Adsorption-Induced Step Formation

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Through an interplay between density functional calculations, Monte Carlo simulations and scanning tunneling microscopy experiments, we show that an intermediate coverage of CO on the Pt(110) surface gives rise to a new rough equilibrium structure with more than 50% step atoms. CO is shown to bind so strongly to low-coordinated Pt atoms that it can break Pt-Pt bonds and spontaneously form steps on the surface. It is argued that adsorption-induced step formation may be a general effect, in particular at high gas pressures and temperatures.

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A crystalline material usually exposes planar facets at low temperatures. The reason for this is that defects on the crystal surface, i.e., steps and kinks, are energetically expensive and therefore infrequent. The defect formation energy is given by the energy required to break the bonds between atoms in the surface layer. For a Pt crystal, for instance, this is of the order 0.25 eV per bond. On such a surface very high temperatures are needed before a sizable fraction of surface Pt-Pt bonds are broken spontaneously [1]. We show in this Letter that, by exposing a Pt(110) surface to CO, the energy required to break Pt-Pt nearest-neighbor (NN) bonds in the surface approaches zero and consequently the equilibrium structure of the surface with CO adsorbed is one where the surface is microscopically rough with more than 50% of the atoms associated with steps. We suggest this adsorption-induced microroughening to be a general phenomenon which may control the properties of metal surfaces under high gas pressures.

The system we have chosen to study in detail is CO/Pt(110). The equilibrium structure of the clean surface is the missing-row (1×2) reconstruction [2] shown in Fig. 1a. In the [001] direction, perpendicular to the close-packed rows, interactions are weak. High energy steps are associated with the breaking of Pt bonds in the $(1\bar{1}0)$ direction, cf. Fig. 1b.

We have studied the CO-induced lifting of the Pt(110)-(1×2) reconstruction by following with scanning tunneling microscopy (STM) the process in real time at room temperature (RT) as well as at elevated temperatures. (For further details see [3].) In Fig. 1b an atomic-scale STM image of the first steps in the structural transformation at RT is shown. It is seen that the process occurs through the breaking of Pt-Pt bonds in the close-packed direction, leading to the creation of "holes" when the CO coverage reaches a critical value of $\theta_{CO} \approx 0.2$ [4], consistent with previous findings [5–8]. At RT the process is kinetically limited and the thermodynamical equilibrium structure is therefore obtained only at elevated temperatures, ~400 K.

In Fig. 2 we show the observed structures at two different CO coverages. The first is a structure that forms after saturating the surface with CO at RT followed by annealing to 400 K. This temperature is high enough to make the surface atoms mobile, as observed when imaging the response of the surface to CO. This means that the system approaches equilibrium, but some of the CO also desorbs. The absolute coverage after annealing was determined as the ratio between the integrated areas of thermal desorption spectra from the annealed structure and the full coverage (2×1)-$p2mg$ phase and was determined to be $\theta_{CO} = 0.8 \pm 0.1$. The second equilibrium structure is the ordered (2×1)-$p2mg$-CO phase, obtained by cooling the Pt(110) crystal from ~600 K in an ambient pressure of 10^{-7} Torr CO. In this structure the metal surface forms a (1×1) structure with CO adsorbates sitting on top of every Pt atom and nearest-neighbor CO molecules being tilted ~25° in opposite directions [6,7]. At coverages lower than 1, the CO molecules are not imaged with STM due to the adsorbate's frustrated motion. For the dense, ordered (2×1)-$p2mg$-CO structure with $\theta_{CO} = 1$, the CO molecules are, however, imaged since they are locked into place by mutual repulsive interactions.

