Influence of Step Sites on Thermal Behavior of NO on Stepped Pd(112) Studied by AES, XPS and UPS

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(Received 21 July 2009; Accepted 10 August 2009; Published 19 September 2009)

The adsorption and thermal dissociation of nitric oxide on a stepped Pd(112) surface has been investigated by Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and ultraviolet photoelectron spectroscopy (UPS). NO undergoes molecular adsorption on a stepped Pd(112) surface at 300 K. With increasing temperature, some NO adsorbed on the surface desorbs molecularly and the remaining NO starts to dissociate into nitrogen and oxygen. The NO dissociation takes place preferentially at the step sites. All NO molecules adsorbed on the surface dissociate above 423 K. Nitrogen desorbs from the surface above 700 K but oxygen exists on the surface or subsurface. UPS results show that the peak at 11.2 eV below Fermi level ($E_F$), originating from the $\pi$+5$\sigma$ orbital of NO adsorbed on step sites of Pd(112), disappear at a lower temperature than does the peak of NO adsorbed on terrace sites. This indicates that NO molecules adsorbed on step sites are dissociated at a temperature lower than those at terrace sites. The dissociation activity of NO on Pd(112) is stronger than on the (111) and (110) surfaces, but weaker than on the (100) surface. The order of the dissociation activity is Pd(100) > Pd(112) > Pd(111) > Pd(110). [DOI: 10.1380/ejssnt.2009.851]

Keywords: Nitric oxide; Palladium; Dissociation; Stepped single-crystal surfaces; XPS; UPS

I. INTRODUCTION

It is very important to investigate the catalytic activity on a surface for both fundamental and applied studies of catalysis. The existence of atomic steps is expected to lead to a high reaction activity in comparison with a flat surface. The adsorption of diatomic molecules on a well-defined stepped surface is a suitable model system for studying the surface reaction. Zambelli et al. observed, by scanning tunneling microscopy (STM), that NO dissociates at the step edge and the N and O atoms diffuse from the step edge in the case of the dissociative adsorption of NO on Ru (0001) [1].

The adsorption of NO on a stepped Pd(112) surface, which is composed of three-atom-wide (111) terraces and monatomic (001) steps, has been studied by several authors [2–6]. The experimental results of temperature-programmed desorption (TPD) and electron-stimulated desorption ion angular distribution (ESDIAD) showed that NO is adsorbed on terrace sites with the NO axis perpendicular to the terraces at low coverage, whereas NO is adsorbed on step sites with NO tilted downwards with increasing coverage [2]. Subsequently, the chemisorption energies and geometries of NO were calculated using density-functional theory and the stable chemisorptions sites were found [3]. In the first stage of adsorption, NO is preadsorbed at threefold hollow sites on the (111) terrace near a step edge. With increasing coverage, NO is adsorbed on threefold hollow sites at the terrace, and the preadsorbed NO changes from the threefold hollow sites to the twofold bridge sites with a slight downward tilt of steps. In a previous paper, we reported the electronic structure of NO adsorbed on a stepped Pd(112) surface [4]. The molecular orbital $1\pi+5\sigma$ of NO molecules adsorbed on step sites of Pd(112) was observed at 11.2 eV below the Fermi level. This result supports the microscopic picture of adsorption predicted by the theoretical calculation and shows that the N-O bond of NO molecules adsorbed on terrace sites is weaker than that of molecules on step sites.

A comparative TPD study of Pd(100) and Pd(112) was performed by Ramsier et al. [5], who observed that NO predominantly desorbs molecularly from Pd(111), whereas relatively large amounts of N and N$_2$O desorb from Pd(112) in the temperature range 450-550 K upon heating. They concluded that the stepped Pd(112) surface is more active for NO decomposition than the Pd(111) surface. Their explanation, however, is based on the NO molecules preferentially binding to terrace sites instead of step sites. Subsequently, pathways and energy barriers for the dissociative adsorption of NO on the Pd(111) and Pd(112) surfaces are calculated using density functional theory [6]. It was shown that on the stepped...
Pd(112) surface, the dissociation of NO is facilitated owing the stronger bonding of molecular NO and atomic N and O.

In this work, to study the influence of step sites on the dissociation and desorption of NO molecules, the thermal behavior of NO adsorbed on a stepped Pd(112) surface has been investigated by AES, XPS and UPS.

II. EXPERIMENTAL

All experiments were performed in an ultrahigh-vacuum (UHV) system with a base pressure of $1 \times 10^{-10}$ Torr. The chamber was equipped with AES, XPS, and UPS facilities. AES, XPS and UPS spectra were observed using a double-pass cylindrical mirror analyzer (CMA, model 15-255, Physical Electronics Industries). The photon energies used for UPS and XPS were 40.81 eV (He II) and 1253.6 eV (Mg Kα), respectively.

