Electrochemical STM observation of new structures of CO adsorbed on a Pt(111) electrode surface

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Received (in Cambridge, UK) 28th February 2006, Accepted 3rd April 2006
First published as an Advance Article on the web 21st April 2006
DOI: 10.1039/b603033e

Presented are two newly observed adstructures of adsorbed CO onto Pt(111), (2 × 2)-3CO-β and (2 × 2)-4CO, observed during the structural evolution from the well-known (2 × 2)-3CO-α structure to the $(\sqrt{19} \times \sqrt{19})$-13CO structure.

The oxidation of CO is one of the important subjects concerning electrocatalysis.[1–3] The reason for the importance is that CO is a model molecule, identical or similar to the catalytic poison formed during the electrochemical oxidation of small organic molecules like methanol on Pt electrode surfaces.

The oxidation of CO on a Pt(111) surface is known to be accompanied by a structural change of the adsorbed CO.[4–6] For example, a (2 × 2)-3CO structure evolves into a $(\sqrt{19} \times \sqrt{19})$-13CO structure during the pre-oxidation of CO. During the oxidative process, the coverage of CO decreases from 0.75 to 0.68, and CO molecules on bridge sites appear at the expense of CO molecules on three-fold sites. However, details of the structural evolution, such as the reaction site, are not understood clearly yet.

In this work, we present new structures for CO adsorbed onto a Pt(111) electrode surface during the structural evolution from the (2 × 2)-3CO structure to the $(\sqrt{19} \times \sqrt{19})$-13CO structure. The newly observed structures of adsorbed CO are discussed in terms of precursor structure and diffusion during the pre-oxidation.

The Pt(111) electrode used in this work was made by the bead method. One of the (111) facets of the bead was imaged after annealing with a flame and quenching with hydrogen-saturated water. In the electrochemical scanning tunnelling microscopy (EC-STM) experiment, W tips, electrochemically polished and coated with a molten polyethylene, were used with an STM instrument (Nanoscope III, Digital Instrument). The adsorption of CO was carried out by contacting a 0.05 M H_2SO_4 solution (Merck, Suprapur) saturated with CO (99.99%, Air Products and Chemicals, USA) at 0.05 V for 10 min in a home made EC-STM cell, and the CO-containing solution then replaced with a CO-free 0.05 M H_2SO_4 solution without any loss of potential control. The electrode potential was controlled against a Ag/AgCl reference electrode and reported here as measured.

Fig. 1 shows three STM images, observed in 0.05 M H_2SO_4 solution at an atomic level, of the Pt(111) surface saturated with CO. Because of the relative arrangements of the spots and because the apparent coupling between them differs, the STM images represent different adstructures of CO on the Pt(111) surface. However, a close examination of the images indicated that the periodicities of the observed spots in all of them were identical:

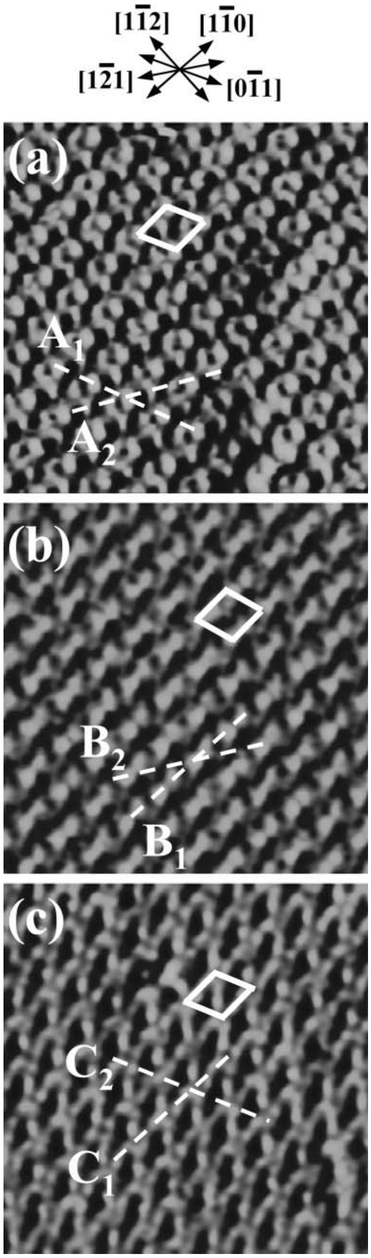

Fig. 1 EC-STM images of the Pt(111) electrode surface saturated with CO in 0.05 M H_2SO_4 solution: (a) (2 × 2)-3CO-α structure at 0.05 V, (b) (2 × 2)-3CO-β structure at 0.10 V and (c) (2 × 2)-4CO structure at 0.15 V. The parallelograms in the images are the (2 × 2) unit cells. The profiles along the dashed lines are shown in Fig. 3. Image sizes: 5 × 5 nm.