Our STM experiments agree with previous experiments about the structure at saturation ($\theta_{CO} = 1$). A very rough structure is, however, observed at an intermediate coverage
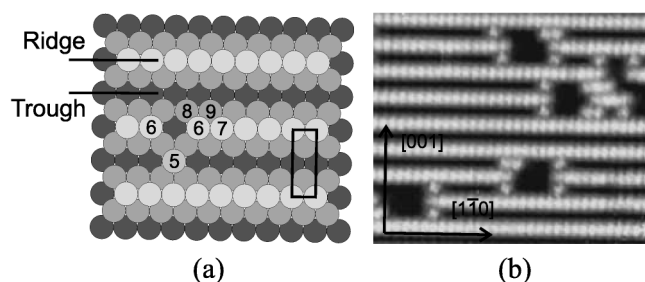

FIG. 1. (a) Model of the missing-row Pt(110)-(1×2) reconstructed surface. Pt coordination numbers for the perfect surface as well as for various defects are also shown. (b) STM image showing both the clean Pt(110) structure and the first steps in the transformation observed upon CO exposure at RT.
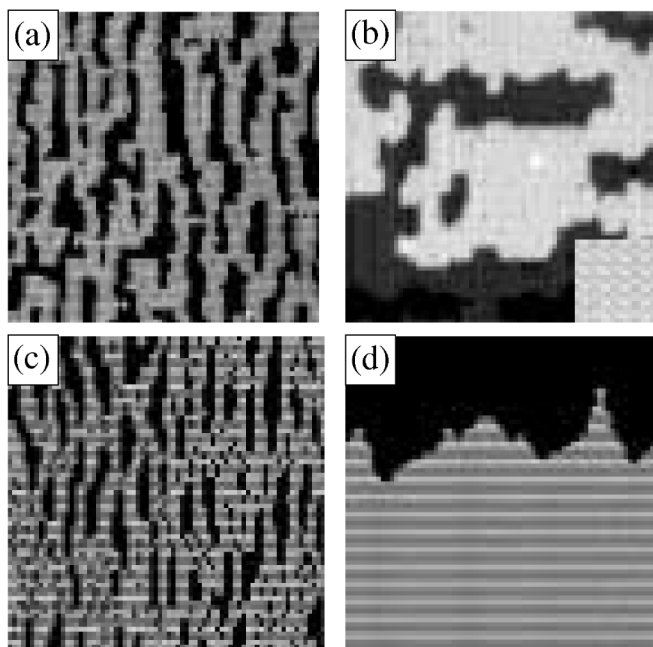

FIG. 2.   STM images of Pt(110) at a CO coverage of (a) $\simeq 0.8$ and (b) 1, the latter imaged in a 10^{-7} Torr CO background. The inset shows individual CO molecules in the (2×1) structure. The images are taken at 300 K as explained in the text. (c),(d) Snapshots from a Monte Carlo simulation of the surface structure at 300 K and at the same two coverages. All parameters are deduced from DFT calculations.
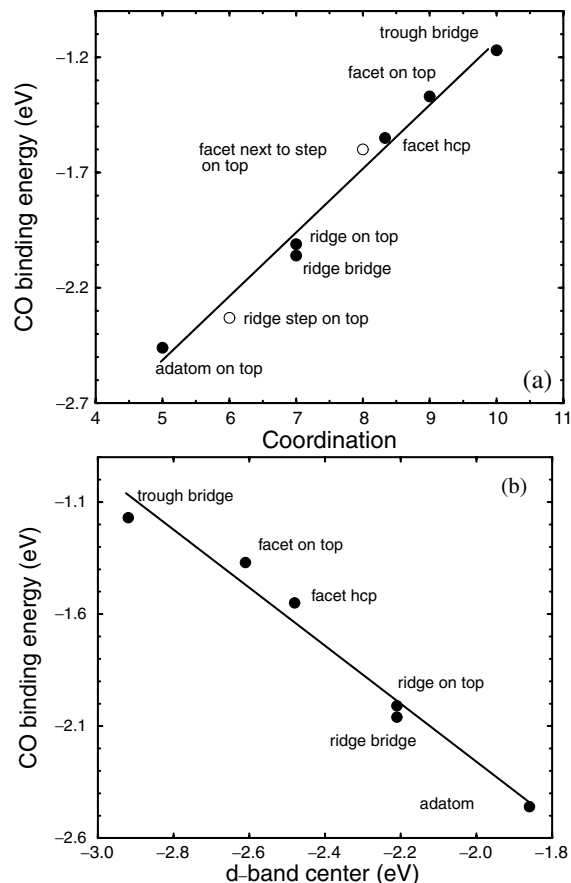

