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Unusual Adsorption Site Occupation Sequence: NO Adsorption on Stepped Pd(112)

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Abstract: The adsorption of NO on a stepped Pd(112) surface has been investigated at 300–373 K with high resolution electron energy loss spectroscopy (HREELS) and electron stimulated desorption ion angular distribution (ESDIAD) techniques. At exposures below 5.7×10^{14} NO/cm^2, NO molecules preferentially adsorb on the terrace sites, with an NO stretching mode observed by HREELS at 1535–1550 cm^{-1}, and an O^+ ESDIAD beam directed near the (111) terrace-normal direction. For NO exposures above $\sim 6 \times 10^{14}$ molecules/cm^2, step sites are occupied in addition to the terrace sites, with an NO stretching mode observed in HREELS at ~1655–1670 cm^{-1} and an additional O^+ ESDIAD beam oriented in the "downstairs" direction. This is an unusual reversal of the site occupation sequence since one usually expects stronger adsorbate bonding on the step sites causing the steps to fill first. The N–O bond stretching frequencies observed in HREELS are indicative of weaker bonding of NO molecules on the step sites than on the terrace sites.

1. Introduction

One of the central goals in surface science is to identify the adsorption sites, and especially the active sites for surface reactions. It is observed in many surface reactions that surface defects, with low metal–metal coordination numbers, serve as preferential adsorption and reaction centers.[1–3] The unsaturated coordination of the defect site atoms, a property of the local surface structure, is often thought to determine the chemical reactivity. The most abundant defects found on single-crystal surfaces are steps. In general, one anticipates that a molecule will bond preferentially to the step sites compared to the terrace sites. This has been observed for example in the adsorption of CO on stepped Pt(335) and Pt(112) surfaces, where at low coverage CO adsorbs on the step edges and at high coverage the terrace sites begin to be occupied.[4–9]

In this report, we describe an unusual reversal of the expected adsorption site occupation sequence for NO on Pd(112). This surface presents a [3(111) × (001)] structure. NO adsorbs exclusively at 373 K on the (111) terrace sites at low coverage and occupies both terrace and (001) step sites at high coverage. To our knowledge, this is the first report of a reverse sequence of chemisorption site occupancy on stepped metal crystal surfaces.

2. Experimental Section

The Pd crystal was oriented, cut and polished in the (112) direction to within 0.5° using Laue X-ray diffraction. The surface plane orientation has also been checked with low-energy electron diffraction (LEED). The periodicity of the terrace-step structure shows a splitting of LEED beams with a vector $\sim {}^1/_3$ of that for the (111) beams. The crystal is cleaned by the following cycles: (1) ion sputtering at 1000 K (beam energy of 2 keV, $I_{crystal} = 2 \times 10^{-6}$ A) in Ar and O_2 gas mixtures with $P_{O2} = 5 \times 10^{-8}$ Torr and $P_{Ar+O2} = 6 \times 10^{-5}$ Torr; (2) annealing in oxygen with $P_{O2} = 5 \times 10^{-7}$ Torr at 1000 K; and (3) 1200 K annealing in vacuum. The major bulk contaminants are identified as S, C, and O by Auger electron spectroscopy (AES). These impurities strongly segregate onto the surface and are removed. The final surface concentration of impurities within the depth of Auger sampling is estimated to be S <0.1 atom % and O <0.5 atom %. In the case of carbon, an overlap of C(KLL) Auger features with Pd(MNN) Auger features requires an Auger line shape analysis to ensure the surface cleanliness. In addition, the lack of CO production (<0.01 mL) upon oxygen adsorption followed by heating to 1000 K indicates that our Pd(112) crystal is carbon free. Using high resolution energy loss spectroscopy (HREELS), impurities beyond the AES detection limit are observed to produce a lower counting rate and a broad beam profile due to phonon losses around the elastic peak. A clean surface shows a sharp elastic beam profile in HREELS with a counting rate of $\sim 2 \times 10^5$ counts/s.

