High Pressure Adsorbate Structures Studied by Scanning Tunneling Microscopy: CO on Pt(111) in Equilibrium with the Gas Phase

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Scanning tunneling microscopy was applied to studies of adsorbates on model catalysts at elevated pressures where dense overlayers in equilibrium with the gas phase can be formed. A structure due an incommensurate hexagonal overlayer is observed for CO on the Pt(111) surface in the 200–750 Torr pressure range. This structure has not been observed before at similar coverage under low pressure and temperature conditions. The results illustrate the inequivalence in this case between the study of surfaces in catalytic conditions of high pressure and the surface science studies carried out in high vacuum. [S0031-9007(98)05308-3]

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The development of new atomic resolution imaging and spectroscopic techniques that can operate in environments other than vacuum is opening the important area of surface science at high pressures. Scanning tunneling microscopy (STM) is capable of atomic scale resolution in atmospheric pressure regimes, providing a much sought-after link between decades of ultrahigh vacuum (UHV) studies and the results of catalysis research performed in the more industrial conditions of high reactant pressure [1]. The link over the pressure gap of many orders of magnitude that separates these two complementary fields is extremely important because many of the UHV results cannot be extrapolated to high pressure and *vice versa.* Examples of advances in high pressure imaging are the studies of the atomic structure of passivating sulfur monolayers on Mo(001) in air [2], the high pressure driven reconstructions of Pt(110) in atmospheric pressures of O_2, H_2, and CO [3] and the opening of the new field of tip-catalyzed reactions in O_2 and H_2-hydrocarbon mixtures [4,5].

None of these previous high pressure STM studies have determined the structure of molecular adsorbates in equilibrium with the gas phase. It has often been argued that the high surface coverage of adsorbates that is prevalent at high pressures can be simulated by operating at cryogenic temperatures in high vacuum conditions. However, the structures formed under these conditions are necessarily not in equilibrium with the gas phase. They might correspond to kinetically trapped structures with no similarity to structures that are thermodynamically stable only at high pressure and temperature. An example of this is the adsorption of CO on metal surfaces, which has been the object of numerous studies in the past [6,7]. Here we present the results obtained for this molecular adsorbate on Pt(111) in the pressure range of 200–750 Torr. Our data illustrate very clearly the fundamental differences that can be expected between the low temperature/low pressure and ambient temperature/high pressure regimes even if they correspond to a similar surface coverage.

The UHV apparatus employed for these experiments is divided into two parts: a UHV analysis/preparation chamber (base pressure in the 10^{-10} Torr range) equipped with surface techniques, including Auger spectroscopy, low energy electron diffraction (LEED) and ion sputtering, and an STM chamber that can be isolated from the vacuum system and subjected to atmospheric pressures. The STM is a commercial unit equipped with *in situ* tip exchange and sample heating and cooling [8]. The sample is moved between the UHV and STM chambers by a magnetically coupled transfer rod. All STM experiments were performed at room temperature.

A flat and a stepped platinum single crystal sample of (111) orientation were used. The stepped crystal was cut 5° off from the (111) orientation. This stepped sample was chosen in order to increase the likelihood of observing changes in step morphology and refaceting caused by high pressure adsorbates. However, such effects were not observed. Both samples were cleaned by successive cycles of Ar^+ sputtering, heating in oxygen (700–750 °C in 1×10^{-7} Torr O_2), and annealing to 950 °C in vacuum. The STM tips were electrochemically etched tungsten treated in vacuum by field emission. A typical experiment was performed as follows: After preparation, the sample was transferred to the STM chamber and imaged first under vacuum. In the stepped crystal the images revealed a surface topography consisting of arrays of (111) terraces separated by single atomic steps with an average terrace width distribution of 40–100 Å. The STM chamber was then isolated from the rest of the system and CO was introduced at a rate of ~1 Torr/sec. The surface was allowed to equilibrate in the high pressure of CO for 1 h prior to imaging. This greatly improved tip stability for imaging presumably due to the formation of a stable passivating thin oxide or carbide.

In the stepped crystal, the images acquired in up to 750 Torr of CO revealed a step morphology that was similar to that seen in vacuum in the absence of CO (not shown). Enlarged views of the terraces showed no ordered structures due to CO until the pressure reached 200 Torr. At this pressure and above, a nearly hexagonal periodic structure was formed, as shown in Fig. 1, obtained under 200 Torr of CO. This structure is observed only in the presence of CO, and has a periodicity of 12 ± 2 Å, with a corrugation of 0.30 ± 0.05 Å. The large error bar is due to the short terrace widths and also to the presence of a few impurities that modify locally the periodicity. Imaging was performed at 0.1–0.2 V sample bias and 0.5–1.0 nA tunneling current with a gap resistance of 200–240 MΩ. Changing either bias or current so that the gap is less than 200 MΩ caused the hexagonal pattern to disappear. It was recovered, however, upon restoring the initial high gap condition. Presumably the tip gets too close to the surface at low gap resistance and displaces the CO. Evacuation of the CO gas to 1×10^{-4} Torr base pressure completely removed the hexagonal pattern. An important observation is that the angular orientation of the pattern is maintained rigidly from one terrace to the next, as seen in Fig. 1. Separate STM experiments on the same surface covered with a sulfur (2×2) layer [9] indicate that the average step direction is roughly parallel to the $[11\bar{2}]$ direction (within 5°–10°). This indicates that the hexagonal structure close-packed rows are aligned with the Pt(111) compact [110] directions.