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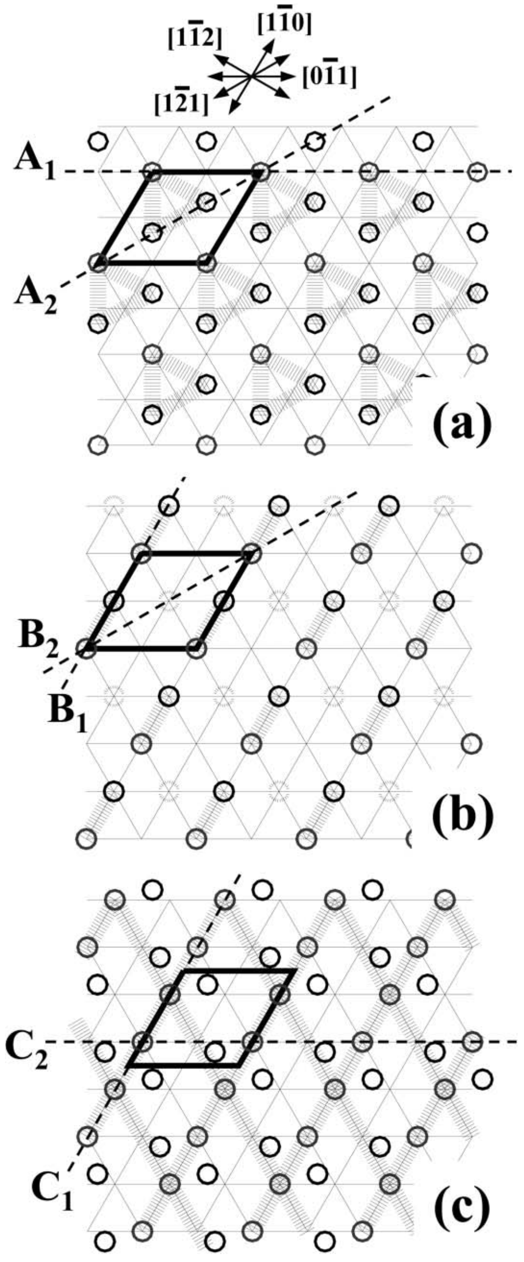

Fig. 2 Schematics of the superlattices of CO on Pt(111): (a) (2 × 2)-3CO-α structure, (b) (2 × 2)-3CO-β structure and (c) (2 × 2)-4CO structure. The dashed lines correspond to those in Fig. 1.

0.52 ± 0.02 nm in the $[1\bar{1}0]$ direction and 0.55 ± 0.02 nm in the $[0\bar{1}1]$ direction. Thus, it was clear that the CO molecules in the three different images were arrayed in (2 × 2) patterns, as shown in Fig. 1.

In spite of the identical (2 × 2) patterns, the spot distributions inside each unit cell were different in detail. Further inspection of the spot locations in each (2 × 2) unit cell in Fig. 1 led us to the schematics shown in Fig. 2. The superlattice of CO, corresponding to Fig. 1 (a), is the well-known (2 × 2)-3CO structure,[4] as shown in Fig. 2 (a). In this particular (2 × 2)-3CO structure, four CO molecules were located on the on-top sites and two CO molecules were located on the two three-fold sites for the coverage to be 0.75. On the other hand, in Fig. 2 (b), a schematic of Fig. 1 (b), three CO molecules were located on the on-top sites at the period of *a* (one Pt–Pt distance unit, 0.277 nm) along the $[0\bar{1}1]$ direction, concomitantly with four CO molecules at the corners of the (2 × 2) unit cell. The CO molecule at the center of the (2 × 2) unit cell, *i.e.* the one on the on-top site at the center of the unit cell in Fig. 2 (b), was imaged much dimmer than the other ones in Fig. 1 (b). The CO coverage in this particular schematic was 0.75, the same as in the schematic of Fig. 2 (a). To distinguish these two adstructures of identical CO coverage, the schematics in Fig. 2 (a) and 2 (b) were assigned to the structures of (2 × 2)-3CO-α and (2 × 2)-3CO-β, respectively. In contrast to the CO adstructures of 0.75 coverage, the spot coverage of Fig. 1 (c) was 1.0, and Fig. 2 (c) is suggested as a schematic of Fig. 1 (c). Specifically, four CO molecules were located near a corner of the (2 × 2) unit cell, two CO molecules were on the on-top sites along the $[1\bar{1}0]$ direction and two CO molecules, separated by a distance of 0.75*a*, were on the sites slightly off from the on-top sites in the $[1\bar{1}2]$ direction. The groups of four CO molecules were therefore arrayed in a (2 × 2) pattern for the CO coverage to be 1.0. This particular superlattice of CO, in Fig. 2 (c), is named (2 × 2)-4CO. The hatched lines in Fig. 2 represent the apparent couplings, as observed in Fig. 1, for easy recognition of the regular patterns of the observed CO structures.

