.

To quantify the strain, we modeled the facets as triangular prisms with $(1\,1\,1)$ and $(1\,1\,-1)$ lateral faces as shown in Fig. 4. Following [8], the interatomic distance along the A_2 axis was allowed to vary quadratically with height from zero strain at the base of the prism to a maximum strain at the apex. The deformations along the A_3 axis were deduced from the Poisson ratio. The continuous lines in Fig. 4, which approximately fit the data, were obtained for strain values of 4% at the apex. This value of the strain is consistent with a solid solution of about 1% carbon atoms in the Ni crystal [9]. The characteristic dimensions of the facets as obtained from the fit are about 120 Å in width and 90 Å in height.

Our understanding of the surface morphology was enlarged by *ex situ* atomic force microscopy (AFM) of a 1 μm^2 area in Fig. 5. In Fig. 5(a), a cross section of the local surface height shows large local height variations in the form of steeply sloped valleys up to 20 nm deep, which outline hills of 50–200 nm diameter. Figure 5(b) reveals the morphology more clearly and allows further characterization. In this image, the height data is transformed as the local slope so that the bottom of each valley is necessarily black (approximately zero slope). Notice on top of each hill that there is only a small flat area of zero slope, which indicates how little the Ni(110) terraces persist after the CO reaction. Most surface area has instead transformed to other surface orientations such as Ni(111) microfacets, as follows. White areas deep in the valleys have the steepest slope. The measured slope, up to 25°, probably corresponds to the expected angle of 35° between $(1\,1\,1)$ and $(1\,1\,0)$ planes modified by the AFM tip resolution. Note also the preferred orientation (parallel to dashed line) of

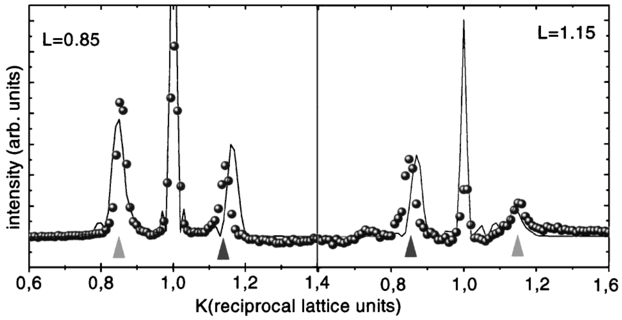

FIG. 4. The data points correspond to facet peaks as in Fig. 3. The calculated continuous line results from a simplified model of the facets as indicated in the figure. The dimensions of the $(1\,1\,1)$ and $(1\,1\,-1)$ sides are of 110 Å, and there is a strain of 4% in the outer facet surfaces along the A_2 direction.

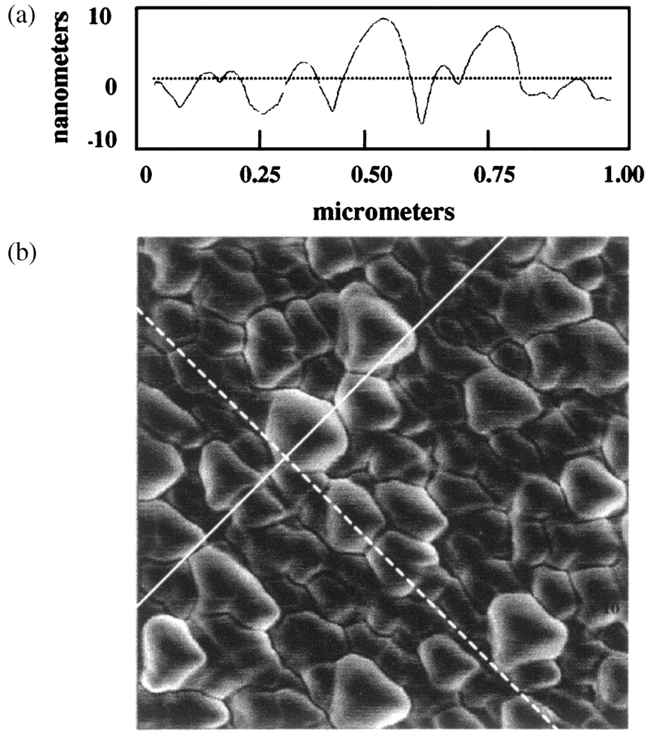

FIG. 5. AFM results on surface morphology of (1 × 1) μm^2 area of partially reacted CO/Ni(110). (a) Cross section of surface height along solid line in (b). (b) Surface image of local slope obtained from height data. Black areas have zero slope and white ~25°. Dashed line indicates a preferred direction of valleys, hill tops, and white steeply sloped area.

many valleys, steeply sloped white areas, and hill tops. This is probably the A_1 direction along the imperfect microfacets. The AFM image illustrates that the surface is otherwise rather disordered and complex.

It is well-known that Ni reacts with CO at elevated pressures forming the volatile Ni(CO)$_4$. An earlier work [10] (that was later questioned [11]) reported the observation of (1 1 1) microfaceting due to the reaction of CO with Ni(110) in agreement with our findings. Likely, the faceting simply reflects the different reactivities of different crystal faces. The morphology is dominated by (1 1 1) faces since these dense planes are probably the most inert ones and survive the etching by the CO molecules.

In conclusion, the interaction of CO with Ni(110) surfaces at temperatures around 130 °C and pressures around one atmosphere causes a restructuring of the Ni surface consisting in the appearance of (1 1 1) facets and possibly the incorporation of C atoms into Ni crystal.

We thank E. Paiser and L. Petit for technical assistance and S. Decossas and M. Salome for help with the AFM and image treatment.

---

*Author to whom correspondence should be addressed. Email address: ferrer@esrf.fr

[1] G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis* (Wiley, New York, 1994).
[2] C. Zhao and M. A. Passler, Surf. Sci. **320**, 1–6 (1994).
[3] K. Y. Kung, P. Chen, F. Wei, Y. R. Shen, and G. A. Somorjai, Surf. Sci. **463**, L627–L633 (2000).
[4] T. Dellwig, G. Rupprechter, H. Unterhalt, and H. J. Freund, Phys. Rev. Lett. **85**, 776–779 (2000).
[5] P. Cernota, K. Rider, H. A. Yoon, M. Salmeron, and G. A. Somorjai, Surf. Sci. **445**, 249–255 (2000).
[6] P. Bernard, K. F. Peters, J. Alvarez, and S. Ferrer, Rev. Sci. Instrum. **70**, 1478–1480 (1999).
[7] I. K. Robinson, *Surface Crystallography,* Handbook on Synchrotron Radiation, edited by G. S. Brown and D. E. Moncton (Elsevier, Amsterdam, 1991), Vol. 3, Chap. 3.
[8] A. J. Steinfort, P. M. L. O. Scholte, A. Ettema, F. Tuinstra, M. Nielsen, E. Landemark, D. M. Smilgies, R. Feidenhans'l, G. Falkenberg, L. Seehofer, and R. L. Johnson, Phys. Rev. Lett. **77**, 2009–2012 (1996).
[9] B. Predel, in *Zahlenwerte und Funktionen aus Naturwissenschaften und Technik,* Landolt-Bornstein, New Series, Group IV, Vol. XX, Pt. 5b (Springer-Verlag, Berlin, 1992).
[10] P. de Groot, M. Coulon, and K. Dransfeld, Surf. Sci. **94**, 204–220 (1980).
[11] K. Lascelles and L. V. Renny, Surf. Sci. **125**, L67–L72 (1983).