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Orientation of nitrous oxide on palladium(1 1 0) by STM

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Abstract

The adsorption structure of N_2O on Pd(1 1 0) was analyzed below 14 K by scanning-tunneling microscopy. The N_2O monomer was oriented along the [0 0 1] direction in the on-top form. Furthermore, the formation of small aggregates extending along the [1 $\bar{1}$ 0] direction was observed. The observed images were well-simulated for two types of cluster structures optimized by density-functional theory calculations. The components in the aggregates are proposed to be in a tilted form either on bridge sites or on-top sites.

1. Introduction

The nitrous oxide (N_2O) decomposition on rhodium and palladium surfaces has received much attention because N_2O, which is harmful with a remarkable greenhouse effect, is concomitantly produced in catalytic deNO_x treatments in automobile gas converters [1]. This species has recently been assigned as the key intermediate in controlling the selectivity to N_2 [2]. Its decomposition highly shares surface-nitrogen removal pathways in the catalyzed NO reduction and emits the product N_2 in an inclined way far from the surface normal [3]. This peculiar desorption was proposed to be due to the decomposition of N_2O oriented along the [0 0 1] direction. Here, we deliver the first scanning-tunneling microscopy (STM) observation of N_2O adsorbed on Pd(1 1 0). In addition to the monomers, small aggregates of N_2O were imaged for the first time. Their molecular orientations are discussed by referring to the results from density-functional theory (DFT) calculations in a generalized gradient approximation (GGA).

The collimated fragment desorption has frequently been reported in electron-stimulated desorption ion angular distribution [4]. In thermal reactions of adsorbed molecules, however, the collimated desorption has been limited to associative processes, such as $2N(a) \rightarrow N_2(g)$ and $CO(a) + O(a) \rightarrow CO_2(g)$ [2]. Therefore, the peculiar N_2 emission from N_2O on Pd(1 1 0) is the first example to show collimated fragment desorption in thermal decompositions [5]. It is indeed useful to analyze the reaction pathways [6].

The structure of adsorbed N_2O was studied on Pt(1 1 1) and Pd(1 1 0) by vibrational spectroscopy, showing the terminal nitrogen atom interacting with the surface [7,8]. Near-edge X-ray absorption-fine structure (NEXAFS) work on Ni(1 1 1), Cu(1 0 0), and Ag(1 1 0) has showed largely inclined forms [9,10]. However, no studies have discussed the presence of the form lying along the [0 0 1] direction

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which is inactive to vibrational spectroscopy. Recent DFT–GGA calculations on Pd(1 1 0) predict two stable adsorption forms, i.e., one lying along the [0 0 1] direction and the other standing with the terminal nitrogen–metal bond [11]. In recent careful NEXAFS work on Pd(1 1 0) at around 60 K, N_2O(a) showed significant anisotropy of the polarization dependence of π resonance [12]. This anisotropy is explained by the mixture of the standing and the lying forms along the [0 0 1] direction.

2. Experiments and calculations

The experiments were performed in an ultrahigh vacuum system (base pressure $<5\times10^{-11}$ Torr) consisting of three chambers for sample preparation, load-lock transfer and analysis (with low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES)), and two additional chambers with helium-cooled STM heads, A and B (UNISOKU). The STM-A had a gas doser directed to the sample surface. Its lowest operating temperature was 8 K (20 K) with a closed (open) inner-cooled radiation shield. The STM-B with no view ports operative at various temperatures was not used in this study. The sample temperature was monitored by either a thermocouple attached on the STM head during measurements or a radiation thermometer during cleaning procedures. An electrochemically etched tungsten tip was used for imaging. All the STM images were recorded in the constant current mode. A typical scan time was 6 min per image. A polished Pd(1 1 0) crystal (5 mm in diameter) was spot-welded to a pair of tantalum wires fixed on a sample holder. The crystal was heated by electron bombardments with a tungsten filament behind. The surface was cleaned by repeated cycles of Ar^+ bombardments at 850 K (2.0 kV, 4 μA, 1 h) and annealing at 1100 K followed by oxidation at 800 K (1×10^{-7} Torr of O_2, 1 h). The surface structure and cleanness were checked by LEED/AES.

The calculations were performed in the framework of DFT–GGA [13] using the plane-wave basis set and ultrasoft pseudopotentials [14], and the PWSCF package [15], while molecular graphics were generated using the XCRYSDEN program [16]. Further computational details are described elsewhere [11]. The STM images have been simulated using the Tersoff–Hamann approach [17]. Within this approximation, the tunneling current is proportional to local density of states at Fermi level (ε_F). We have integrated the local density of states (ILDOS) in the energy window [ε_F, ε_F + 0.3 eV] and plotted the corrugation of the isosurface of constant ILDOS at an average height of about 0.5 nm from the clean surface. This simplified approach merely reproduces the qualitative features.

3. Results

The clean Pd(1 1 0) surface prepared above showed a sharp (1 × 1) LEED pattern and clear (1 × 1) planes in STM images. Immediately after flashing to 1100 K, the crystal was transferred to the STM chamber to avoid the adsorption of residual gases. The surface was then exposed to 2.4 L N_2O (1 L = 10^{-6} Torr s) through the doser at between 90 and 80 K in the course of cooling. This adsorption temperature prevents the formation of N_2O multilayers [18]. Fig. 1 shows an STM image over a 24 nm × 24 nm region of the N_2O-covered Pd(1 1 0). In the upper left part of the image, a step edge of the Pd(1 1 0) substrate is seen along the [1 $\bar{1}$ 0] direction. The N_2O adsorbates and the defect sites are imaged as brighter and darker spots, respectively, than the Pd atoms. The average coverage of N_2O was estimated around 0.15 monolayer by assuming no multilayers. The majority of the N_2O is found to form small aggregates along the [1 $\bar{1}$ 0] direction whereas only a relatively small number of N_2O monomers are seen.

The step height was estimated to be 0.13 nm by referring to the STM image of the Au(1 1 1) planes on particles on mica at 12–14 K. The defect sites were 0.13–0.17 nm deep, indicating that they were due to missing Pd atoms. The local structures of the N_2O adsorbates are displayed in Fig. 2, which is the 6 nm × 10 nm part marked in Fig. 1. The Pd atoms and defects are clearly seen and the N_2O monomers are observed as dim oval spots with the long axis along

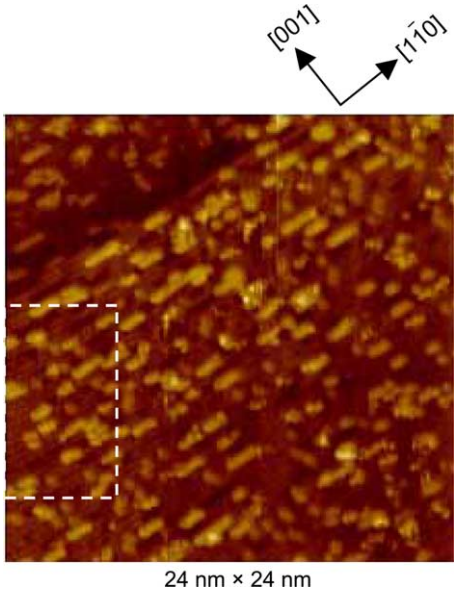

Fig. 1. STM picture of a wide range of Pd(1 1 0) surfaces at 8 K with sample bias V_{bias} = 0.05 V and tip current I_{set} = 0.25 nA. The surface was exposed to N_2O at 90–80 K in the course of cooling. The average N_2O coverage is ca. 0.15 monolayer. The part marked by the broken line is expanded in Fig. 2.