FIG. 3.   (a) Calculated CO chemisorption energies at different positions on the Pt(110) surface versus the mean coordination number of the nearest platinum atoms. With the open symbols we include data for CO adsorption on a Pt dimer on Pt(110) (coordination number 6) from Feibelman [25], and on a Pt(100) surface (coordination number 8) from Hammer *et al.* [16]; see Table I for details. (b) Data for Pt(110) plotted as a function of the average energy of the *d* states to which the CO interacts. As the metal coordination number is reduced the local *d* band moves up and narrows leading to stronger bonding.

($\theta_{CO} = 0.8$) in which case there is a large number of steps—in fact 52% of the Pt surface atoms have fewer than seven Pt nearest neighbors; or, equivalently, 52% of the surface atoms are associated with steps in the close-packed direction. There is also a tendency for an attractive next-nearest-neighbor (NNN) interaction indicated by alignment of Pt islands perpendicular to the close-packed rows.

In the following we focus primarily on the rough surface structure at intermediate CO coverages. We will show that it indeed represents an equilibrium structure of the system, where adsorption has lowered the step formation energy to a value close to zero. Steps and other defects on the surface are characterized by Pt atoms with a low Pt coordination number, cf. Fig. 3a. We have studied the adsorption energy of CO on Pt(110), as a function of the Pt coordination number, using density functional theory (DFT) [9–11]. The calculations are performed with electronic exchange and correlation described within the generalized gradient approximation (PW91) [12]. The surface is modeled by slabs of nine Pt(110) layers, where the top three layers and the CO coordinates are fully relaxed. The numerical setup is identical to the one described in Ref. [13].

Figure 3a shows that CO molecules bond strongly to Pt atoms with a low Pt coordination number, while Pt atoms with a high coordination number bind CO more weakly. On the unperturbed Pt(110)-(1×2) surface, CO prefers to bond to Pt atoms at ridges, since these Pt atoms have

a coordination number of 7 in contrast to the Pt atoms on the sides of the troughs with a coordination number of 9. A Pt atom at a step perpendicular to the close-packed direction or a single Pt atom in the troughs have coordination numbers 6 and 5, respectively (see Fig. 1), and they therefore bind CO even stronger than Pt atoms at the ridges. The important point in the present context is that the extra bonding of CO to the low coordinated Pt atoms is of the same order of magnitude as the energy required to form the defect with a low coordinated Pt atom. The difference in adsorption energy on, e.g., an adatom (coordination number 5) and on the ridge (coordination number 7) is found to be 0.45 eV. This should be compared to the energy of forming an adatom, which we calculate to be essentially the same, 0.45 eV. The accuracy of the DFT calculations allows us to say only that the effective defect formation energy in the presence of CO becomes

close to zero. Nonetheless, we note that even a slightly positive step formation energy will lead to a surface with many steps at finite temperatures due to the higher entropy of the defected surface. Based on the DFT calculations it therefore seems very likely that CO adsorption should be able to break up the Pt(110)-(1 × 2) surface completely at RT, as is indeed observed experimentally.