Two UHV chambers were employed for the adsorption study with base pressures $\leq 1 \times 10^{-10}$ Torr. The Pd(112) crystal was transferred between the two chambers and recleaned after each transfer. The first chamber was equipped with a HREEL spectrometer, a shielded line-of-sight quadrupole mass spectrometer (QMS) for temperature-programmed desorption (TPD) studies, a cylindrical mirror analyzer (CMA) Auger electron spectrometer (AES), a low-energy electron diffraction (LEED) apparatus, an ion sputtering gun, and a calibrated multicapillary array beam doser.[10–13] The primary energy used for HREELS was ~4.5 eV with a full width at half maximum (fwhm) of ~60 cm^{-1}.

The second chamber housed a digital electron stimulated desorption ion angular distribution (ESDIAD) and LEED apparatus, an unshielded QMS for TPD studies, an ion sputtering gun, a CMA for AES, and a calibrated multicapillary array doser. The absolute dosing rate of the dosers on the two chambers was calibrated with N_2 gas and absolute errors estimated for NO dosing are in the 10% range. The electron beam energy used for the ESDIAD study was 1000 eV. A very small beam current was used (~5 nA) to avoid significant electron beam damage on the surface during the measurements. The ion desorbed during ESD of NO(a) was determined to be O^+ using the QMS, with no NO^+ or N^+ detected. The ESDIAD patterns are obtained under field-free conditions

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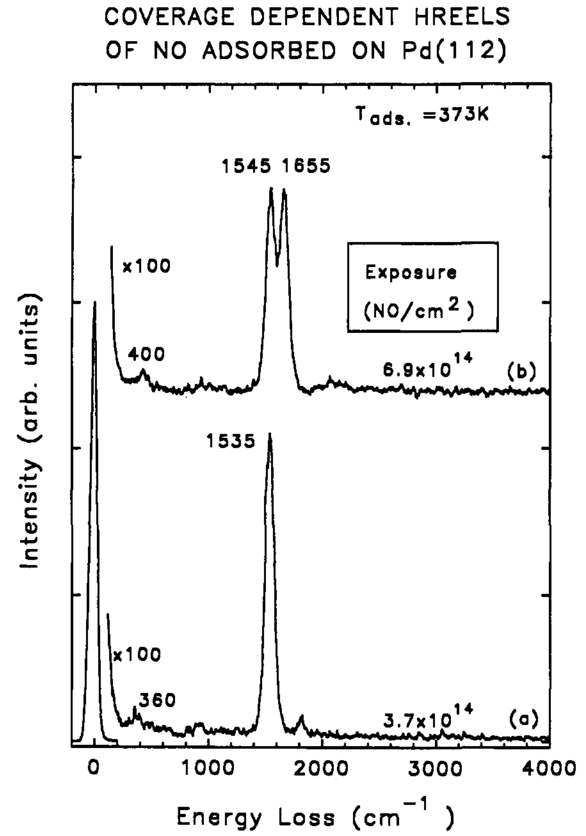

Figure 1. HREEL spectra of NO adsorbed on Pd(112) at 373 K with NO exposures of (a) 3.7 × 10^{14} and (b) 6.9 × 10^{14} molecules/cm^2.

with the crystal and the first grid of the detection optics grounded. The final pattern is processed by background subtraction to remove a large soft X-ray contribution and by least-squares digital smoothing. The presence of the large X-ray background degrades the quality of the O^+ ESDIAD pattern to below normal levels.

Nitric oxide (NO) (Matheson, 99.0% purity) was purified several times by freeze–pump–thaw cycles using a liquid nitrogen–ethanol bath (156 K). The purity of this as-prepared NO gas was confirmed using the QMS.

