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Adsorption states of NO on the Pt(1 1 1) step surface

N. Tsukahara [a], K. Mukai [a], Y. Yamashita [a], J. Yoshinobu [a,*], H. Aizawa [b]

[a] The Institute for Solid State Physics, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277 8581, Japan
[b] Creative Research Initiative "Sousei", Hokkaido University, N21W10 Kita-ku, Sapporo, Hokkaido 001 0021, Japan

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Abstract

Using infrared reflection absorption spectroscopy (IRAS) and scanning tunneling microscopy (STM), we investigated the adsorption states of NO on the Pt(9 9 7) step surface. At 90 K, we observe three N–O stretching modes at 1490 cm^{-1}, 1631 cm^{-1} and 1700 cm^{-1} at 0.2 ML. The 1490 cm^{-1} and 1700 cm^{-1} peaks are assigned to NO molecules at fcc-hollow and on-top sites of the terrace, respectively. The 1631 cm^{-1} peak is assigned to the step NO species. In the present STM results, we observed that NO molecules were adsorbed at the bridge sites of the step as well as fcc-hollow and on-top sites of the terrace. To help with our assignments, density functional theory calculations were also performed. The calculated results indicate that a bridge site of the step is the most stable adsorption site for NO, and its stretching frequency is 1607 cm^{-1}. The interactions between NO species at different sites on Pt(9 9 7) are also discussed.

Keywords: Platinum; Steps; Nitric monoxide; Adsorption; Infrared reflection absorption spectroscopy; Scanning tunneling microscopy; Density functional theory calculations

1. Introduction

The adsorption and reaction of nitric monoxide (NO) on transition metal surfaces are important from industrial, environmental, and scientific viewpoints. The unpaired electron in the antibonding 2π orbital of NO increases the variety of surface reactions as compared to the case of CO. So far many studies have been carried out to determine the adsorption states of NO on metal surfaces [1].

The adsorption states of NO on the Pt(1 1 1) surface were studied using several experimental techniques. Using electron energy loss spectroscopy (EELS) and infrared reflection absorption spectroscopy (IRAS), 1490 cm^{-1} and 1690 cm^{-1} peaks were observed at low and high coverages at 100 K, respectively. Ibach and Lehwald concluded that NO adsorbed as a monomer at low coverage, and with increasing coverage NO molecules adsorbed as dimer species near the saturation coverage [2]. Gland and Sexton [3] and Hayden [4] proposed an adsorption model based on the comparison of the stretching vibrational energy of the adsorbed NO with that of NO in nitrosyl complexes. In their model, NO adsorbs at a twofold bridge site at low coverage and switches to an on-top site as the coverage increases. On the other hand, Kiskinova et al. found an O 1s peak at 530.6 eV, which was assigned to NO on a bridge site at low coverage, and the second peak at 532.5 eV which was assigned to the on-top NO at high coverage. At the saturation coverage, only one broad peak at 531.1 eV was observed, which was assigned to disordered NO [5]. The transition from the bridge to the on-top sites, as suggested from EELS and IRAS results [3,4], does not agree with the XPS results.

On the contrary, using dynamical low energy electron diffraction (LEED), Materer et al. reported that at 0.25 ML the $p(2\times2)$ NO fcc-hollow site model gave the best fit between LEED experiment and calculation. (1 ML is defined as one adsorbate molecule per surface atom) [6,7]. Ge and King calculated the adsorption energies of NO on

* Corresponding author. Tel.: +81 4 7136 3320; fax: +81 4 7136 3474.
E-mail address: yoshinobu@issp.u-tokyo.ac.jp (J. Yoshinobu).

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Pt(1 1 1) based on density functional theory (DFT) with generalized gradient approximation (GGA) [8]; they also found that the fcc-hollow site was the most stable site for NO.

Recently, the adsorption states of NO on Pt(1 1 1) have been studied in detail [9–14]. Using dynamical LEED analysis, with the aid of scanning tunneling microscopy (STM) and high resolution EELS, Matsumoto et al. investigated the adsorbed states of NO on Pt(1 1 1) as a function of coverage. First, NO molecules are adsorbed at fcc-hollow sites up to 0.25 ML and form the $p(2\times2)$ ordered structure. Next, NO is additionally adsorbed at on-top sites up to 0.5 ML. Finally up to saturation coverage (0.75 ML), NO occupied fcc-hollow, hcp-hollow and on-top sites [9–11]. By the latest DFT calculation, Aizawa et al. also supported these results [12]. Furthermore, they calculated the peak intensities (i.e. square dynamic dipole moments) and the wavenumbers of N–O stretching vibrations as a function of the coverage.