To further substantiate that the experimentally observed rough structure at $\theta_{CO} < 1$ is indeed the equilibrium structure, we compare it in more detail to the structure expected from DFT calculations. We have performed Monte Carlo (MC) simulations of the equilibrium structure corresponding to the energetics of the DFT calculations. In the simulations the total energy of the system is written as

$$E = \frac{1}{2} \sum_{i,j} V_{ij}, \qquad (1)$$

where i and j run over all Pt atoms in the first two layers and over the CO molecules. CO can adsorb on all Pt atoms in the two outermost layers. All interaction energies are deduced from DFT calculations, as shown in Table I [14]. We simulate 100×100 surface unit cells starting from the perfect missing row (1 × 2) reconstructed surface. We then adsorb CO molecules to a specific coverage and equilibrate at 300 K by running 10^4 trial moves per site. Snapshots at two coverages are shown below the corresponding STM pictures in Fig. 2. Clearly a good qualitative agreement is found.

From the simulations we calculate the equilibrium number of defects/steps as a function of CO coverage, Fig. 4a [15]. The number of steps shows a maximum around a CO coverage of 0.7. Here the number of steps is as high as 90%. We have not investigated this extreme coverage experimentally but at a coverage of 0.8 the MC simulation shows about 60% steps, in good agreement with the experimental value. At a more detailed level, we can compare the experimental and theoretical values for the frequency

TABLE I. Parameters used in MC simulations. NN: nearest neighbors. NNN: next-nearest neighbors. a: This work. b: The energy difference $V_{CO/Pt}(\text{coord.} = 6)$-$V_{CO/Pt}(\text{coord.} = 5) = E_{dis}$("empty" dimer)-$E_{dis}$(dimer with 1 CO on top) is estimated from calculations by Feibelman [25]. c: The energy difference $V_{CO/Pt}(\text{coord.} = 7)$-$V_{CO/Pt}(\text{coord.} = 8, 9)$ is estimated from calculations on Pt(11 8 5) [16]. d: Estimated from calculations by Feibelman [25]. e: Estimated from calculations on Au(110) [23].

Parameter	Value (eV)	Remarks
$V_{CO/Pt}(\text{coord.} = 5)$	−2.46	a
$V_{CO/Pt}(\text{coord.} = 6)$	−2.33	b
$V_{CO/Pt}(\text{coord.} = 7)$	−2.01	a
$V_{CO/Pt}(\text{coord.} = 8)$	−1.60	c
$V_{CO/Pt}(\text{coord.} = 9)$	−1.37	c
$V_{Pt,Pt}(\text{NN})$	−0.45	a
$V_{CO,CO}(\text{NN})$	0.06	d
$V_{Pt,Pt}(\text{NNN})$	0.10	e

of Pt rows of different lengths at the coverage 0.8, Fig. 4b. The experimental results show a most probable chain length of three while the MC simulations find this number to be two, but given the fact that no fitting of the parameters has been made and the fact that the experimental determination of the CO coverage is somewhat uncertain, the agreement is quite satisfactory. We therefore suggest that the rough surface observed at a CO coverage at about 0.8 is a direct observation of adsorption-induced roughening.

