Coadsorbate Induced Reconstruction of a Stepped Pt(111) Surface by Sulfur and CO: A Novel Surface Restructuring Mechanism Observed by Scanning Tunneling Microscopy

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The chemisorption of sulfur and CO was found to have profound effects on the structure of a stepped platinum surface. By itself, sulfur chemisorbs, forming a $p(2 \times 2)$ ordered structure, and induces doubling of the terrace widths and step heights. Subsequent coadsorption of CO displaces the sulfur, compressing it to distances of $\sqrt{3}$ times the Pt lattice spacing, and induces surface restructuring. New terraces form which contain exclusively CO and are separated by monatomic steps from the terraces containing the compressed sulfur overlayer. This coadsorbate induced restructuring phenomenon has strong implications in the mechanisms of surface catalyzed reactions. [S0031-9007(96)00578-9]

Chemisorbed atoms and molecules can have a profound influence on the structure of metal surfaces. Small displacements of the metal atoms due to the formation of chemical bonds with the adsorbate, known as relaxations, are common [1]. A more dramatic effect of chemisorption is the extensive restructuring of the substrate involving the displacement of many substrate atoms that form completely new surface structures. Such is the case in the reconstructions of the low Miller index surfaces of noble metals such as Ir and Pt. On these metals, CO chemisorption has been shown to remove the hexagonal overlayer reconstruction of the clean (100) surfaces and the missing row reconstruction of the clean (110) surfaces, returning them to bulk terminated (1 × 1) structures [2–5].

Vicinal surfaces of these low Miller index orientations are even more prone to restructuring because the stability of step structure is greatly affected by adsorbates [6,7]. Such phenomena imply that, during chemical reactions, the surface of a catalyst must adapt its structure in a dynamic fashion to the chemisorption events taking place. This is indeed observed during the catalytic oxidation of CO on platinum [8]. Additionally, atmospheric pressures of O_2, H_2, or CO have been shown to have profound effects on the structure of the Pt(110) surface by *in situ* scanning tunneling microscopy (STM) [9].

In this article, we describe a completely new type of surface restructuring that occurs as a result of the *coadsorption* of two mutually repelling adsorbates: sulfur and CO, on a stepped Pt(111) surface. Coadsorption results in segregation of these two species and a restructuring of the surface via step splitting, leading to the surprising formation of new metal terraces, each containing a different adsorbate.

All of the experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure $< 7 \times 10^{-10}$ Torr. The single crystal Pt(111) was cut at an angle of approximately 5° from the (111) direction. STM topographic images of the clean Pt surface show that it consists of single atomic height steps 2.20 Å high and terraces with widths on the order of 20–60 Å, which var-

ied somewhat with the particular location on the surface. Sulfur was added to the surface via an electrochemical source ($Ag/AgI/Ag_2S$) [10] at room temperature, followed by annealing to 600 °C for 30 sec. Upon cooling, the surface exhibited a well-ordered $p(2 \times 2)$-S structure as determined by low-energy electron diffraction (LEED). The sulfur coverage in this structure is 0.25 ML. Splitting of the LEED diffraction beams due to the steps from the 5° miscut was observed in the original clean surface but was less discernible after formation of the $p(2 \times 2)$-S structure, indicating that the terrace widths had increased. The STM images confirmed this result and showed that the surface was uniformly covered by the $p(2 \times 2)$-S structure on terraces of 40–120 Å wide, separated by steps 4.5 Å high, indicating a doubling of the step heights and terrace widths had occurred. An example is shown in Fig. 1. Typical tunneling conditions were 1 nA of current and 100–200 meV sample bias. The doubling of steps heights induced by sulfur on many metal surfaces and the simultaneous increase in terrace widths are well-known effects and have been previously observed for sulfur chemisorbed on Pt(755) [6,7]. This effect has been explained as a result of a decrease in the repulsive interaction which makes it energetically favorable for steps to coalesce [11].

