ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Surface Science 575 (2005) 343–357

SURFACE SCIENCE

www.elsevier.com/locate/susc

The surface geometries of the medium and high coverage carbon monoxide structures $c(2\times4)$–(2CO) and $p(\sqrt{7}\times\sqrt{7})R19°$–(4CO) on Ni{1 1 1}

W. Braun [a], H.-P. Steinrück [a], G. Held [a,b,*]

[a] *Universität Erlangen-Nürnberg, Physikalische Chemie II, Egerlandstr. 3, D-91058 Erlangen, Germany*
[b] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK*

Received 5 October 2004; accepted for publication 23 November 2004

Abstract

The surface geometries of the $p(\sqrt{7}\times\sqrt{7})R19°$–(4CO) and $c(2\times4)$–(2CO) layers on Ni{1 1 1} and the clean Ni{1 1 1} surface were determined by low energy electron diffraction structure analysis. For the clean surface small but significant contractions of d_{12} and d_{23} (both 2.02 Å) were found with respect to the bulk interlayer distance (2.03 Å). In the $c(2\times4)$–(2CO) structure these distances are expanded, with values of $d_{12} = 2.08$ Å and $d_{23} = 2.06$ Å and buckling of 0.08 and 0.02 Å, respectively, in the first and second layer. CO resides near hcp and fcc hollow sites with relatively large lateral shifts away from the ideal positions leading to unequal C–Ni bond lengths between 1.76 and 1.99 Å. For the $p(\sqrt{7}\times\sqrt{7})R19°$–(4CO) layer two best fit geometries were found, which agree in most of their atomic positions, except for one out of four CO molecules, which is either near atop or between bridge and atop. The remaining three molecules reside near hcp and fcc sites, again with large lateral deviations from their ideal positions. The average C–Ni bond length for these molecules is, however, the same as for CO on hollow sites at low coverage. The average C–Ni bond length at hollow sites, the interlayer distances, and buckling in the first Ni layer are similar to the $c(2\times4)$–(2CO) geometry, only the buckling in the second layer (0.08 Å) is significantly larger. Lateral and vertical shifts of the Ni atoms in the first layer lead to unsymmetric environments for the CO molecules, which can be regarded as an imprint of the chiral $p(\sqrt{7}\times\sqrt{7})R19°$ lattice geometry onto the substrate.

Keywords: Nickel; Carbon monoxide; Low energy electron diffraction (LEED)

---

1. Introduction

The adsorption of carbon monoxide on Ni{1 1 1} has been studied extensively over the last

---

[*] Corresponding author. Address: Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK. Tel.: +44 1223 336344; fax: +44 1223 762829.
E-mail address: gh10009@cam.ac.uk (G. Held).

0039-6028/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2004.11.034

thirty years [1–19]. Despite this, a clear picture of the adsorption geometry only emerged over the last decade. Recent surface crystallographic studies show that for coverages up to 0.5 ML the molecules adsorb in a near-upright orientation on hcp and fcc hollow sites [10–12,14]. This replaced the earlier assignment to bridge sites by vibrational spectroscopies [3–5,7–9].

Five ordered structures of CO on Ni{1 1 1} under ultra high vacuum (UHV) conditions have been reported in the literature (see Ref. [15] and references therein). The low and medium coverage structures p(2 × 2)–(CO) (0.25 ML), $p(\sqrt{3}\times\sqrt{3})R30°$–(CO) (0.33 ML), and c(4 × 2)–(2CO) (0.50 ML) have been studied in detail by Photoelectron Diffraction (PhD) [11,14] and low energy electron diffraction (LEED) [12]. To our knowledge, no detailed experimental structure analyses exist, however, of the ordered high coverage $p(\sqrt{7}\times\sqrt{7})R19°$–(4CO) and $c(2\sqrt{3}\times 4)$rect–(5CO) structures with coverages of 0.57 and 0.62 ML, respectively. There are strong indications from vibrational spectroscopies [7–9], X-ray photoelectron spectroscopy (XPS) [15] and X-ray diffraction (XRD) [19] that at least two adsorption sites are occupied by CO, one near the atop site and another higher co-ordinated site. A recent density functional theory (DFT) study by Eichler arrived at a similar conclusion [16]. Obviously, the energy difference between adsorption on hollow sites and alternative adsorption sites, such as atop or bridge, must be very high. Otherwise the 0.5 ML c(4 × 2)–(2CO) structure, an uniaxially compressed layer of CO molecules with very small intermolecular distances around 2.88 Å [10,12], could not be explained easily. Recent DFT studies predict energy differences between 0.1 and 0.3 eV between adsorption on hollow and atop/bridge sites [16–18] for low coverages. As the coverage increases, the adsorption energy of the bridge site and the hollow sites become more and more similar. These values have to be taken with caution, however, since DFT tends to overestimate surface bond energies for CO [17,20].

One of the reasons why the high density structures have not yet been analysed by diffraction methods such as PhD or (LEED) is the large number of structural parameters that have to be determined with over 20 atoms in the adsorbate layer and the top-most two substrate layers per surface unit cell. This leads to time-consuming model calculations, which inherently bear the risk of becoming unreliable when too many parameters have to be optimised simultaneously. With increased computer power available, the time spent on model calculations is less of a problem now. However, the size of the parameter space to be searched in relation to the amount of data available for comparison with model calculations can still lead to ambiguities in the results of the structure determination.

This study concentrates on the surface geometry of the high density Ni{1 1 1}–$p(\sqrt{7}\times\sqrt{7})R19°$–(4CO) structure. For comparison, we have also repeated earlier structure determinations of the c(4 × 2)–(2CO) structure [12] and the clean surface [21,22], using the same non-geometrical parameters in order to ensure optimum comparability.

2. Experiment and data analysis

The experiments were carried out in an UHV chamber described elsewhere [23–25]. The sample was cleaned using standard procedures [25]; high purity carbon monoxide (Messer–Griessheim, purity 99.99%) was dosed through a capillary array gas doser. The sample cleanliness and CO coverage were checked by XPS and temperature programmed desorption (TPD).

The LEED-IV data were recorded at a sample temperature of 85 K with electron energies between 70 and 280 eV (500 eV for the clean surface) at normal incidence using a standard Video-LEED system (AutoLEED by Omicron). In order to reduce electronic noise, the IV-curves were extracted directly from the camera signal without intermediate storage on video tape. Electron-induced damage was kept at a minimum by using beam currents of typically less than 1 μA and data acquisition times of around 3 min. Experimental IV-curves of symmetry equivalent spots were averaged within each data set and smoothed. The experimental input data for the structure analyses presented in this paper are the average of several independent data sets. For the (1 × 1) structure