Real metal surfaces contain various defects, such as steps and kinks, and thus adsorption states become more complex than those on a flat surface. Since molecules often interact strongly with the defect sites, the defects on the surface have a strong influence on chemical reactions on inhomogeneous surfaces [15,16]. Thus, as a model of defect surfaces, it is important to study surface chemical reactions on well-defined step surfaces.

Recently, using temperature programmed desorption (TPD), Sugisawa et al. [17] and Mukerji et al. [18] found that NO was dissociated at the step on Pt(2 1 1) above 230 K and then N_2 and N_2O were observed as desorption products. In addition, Mukerji et al. studied the adsorption states of NO on Pt(2 1 1) using DFT calculation and IRAS [19]. They reported that NO adsorbed at a bridge site of the step and its stretching energy was 1620 cm^{-1} at 120 K; at 307 K NO–O complexes were formed and the absorption band was observed at 1801 cm^{-1}. Backus et al. reported similar results for NO on Pt(5 3 3) using TPD, IRAS and DFT calculations [20]. However, so far there is no direct experimental evidence that NO adsorbs at a bridge site of the step.

In this study, we investigated the adsorption states of NO molecules on the Pt(9 9 7) surface at low temperature, using IRAS and STM. The DFT calculation was performed to evaluate the adsorbed states of NO on Pt(5 5 3).

2. Experiments and calculations

The Pt(9 9 7) surface has a periodic step-terrace structure; miscutting about 6.5° from the [1 1 1] direction. The terrace of this surface has a (1 1 1) close-packed structure constituted by nine rows of Pt atoms, and the monoatomic step is formed by a (1 1 1) microfacet.

The IRAS and STM experiments were carried out in an ultrahigh vacuum chamber. The base pressure of the chamber was less than 1×10^{-10} Torr. The Pt(9 9 7) clean surface was carefully prepared by repeated cycles of 800 eV Ne-ion sputtering and annealing at 800 K, and repeated cycles of oxidation under 1×10^{-7} Torr O_2 and flashing to 1300 K in the preparation chamber. The sample was transferred to the main chamber in which the sample holder was connected to a liquid He/liquid N_2 reservoir and surrounded by triple thermal shields. Gaseous NO molecules at room temperature were introduced to the cold sample surface through a pulse gas dosing system, at an angle of about 45° from the surface normal direction. With constant pressure in the gas line and a constant duration for opening the valve, the exposure was accurately controlled by the number of shots.

First-principles calculations were performed for NO molecules adsorbed on the Pt(5 5 3) surface. The Pt(5 5 3) surface is similar to the Pt(9 9 7) surface in the sense that both surfaces consist of (1 1 1) terraces and (1 1 1) monoatomic steps. The only difference is in the width of the terrace; the Pt(9 9 7) surface involves nine atom wide terraces, while on the Pt(5 5 3) surface the terrace is only five atom wide. We consider that the calculations for the Pt(5 5 3) surface reproduce the essential features of chemical processes taking place on the Pt(9 9 7) surface, because from a chemical perspective the steps usually play a much more important role than terraces.

All the calculations were carried out using a program called STATE, which has been successfully applied to both metal and semiconductor surfaces [25]. The calculations were based upon the DFT with GGA. The PBE-type exchange-correlation functional was employed [26]. Only valence electrons in the 5d, 6s and 6p states for Pt and the 2s and 2p states for N and O were treated explicitly in the present calculations. Ultrasoft pseudopotentials [27] were used for the N 2p, O 2p, and Pt 5d states, while norm-conserving pseudopotentials [28] were used for the other states. Wavefunctions were expanded by plane waves, whose cutoff energy was taken to be 30.25 Ry. The number of it k-points can be small, as the size of the unit cell is large in the present calculations. We adopted a two-dimensional 2×2 uniform k-point mesh. We used a slab consisting of an NO molecule layer and 15 Pt layers. The NO molecule layer, as well as the upper 10 Pt layers, were allowed to relax in geometrical optimization procedures. The surface unit cell contains one step and one terrace consisting of five atomic rows. The periodicity parallel to the step was set to be three atoms. Spin-polarization effect was not taken into account, because most previous calculations of NO on transition-metal surfaces have indicated that chemisorbed NO is not spin-polarized [29].

3. Results and discussion

3.1. IRAS measurements of NO adsorption on Pt(9 9 7) at 90 K

IRAS spectra of NO on Pt(9 9 7) at 90 K are shown in Fig. 1 as a function of NO exposure. When the valve of the gas line was opened once (=1 shot), a certain amount