The same high pressure studies were performed on the flatter Pt(111) crystal which had terrace widths on the order of 1000 Å. This crystal was exposed to a mixture of 150 Torr CO and 50 Torr O_2, heated to 183 °C for 10 min, and then cooled slowly (for ~1 h) to room temperature and reimaged. Under these conditions, the surface is covered by a saturation layer of pure CO. Treatment in the mixed CO-O_2 atmosphere proved very effective in producing a clean surface. STM images revealed the same hexagonal structure as observed with the stepped crystal; however, it was better ordered with a more uniform spacing of 12 ± 1 Å, as shown in Fig. 2. As on the stepped sample, the hexagonal structure showed only one rotational orientation. The inset in Fig. 2 shows a nearly triangular one-atom deep hole and a neighboring triangular island of platinum of one-atom height. The straight segments of the hole and island step edges form 60° angles, as expected for [110]-type step edges. Comparison of these step directions with the hexagonal structure (shown by the white triangle) indicate that the close-packed rows are aligned (±5°) with the [110]-type directions of the Pt(111) lattice.

From all the observations, we can conclude that the observed hexagonal structure is due to an ordered, hexagonal close-packed layer of CO that is incommensurate with the Pt(111) substrate, forming a moiré-type structure. The consistent orientation of the moiré pattern relative to the platinum lattice indicates that the rows of nearest neighbor CO molecules in the overlayer are parallel with those of the Pt atoms in the substrate. Small changes of density in the CO overlayer that shift even slightly the CO-CO distance are considerably amplified in the moiré periodicity. Although not shown here, this is indeed observed in surfaces with residual impurities that change the local density of CO. The most likely arrangement of CO molecules for the observed 12 ± 1 Å moiré periodicity corresponds to an intermolecular separation of 3.7 Å with three molecules spanning approximately four Pt atoms, which corresponds to a coverage of 0.60 ML. Figure 3

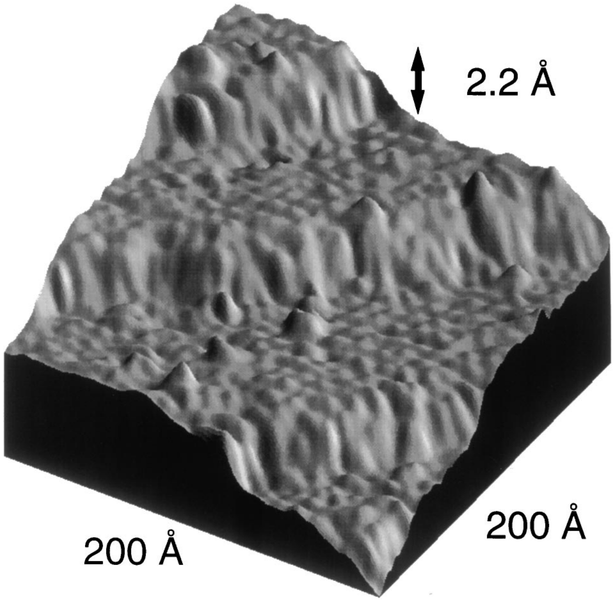

FIG. 1. 3D representation of an STM image obtained in 200 Torr CO. Image size is 200 Å × 200 Å, sample bias is +109 mV, and tunneling current 0.52 nA. Height scale is greatly exaggerated to display corrugation on the terraces. Hexagonal arrays of maxima can be observed on each terrace due to a CO monolayer forming a moiré structure. The alignment of the hexagonal array is the same in each terrace.