3. Results

The NO adsorption temperature on Pd(112) was chosen in the range of 300–373 K to limit the number of NO adsorption states which are occupied at saturation coverage. Adsorption at 100 K on Pd(112) produces more NO adsorption states at higher coverages which complicate the interpretation of the results.[14] Figure 1 shows two typical HREEL spectra of NO/Pd(112) selected from a series of coverage-dependent results.[14] At 3.7 × 10^{14} NO/cm^2 exposure, energy loss peaks at ~1535 and ~360 cm^{-1} are observed (Figure 1a). These peaks correspond to the N–O stretching mode, $\nu_{(NO)}$, and the Pd–NO stretching mode, $\nu_{(Pd-NO)}$, respectively.[15-18] A weak feature at ~1800 cm^{-1} is from the adsorption of background CO during data collection at 90 K. This feature is not present for the initial first few scans. A larger NO exposure (6.9 × 10^{14} molecules/cm^2) produces another adsorbed NO state, with an N–O stretching mode observed at 1655 cm^{-1}, in addition to the previously observed NO mode which shifts slightly to 1545 cm^{-1} (Figure 1b). The $\nu_{(Pd-NO)}$ feature is also observed near 400 cm^{-1}.

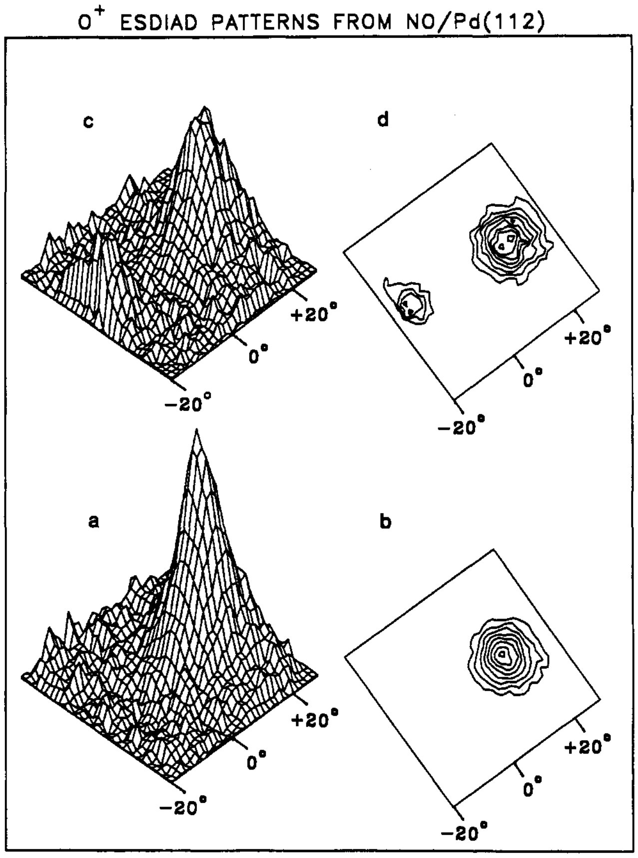

Figure 2. ESDIAD patterns of NO adsorbed on Pd(112) at 300 K, with NO exposures of (a, b) 4.0 × 10^{14} and (c, d) 6.0 × 10^{14} molecules/cm^2. The step edge on the crystal runs parallel to the lower left border of each of the plots. The perspective plots (a and c) are on the same scale. The contour plots (b and d) are generated by 8 equal separations from 25% to 95% of the maximum counts on each plot.