The sample used here was 10 mm in diameter and 1 mm in thickness (Mateck Crystal Ltd., GM, 99.999% purity). The sample was cut within 0.5° using Laue X-ray diffraction and polished to obtain a mirror finish. The surface roughness was less than 0.03 µm. The sample was cleaned by repeated cycles of Ar ion sputtering, annealing in $2 \times 10^{-8}$ Torr of oxygen at 900 K and then flashing at 1200 K in vacuum. The sample was heated by electron back-bombardment. The sample temperature was measured with a chromel-alumel thermocouple spotwelded to the side of the sample. The surface cleanliness was checked for impurities by AES. The sample was exposed to NO gas (99.9% purity) at room temperature introduced through bakeable metal leak valves. All measurements were carried out at room temperature, after the sample had been heated to the target temperature that was then maintained for 5 minutes.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the peak-to-peak intensities of the N(KLL) and O(KLL) Auger electrons as a function of annealing temperature. The sample was exposed to 20 L of NO at room temperature. The intensities of N(KLL) and O(KLL) were in the ratio of 1:1 at 300 K. With increasing annealing temperature, the intensities of N(KLL) and O(KLL) decreased monotonically and then dropped sharply at 400 K. Then the intensity of N(KLL) is decreased gradually and disappeared at about 700 K, within experimental error, whereas the intensity of O(KLL) was almost constant above 450 K and did not fall to zero up to 1200 K. Our results are in rough agreement with the AES data obtained by Ramsier et al. [5], except for the N(KLL) intensity in the temperature range of 550 K to 700 K. Several studies have indicated the presence of nitrogen near 700 K on polycrystalline and low-index single crystal Pd surfaces [7–9]. Although there may be different annealing procedures, we used double-pass CMA, with a higher sensitivity than the single-pass CMA used by Ramsier et
Figures 2 and 3 show the XPS difference spectra of O 1s and N 1s for various annealing temperatures after exposure to 20 L of NO at room temperature, respectively. We show the XPS difference spectra due to the overlap of O 1s and Pd 3p\(^{3/2}\) orbitals. The peak position of O 1s was shifted from 533.8 eV to 532.8 eV at the temperature of 423 K, and that of N 1s from 401.2 eV to 398.2 eV. From the previous XPS results of NO adsorbed on the metal surfaces [8–10], we can assign both the N 1s and O 1s peaks shifted to the lower binding energy side upon heating to the dissociated atomic N and O. These shifts are indicative of the dissociation of NO at 423 K. Another small peak appeared at 405 eV in Fig. 2 seems to be an N 1s shake-up satellite component depending on chemical state of nitrogen. This temperature is lower than those on Pd(111) and Pd(110), but higher than that on Pd(100) [9]. The peak of N 1s was diminished at the temperature of 700 K. This is consistent with the AES result.

The UPS difference spectra for various annealing temperatures after exposure to 20 L of NO at room temperature are shown in Fig. 4. Four peaks were observed at 2.7, 9.4, 11.2 and 14.8 eV below the Fermi level (\(E_F\)) at 300 K. At around 4 eV, a bulk d-band peak remains on difference spectra [4, 9]. The peaks at 9.4 and 11.2 eV were considered to be derived from 1\(\pi+5\sigma\) orbitals of NO adsorbed on terrace and step sites of Pd(112), respectively [4]. According to the d-band model by Hammer and Nørskov, the surface d-band center correlates well with trends in the bond energy of the adsorbate to the transition-metal surface [11, 12]. Because the calculated d-band center for the bridge sites of the step edge is higher below \(E_F\) than that for the threefold hollow sites of the terraces [3, 6], the bonding energy and the adsorbate projected density of states (1\(\pi+5\sigma\) orbitals of NO) of the bridge sites of the step edge should became higher than that for the threefold hollow sites of the terraces. This is also in reasonable agreement with the experimental results.