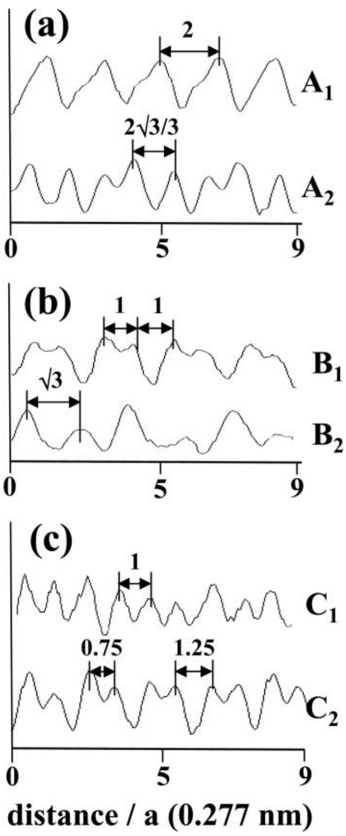

Fig. 3 Line profiles along the individual lines designated in Fig. 1: (a) (2 × 2)-3CO-α structure, (b) (2 × 2)-3CO-β structure and (c) (2 × 2)-4CO structure. The unit of the transverse axis in the profiles is *a* (one Pt–Pt distance, 0.277 nm).

Line profile analysis of the images in Fig. 1 justifies the suggested schematics of the CO adstructures in Fig. 2. The profiles along the lines in Fig. 1 are shown in Fig. 3, and the dashed lines in Fig. 2, corresponding to those designated in Fig. 1, are also drawn for comparison. Concerning the (2 × 2)-3CO-α structure (Fig. 1 (a) and Fig. 2 (a)), the periods in the profiles of lines A_1 and A_2 (Fig. 3 (a)) were coherent with those anticipated from its schematic (Fig. 2 (a)), *i.e.* $2a$ and $(2\sqrt{3}/3)a$, respectively. On the other hand, the periods in the profiles of lines B_1 and B_2 (Fig. 3 (b)) were a and $\sqrt{3}a$, respectively; which, again, were identical to those expected from the suggested (2 × 2)-3CO-β structure. One important observation to distinguish apart the (2 × 2)-3CO structures is the existence of CO molecular rows with the frequency a. In other words, there is no molecular row with the frequency a in the (2 × 2)-3CO-α structure (Fig. 2 (a)). Therefore, it can be confirmed that the (2 × 2)-3CO-β structure was not same as the (2 × 2)-3CO-α structure. A similar logic could be applied to the (2 × 2)-4CO structure; the period of line C_1, as shown in Fig. 3 (c), was observed to be a. In addition, the unique profile of line C_2, not predictable in the two (2 × 2)-3CO structures, supports the notion that the (2 × 2)-4CO structure is different from them. Indeed, the domains of the three different structures were observed, although not shown here, in one STM image. Further increase in the electrode potential induced the appearance of the ($\sqrt{19}$ × $\sqrt{19}$)-13CO structure.

The newly observed (2 × 2)-3CO-β and (2 × 2)-4CO structures were less populated than the well-known the (2 × 2)-3CO-α structure. In the hydrogen region, *e.g.* 0.05 V, only the (2 × 2)-3CO-α structure was observed. However, in the pre-oxidation region of CO (0.30–0.60 V *vs.* RHE),[6,7] the two new CO structures were found, in addition to the (2 × 2)-3CO-α structure. The populations of the (2 × 2)-3CO-β and (2 × 2)-4CO structures in the potential region were ~8% and ~2%, respectively. The low populations are probably due to anticipated high lateral repulsions in the molecular rows of CO, with a periodicity of a or less than a, as shown in Fig. 2 (b) and (c). Therefore, the presumably repulsive domains of (2 × 2)-3CO-β and (2 × 2)-4CO would be relevant to the pre-oxidation process of CO.

In summary, two new adstructures of adsorbed CO, the (2 × 2)-3CO-β and (2 × 2)-4CO structures, were found on Pt(111) in the pre-oxidation potential region. The CO domains of the newly observed structures may be connected to the pre-oxidation of adsorbed CO.

The authors appreciate the permission of Central Research Facility, Chungnam National University, Korea for the use of the STM instrument. This work was supported by a Korea Research Foundation Grant, funded by the Korean Government (MOEHRD) (R05-2004-000-10247-0).

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