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Low-temperature STM investigation of acetylene on Pd(1 1 1)

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Abstract

The adsorption of individual acetylene molecules at a Pd(1 1 1) surface has been studied with scanning tunneling microscopy (STM) at 4.7 K. The adsorbed acetylene molecules appear in the STM images as a combination of a protrusion and a pair of depressions. To determine the adsorption site and configuration of the molecule, we performed rotational manipulation of the molecule by injecting tunneling electrons into the molecule as well as performing atomically resolved STM imaging. The STM images revealed that the molecules have a total of six equivalent adsorption orientations on Pd(1 1 1), indicating three equivalent rotational states on two (both fcc and hcp) 3-fold hollow adsorption sites. From the atomically resolved STM images of the surface with a monatomic step edge, we have distinguished the two types of 3-fold hollow sites and confirmed that the fcc site is more stable than the hcp site at a low temperature.

Keywords: Scanning tunneling microscopy; Low temperature; Acetylene; Palladium; Rotation; Adsorption site

1. Introduction

Microscopic studies of the bonding and orientation of unsaturated hydrocarbon molecules at transition metal single crystal surfaces provide molecular-level insights into heterogeneous hydrocarbon catalysis. The adsorption and reaction of acetylene on metal surfaces has been extensively studied as a prototypical catalytic system, such as hydrogenation and dehydrogenation. The (1 1 1) surface of palladium has attracted special interests since it has the unique catalytic property of producing a benzene molecule from three acetylene molecules through a cyclotrimerization reaction [1–3].

The adsorption structure of acetylene on Pd(1 1 1) has been extensively studied by experimental techniques such as high-resolution electron energy loss spectroscopy (HREELS) [4], near-edge

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X-ray absorption fine structure (NEXAFS) [5], scanned-energy mode photoelectron diffraction [6], and scanning tunneling microscopy (STM) [7] as well as theoretical approaches based on density functional theory (DFT) calculations [7–12]. It has been commonly found in the structural studies that (1) the C–C bond is elongated on Pd(1 1 1) compared to the value in the gas phase, (2) the C–H bonds are distorted out of the plane where the hydrogen atoms are tilted away from the surface, and (3) the C–C bond is located on either an fcc or hcp 3-fold hollow site being parallel to the Pd–Pd bridge. These findings indicate that the carbon atoms in acetylene are rehybridized from an sp to an sp^2 configuration [11] and the carbon–carbon bond strength is weakened upon its adsorption on the Pd(1 1 1) surface. Although there is no doubt that adsorption at 3-fold hollow sites is strongly favored, there has been a controversial issue whether the acetylene molecules energetically prefer to bind at fcc [12] or at hcp [6–8,13] hollow sites.

STM imaging at cryogenic temperatures provides direct information about local structure and dynamics of individual molecular adsorbates on surfaces. Janssens et al. reported the low-temperature cyclotrimerization of acetylene molecules in the $(\sqrt{3}\times\sqrt{3})R30°$ phase on the Pd(1 1 1) surface at 140 K [14]. Dunphy et al. imaged single acetylene molecules on Pd(1 1 1) and determined their adsorption sites by combining STM imaging at 44 K and total-energy calculations [7]. In spite of the good agreement between these experimental findings and the results of theoretical studies, there still needs to be a closer look at the adsorption structure of an isolated acetylene molecule at much lower temperatures since thermally activated rotational motion of individual molecules occurs even at 44 K.

Here, we present direct determination of adsorption site and bonding configuration of "suspended" acetylene molecules on Pd(1 1 1) at 4.7 K with a dynamical method [15] of rotating the molecule by injecting tunneling electrons.

2. Experimental

All experiments were performed with a low-temperature STM (LT-STM, Omicron GmbH) equipped in an ultrahigh vacuum ($<3\times10^{-11}$ Torr) chamber at 4.7 K. A clean Pd(1 1 1) surface was prepared by repetitive cycles of Ar^+ sputtering and annealing to 1100 K followed by O_2 treatment at 850 K. The acetylene molecules were dosed on the surface through a dosing tube below 50 K. An electrochemically etched tungsten tip was used for imaging and manipulating acetylene molecules.

3. Results and discussion

Fig. 1(a) shows a topographic STM image of an isolated acetylene molecule obtained at 4.7 K. The Pd(1 1 1) surface was dosed with a small amount of molecules ($\theta = 0.01$ ML) at 50 K. At the sample temperature of 4.7 K, molecular motions are thermally quenched and the molecules do not move or rotate at all. The acetylene molecule appears as a combination of a protrusion and a pair of depressions in the STM images, which is worth comparing with previous results of STM observation at a cryogenic temperature. The saturated surface with acetylene molecules at 140 K revealed single protrusions [14] and the low-coverage structure of

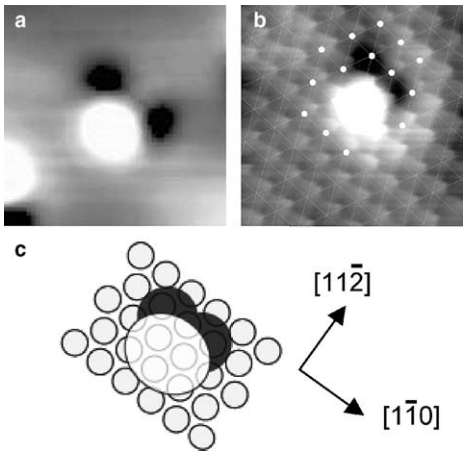

Fig. 1. STM images of an acetylene molecule adsorbed on Pd(1 1 1) obtained with (a) a normal bare tip ($I_t = 0.8$ nA, $V_s = 20$ mV, 1.2×1.2 nm^2) and (b) a molecular tip ($I_t = 0.8$ nA, $V_s = 20$ mV, 1.0×1.0 nm^2). The cross points and white dots represent the position of Pd atoms of the substrate. (c) Schematic model of acetylene on the Pd(1 1 1) surface showing top views of the molecule consistent with the STM image.