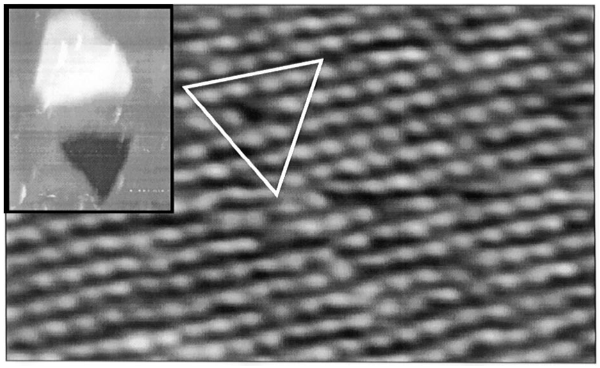

FIG. 2. 560 Å × 360 Å topographic STM image obtained in 150 Torr CO and 50 Torr O_2 after annealing at 183 °C. $V_S = +111$ mV, $I_T = 0.16$ nA. The inset, a 1600 Å × 2000 Å STM image, shows a monoatomic hole and mesa of Pt atoms with triangular shapes. The close-packed row directions of the moiré pattern align parallel to the step edges of the Pt structures which are of the [110] type.

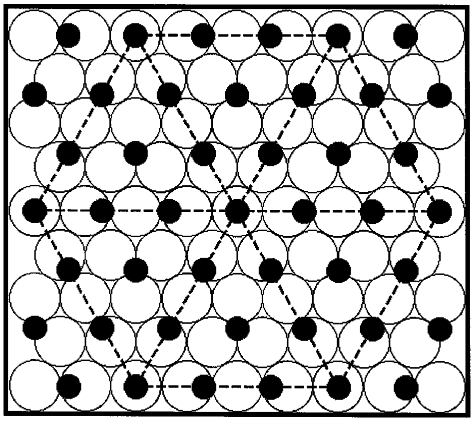

FIG. 3. A possible model of the incommensurate CO overlayer in relation to the Pt(111) lattice (2.77 Å spacing). In this model, three CO molecules span the length of four Pt atoms. Black circles represent CO molecules (3.7 Å spacing) with one molecule chosen to be on the top site.

shows the relationship between such a CO layer and the Pt(111) lattice.

The present structure formed at room temperature in equilibrium with the CO gas pressure has no correspondence with any of those observed in UHV in previous studies. All the dense structures that are stabilized at low temperature form several domains that have been observed by LEED. The domains are due to different angular epitaxies with the Pt substrate. The interpretation of the LEED data corresponding to these structures is still controversial, with two models being debated. One involves formation of incommensurate structures [7]. In the other model, CO occupies only high symmetry top and bridge positions [10]. The latter model is appealing in that it appears to agree better with the observation of two well-defined vibrational bands for the CO stretch mode which have been assigned to the top and bridge sites. It also explains better the intensity of the superlattice spots in the LEED patterns involving large lateral momentum transfers [11].

In the electrochemical cell, where similar high CO coverages can be achieved by virtue of the surface electric field, an incommensurate overlayer with $(\sqrt{19} \times \sqrt{19})R23.4°$ periodicity relative to the Pt(111) was observed at 0.67 ML [12]. This structure was imaged by *in situ* STM, which revealed the presence of two hexagonal close-packed domains rotated 23.4° relative to the substrate lattice. The resulting moiré periodicity is 12.1 Å, in the range of our observed value (12 ± 1 Å). A $(\sqrt{7} \times \sqrt{7})R19.1°$ structure with a CO coverage of 0.57 ML was also observed. This structure has a similar CO spacing as that inferred from our data (3.7 Å), but the close-packed CO layer is rotated relative to the substrate lattice (by 19.1°, in this case). Again, this structure forms multiple rotational domains, which are not observed in the high pressure structure. The presence of water, either coadsorbed or forming an ordered layer above it, appears to be necessary to stabilize these structures [13].

Much more relevant to our work are the vibrational spectroscopy data of CO on Pt(111) at high pressures recently obtained by Su *et al.* [14] using sum frequency generation. They find that the intensity of the 2100 cm^{-1} mode, which corresponds to the on-top site in the vacuum regime, decreases and then disappears when the CO gas pressure reaches 150 Torr. It is replaced by a broad adsorption band in the range of 2050−1900 cm^{-1} which results from a distribution of modes. Above 300 Torr, this broad band tails all the way down to 1700 cm^{-1}. These results are very different from both the vacuum and the electrochemical cell environments where two well-defined peaks are always observed: an atop site in the 2050−2100 cm^{-1} region, and either a bridge site in the 1850 cm^{-1} region (up to 0.67 ML) or a threefold site near 1770 cm^{-1} at the highest coverage of 0.75 ML. A quasicontinuous distribution of CO sites that is proposed from these results best fits our model for an incommensurate CO layer.

In conclusion, the novel use of STM in high pressure gas environments has revealed the existence of dense layers of CO on Pt(111) *in equilibrium* with the gas phase at 200−750 Torr at room temperature, forming a new structure that is incommensurate with the underlying Pt(111) lattice and quite different from the structures formed at low temperature in vacuum conditions. It is this structure that is likely to be relevant in catalytic processes that occur only at high pressures [15].

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