These peaks at 2.7 and 14.8 eV originate from 2\(\pi\) and 4\(\sigma\) orbitals of NO molecules, respectively, as determined by several authors [13–16]. With increasing annealing temperature, the two peaks of 1\(\pi+5\sigma\) orbitals gradually decrease and the peaks at 9.4 and 11.2 eV disappear at 423 K and 393 K, respectively. A new peak appears at 6.0 eV above 333 K. This peak originates from the 2p orbital of oxygen or nitrogen atoms. This indicates that NO molecules dissociate into nitrogen and oxygen atoms. The NO dissociation takes place preferentially at the step sites, because the peak of 1\(\pi+5\sigma\) orbitals of NO adsorbed at the step sites disappears at a lower temperature than does the peak of NO adsorbed on the terrace sites. The peak at 6.0 eV becomes broad above 423 K and disappears at 623 K. Conrad et al. observed the peaks at 6.4, 10.6, and 13.5 eV below \(E_F\), which are due to the formation of PdO on Pd(111) after exposure to \(10^{-6}\) Torr NO at 900 K [14]. The broadening of the peak at 6.0 eV is indicative of the formation of surface oxide (PdO). Taking the difference in the electron escape depth for both AES and UPS techniques into consideration, the disappearance of this peak above 623 K in UPS and the existence of oxygen indicated by in AES imply that the oxygen atoms penetrate into the subsurface on Pd(112).

Figure 5 shows intensities of the 1\(\pi+5\sigma\) orbital of NO
molecules from the Pd surfaces for various annealing temperatures, along with those for previously reported low-index surfaces [9]. The $1\pi + 5\sigma$ intensity is normalized at room temperature. The activity of the dissociation of NO on Pd(112) is stronger than on the (111) and (110) surfaces, but weaker than on the (100) surface. The order of the dissociation activity is Pd(100) > Pd(112) > Pd(111) > Pd(110). The NO adsorbed on step sites of Pd(112) dissociate at a lower temperature than those of terrace sites. The dissociation activity of step sites is stronger than that of terrace sites. The stepped Pd(112) surface is composed of three-atom-wide terraces of (111) orientation and monatomic steps of (001) symmetry. Among the low-index single crystal surfaces, the Pd(100) surface has a high dissociation activity. It is thus suggested that the atomic structure of monatomic steps of (001) symmetry affect the dissociation of NO.

IV. CONCLUSIONS

The adsorption of nitric oxide on a stepped Pd(112) surface has been investigated by Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and ultraviolet photoelectron spectroscopy (UPS). It was found that the peak at 11.2 eV, originating from the $1\pi + 5\sigma$ orbital of NO molecules adsorbed on step sites of Pd(112), disappears at a lower annealing temperature than does the peak of NO adsorbed on terrace sites. This indicates that NO molecules adsorbed on step sites are dissociated earlier than those at terrace sites. The dissociation activity of NO on Pd(112) is stronger than on the (111) and (110) surfaces, but weaker than on the (100) surface. The order of the dissociation activity is Pd(100) > Pd(112) > Pd(111) > Pd(110).

[1] T. Zambelli, J. Wintterlin, J. Trost, and G. Ertl, Science 273, 1688 (1996).
[2] R. D. Ramsier, Q. Gao, H. Neergaard Waltenburg, K.-W. Lee, O. W. Nooij, L. Lefferts, and J. T. Yates, Jr., Surf. Sci. 320, 209 (1994).
[3] B. Hammer, J. K. Norskov, Phys. Rev. Lett. 79, 4441 (1997).
[4] K. Irokawa, S. Ito, T. Kioka, and H. Miki, Surf. Sci. 433-435, 297 (1999).
[5] R. D. Ramsier, Q. Gao, H. Neergaard Waltenburg, and J. T. Yates, Jr., J. Chem. Phys. 100, 6837 (1994).
[6] B. Hammer, Faraday Discuss. 110, 323 (1998).
[7] H. Miki, H. Nagase, T. Nagase, T. Kioka, S. Sugai, and K. Kawasaki, Appl. Surf. Sci. 33-34, 292 (1988).
[8] S. Sugai, H. Watanabe, H. Miki, T. Kioka, and K. Kawasaki, Vacuum 41, 90 (1990).
[9] S. Sugai, H. Watanabe, T. Kioka, H. Miki, and K. Kawasaki, Surf. Sci. 259, 109 (1991).
[10] M. J. Breitschaffer, E. Unbach, and D. Menzel, Surf. Sci. 109, 493 (1981).
[11] B. Hammer and J. K. Norskov, Nature 376, 238 (1995).
[12] B. Hammer and J. K. Norskov, Surf. Sci. 343, 211 (1995).
[13] H. Conrad, G. Ertl, J. Küppers, and E. E. Latta, Surf. Sci. 65, 235 (1977).
[14] H. Conrad, G. Ertl, J. Küppers, and E. E. Latta, Surf. Sci. 65, 245 (1977).
[15] E. Miyazaki, I. Kojima, M. Orita, K. Sawa, N. Sanada, T. Miyahara, and H. Kato, Surf. Sci. 176, L841 (1986).
[16] E. Miyazaki, I. Kojima, M. Orita, K. Sawa, N. Sanada, K. Edamoto, T. Miyahara, and H. Kato, J. Electron Spectrosc. Relat. Phenom. 43, 139 (1987).