The addition of a background pressure of CO (1×10^{-6} Torr) at room temperature produced an immediate and dramatic change in the structure of the sulfur covered surface. STM images showed that the S-induced double atomic height steps split into two monatomic height steps, separated by smooth and flat terraces (10–30 Å wide), alternating with wider (30–90 Å) terraces that show higher contrast, as shown in Fig. 2. The average local slope of the surface was found to be unchanged. The total height difference between *sulfur covered* terraces was within 0.1 Å of a double Pt step, and the mean separation between steps *with sulfur terraces at the top edge* was unchanged within the random variation in step width (from 102 ± 25 to 95 ± 23 Å after CO exposure in one experiment).
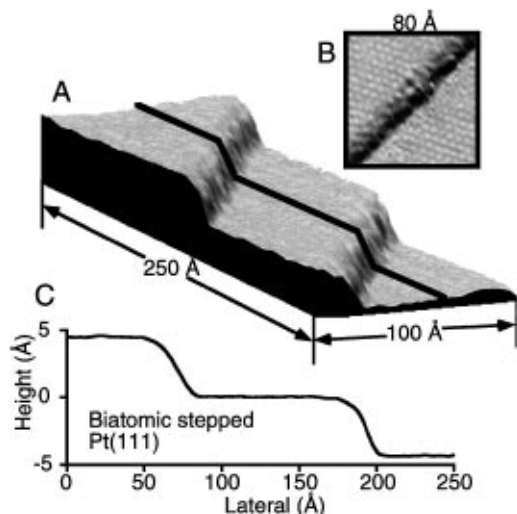
FIG. 1. (A) A 250 Å × 100 Å STM image of the stepped Pt(111) surface after deposition of 0.25 LM of S (from a S_2 source) and annealing to 600 °C. (B) Magnified image showing the $p(2 \times 2)$-S structure covering the terraces. (C) Height profile across the line marked in (A) showing the double step heights formed by S chemisorption. This profile consists of 16 scan lines averaged together to average away much of the atomic corrugation of the sulfur for clarity.

Atomic resolution images on the high contrast terraces show maxima due to the sulfur atoms compressed from a uniform spacing of 5.50 Å, in the original $p(2 \times 2)$ structure, to a disordered overlayer with many neighboring sulfur atoms separated by 4.80 Å, which is the sulfur-sulfur distance in the $(\sqrt{3} \times \sqrt{3})R30°$-S structure. Within this disordered layer some small regions of $(\sqrt{3} \times \sqrt{3})R30°$-S were observed, such as the one shown in Fig. 3. The smooth terraces are covered by CO that could not be imaged, due to its rapid diffusion at room temperature and its low corrugation, in agreement with the literature [12,13]. The ratio of the area of the terraces covered by sulfur before and after CO adsorption was measured to be 1.26 ± 0.12, consistent with the expected limiting value of $\frac{4}{3}$ based on the relative areas occupied by sulfur in the $p(2 \times 2)$ and $(\sqrt{3} \times \sqrt{3})R30°$-S sulfur structures. Following CO desorption from the surface by heating the crystal to 600 °C for a few seconds, the surface returned to the $p(2 \times 2)$-S structure and the steps returned to their original two-atom height.

Attempts to examine the kinetics of the Pt step reconstruction by reducing the background pressure of CO were unsuccessful. Pressures less than 1×10^{-8} Torr did not appear to induce restructuring, while for pressures greater than this, the restructuring occurred faster than the minimum STM image acquisition time of $\sim$20 sec. Also, images of the reconstructed surface in vacuum, immediately after formation, showed no discernible changes over the period that imaging of the same region was possible ($\sim$5 min). This disordered sulfur structure was observed previously [14] and found to eventually order into
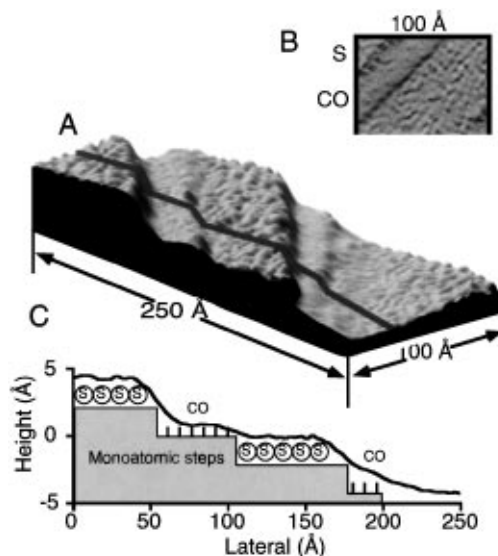

FIG. 2. (A) A 250 Å × 100 Å STM image of the S-covered Pt(111) after adsorption of CO from a background pressure of 1×10^{-6} Torr that is maintained during imaging. The double steps visible in Fig. 1 before CO coadsorption are split into monatomic steps separated by new terraces that contain exclusively CO. These new terraces appear as smooth bands in the image. Sulfur is compressed in the remaining alternating terraces and appears as disordered maxima in the image; (B) close view of the alternating CO and S covered areas; (C) cross section of eight averaged scan lines along the line marked in (A), showing the step heights. The difference in heights of the S- and CO-covered terraces is due to the difference in tunneling probability, which is lower through CO than through S. The large circles represent S atoms and the small lines represent CO molecules.

a $(\sqrt{3} \times \sqrt{3})R30°$-S structure. Figure 3 shows the initial stages of this reordering. After leaving the reconstructed surface in vacuum for several hours, the LEED showed a $(\sqrt{3} \times \sqrt{3})R30°$-S pattern. We attribute this pattern to
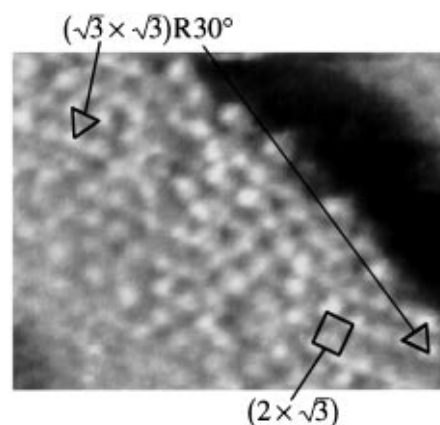