From the discussion above it is clear why the number of step atoms increases with the CO coverage. Since CO adsorption strongly stabilizes Pt step atoms, they increase in number proportional to the CO coverage. The reason for the decrease in the number of step atoms at the highest coverages is equally simple: As the CO coverage approaches 1, every Pt surface atom, including those below
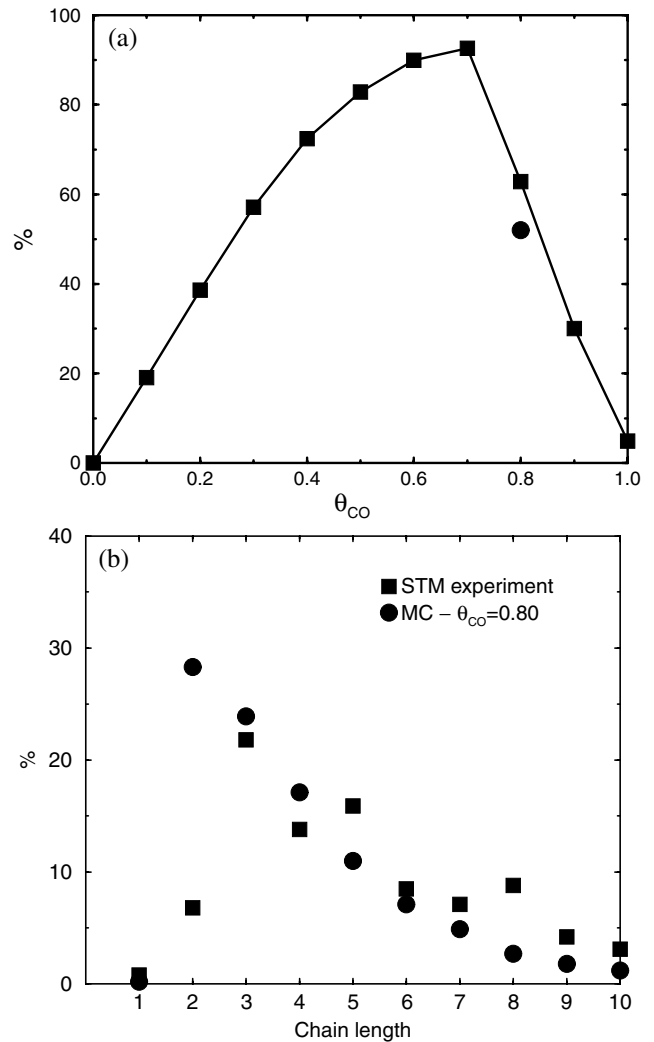

FIG. 4. (a) Step density calculated at 300 K based on the DFT parameters of Table I shown as a function of the CO coverage. The experimental observation at a coverage of 0.8 is included as a circle. (b) A comparison of measured and calculated probabilities of finding Pt rows of different lengths.

steps, must have an adsorbed CO. These Pt atoms have a coordination number higher than 7, and they therefore have a *lower* CO adsorption energy than the first layer of surface atoms. The energy gain associated with step formation disappears because the energy gain from CO adsorption on top of the step is cancelled by the energy loss due to CO adsorption at the bottom of the step. As the CO coverage approaches 1 the surface therefore heals again. This need not be the case if Pt atoms from deeper layers could migrate and form new steps. We suggest that at the high CO coverages of the experiment this process may be too activated to take place at the moderate temperatures reached. If, on the other hand, the CO coverage could be maintained at higher temperatures, it is possible that the surface would roughen completely.

The lineup of Pt islands in the direction perpendicular to the close-packed rows is also related to the relative proportion of coordination number 6 and 8 adsorption sites. By lining up, the number of coordination number 8 adsorption sites is minimized.

Adsorption-induced microroughening is not limited to the CO/Pt(110) system. Any adsorbate which is attracted to a step atom by an energy comparable to the step formation energy should induce disordering on any facet. CO also binds strongly to steps of other Pt surfaces [16], and the same has been established for NO, O, N, and C on a number of different transition metals [17–19]. The underlying reason is that the step atoms with a low coordination number have high energy d electrons, which interact more strongly with adsorbate states [20,21]. This is illustrated in Fig. 3b for CO/Pt(110). It should be stressed, though, that the strength of the effect is system specific [19].

The effect is particularly strong at fcc(110) surfaces because the metal atoms along steps perpendicular to the close-packed rows are so far apart that each of them can accommodate an adsorbate without strong adsorbate-adsorbate interactions. The coverage can become large at high gas pressures, and adsorption-induced step formation may be possible in general. One report of high pressure, CO-induced roughening of Pt(110) exists [22], but such experiments are presently very rare. Our suggestion is that for a number of gas/metal systems high pressures of gases will induce substantial changes in the morphology of the surface at high temperatures. One immediate consequence is that we must expect that, e.g., catalysts can change morphology as a function of gas composition and pressure, and that the distribution of active sites, and thus the catalytic activity, is self-regulated by gas adsorption.

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