FIG. 3. A 70 Å × 55 Å STM topograph of the disordered sulfur overlayer showing the partial reordering of the sulfur into $(\sqrt{3} \times \sqrt{3})R30°$-S islands. Some sulfur atoms, such as those near the bottom indicated by the $\sqrt{3} \times 2$ square, remain separated by twice the Pt lattice distance as in the (2×2) structure.

the sulfur overlayer, indicating that coadsorbed CO still remained on the surface and that the disordered S atoms eventually rearranged into a more compact ordered structure. While CO also forms a diffuse quasi $(\sqrt{3} \times \sqrt{3})$ pattern near one-third monolayer coverage (each diffuse overlayer spot consists of three nearby spots blurred together) [15], the spots observed in the LEED pattern are too sharp to be due to CO at room temperature.

The segregation of S and CO into separate domains had been previously observed on "flatter" (terrace widths >100 Å) Pt(111) and Re(0001) substrates [14,16]. CO was observed to displace S towards the top of the step edges, while CO occupied the remaining terrace region. However, with the wider terraces, sulfur did not induce any step doubling.

We propose a mechanism for the coadsorption induced reconstruction of steps. On the clean surface, the separate monatomic step structure is stabilized by repulsive interactions between steps which arise from several sources. There is a repulsive electrostatic interaction between the nearly vertical component of dipoles at the step edge resulting from the Smoluchowski effect [17]. The mechanical interaction between the stress fields surrounding the steps is repulsive [18]. In addition, an effective repulsive interaction arises from the entropy associated with the step wandering [18]. Sulfur adsorption on the surface weakens the first two of these interactions. These chemisorbed atoms have the opposite dipole moment of the step edge. Sulfur chemisorption also relieves the Pt relaxation, reducing the step stress field. These combined effects reduce the step-step repulsion to the point where it is favorable for steps to coalesce, as this reduces the free energy associated with step edges and kinks.

As CO is added to the surface, it initially bonds to the step edges where the Pt-CO bonding its strongest [19]. The adsorption of CO at the step edges has two important effects. It initiates the compression of the sulfur overlayer which is displaced away from the bottom of the step edges, due to the repulsive interactions between sulfur and CO. This counteracts the effect of sulfur on the step-step interactions, increasing the repulsion between steps so double layer steps are no longer favorable. In addition, CO adsorption enhances the Pt atom diffusion from the step edge, allowing the formation of new terraces even at room temperatures. This enhancement has been well documented in the CO induced reconstruction of Pt(110) [the (2×1) to (1×1) reconstruction] and of Pt(100) [the (5×20) to (1×1) reconstruction] which involve displacement of a large number of Pt atoms at the surface [2–5].

At a CO pressure below 10^{-8} Torr, the reconstruction does not occur because the energy balance between CO adsorption and sulfur compression is unfavorable. At room temperature, the equilibrium CO coverage on clean Pt(111) with a background gas pressure of 10^{-8} Torr is approximately 0.5 monolayers [20]. Each adsorbed CO provides 1.28 eV (29.5 kcal/mole) of energy, but takes up approximately two sites on the Pt surface which must be liberated of sulfur [20]. Compressing the sulfur from the (2×2) structure to the $(\sqrt{3} \times \sqrt{3})R30°$ liberates one site per sulfur atom. Thus the energy necessary to compress the sulfur overlayer can be estimated to be 0.64 eV per atom. The equilibrium CO coverage decays quickly with pressure, so that at lower pressures insufficient energy is released by CO adsorption to compress the sulfur overlayer, and no reconstruction occurs.

In summary, we have shown that a stepped Pt(111) surface may be restructured by the coadsorption of sulfur and CO. This is the first reported coadsorbate induced restructuring of a metal surface. The coalescence of steps from monatomic to diatomic heights induced by sulfur chemisorption can be reversed by coadsorption with CO at room temperature. CO displaces and compresses sulfur atoms closer together from 5.50 Å to 4.80 Å. Additionally, the diatomic height steps found with the $p(2 \times 2)$-S structure split apart and restructured via Pt diffusion (enhanced by CO) from the step edges, forming new terraces, separated by monatomic height steps, on which CO remains segregated from sulfur on the alternating terraces. Such restructuring of the step structure should have important consequences in catalysis, as it provides a mechanism for the dynamic generation of new metallic sites during coadsorption of competing species on the catalyst surface. Such a dynamic restructuring mechanism may be active in real catalysts where the catalytic surface is believed to be constantly changing under reaction conditions.

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