The adsorbed NO produces O^+ ions during electron stimulated desorption (ESD). The angular distribution of these O^+ beams is shown by ESDIAD measurements (Figure 2). The macroscopic surface direction, the surface normal for the (112) plane, corresponds to the 0° polar angle in the figure while +19.5° corresponds to the (111) direction normal to the terraces. Polar angles less than 0° correspond to "downstairs" directions which are characteristic of NO adsorption on step sites on Pd(112). NO is adsorbed at 300 K in Figure 2, but similar ESDIAD patterns are observed for both 373 and 100 K adsorption temperatures for roughly the same exposures. At an NO exposure of 4.0 × 10^{14} molecules/cm^2, a single O^+ ESDIAD beam is observed close to the (111) terrace-normal direction, as shown in the 3-D perspective plot (Figure 2a) and the contour plot (Figure 2b). The peak maximum corresponds to a laboratory polar angle of ca. +14°. A higher NO exposure (6.0 × 10^{14} molecules/cm^2) yields an ESDIAD pattern with two O^+ ion beams at ca. −16° and ca. +16° polar angles (Figure 2c,d). The negative polar angle value corresponds to an N–O bond angle oriented in the "downstairs" direction for the stepped Pd(112) surface.

4. Discussion

The Pd(112) surface is composed of 3-atom-wide (111) terraces and monatomic height (001) steps (Figure 3). Three types of surface Pd atom sites are present with metal–metal coordination numbers of 7, 9, and 10 labeled as sites A, B, and C, respectively (Figure 3). Site B is equivalent in coordination number, 9, to that present for Pd atoms on the Pd(111) surface.

In separate experiments,[14] we have employed a flat Pd(111) surface to compare NO adsorption to that on stepped Pd(112). It is observed that at 373 K, only one adsorption state of NO is

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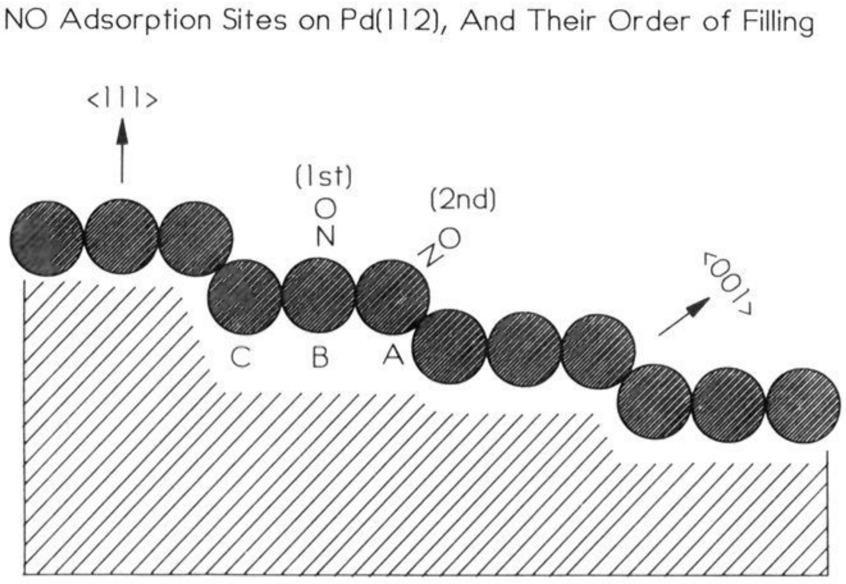

Figure 3. Model of a stepped Pd(112) surface and the stages of occupancy of surface sites by NO. The identification of local site symmetries at A, B, and C (atop; bridged) is not intended in the drawing.

present on Pd(111), with an NO stretching mode observed at ~1540 cm^{-1} at 4.9 × 10^{14} molecules/cm^2 exposure.[14] This mode corresponds closely in frequency to the observed $\nu_{(NO)}$ mode at 1535 and 1545 cm^{-1} on Pd(112) as shown in parts a and b, respectively, of Figure 1. In addition, NO adsorbed on Pd(111) is characterized by a normal O$^+$ ESDIAD beam.[14] This eliminates the possibility of a bent NO species on Pd(111) which exhibits a Pd–N–O bond angle significantly less than 180°. Recent surface reflection FT-IR studies on Pd(111) have also observed one NO stretching mode at ~1564 cm^{-1} at a substrate temperature of 375 K, supporting our assignment.[19]

The ion trajectory in ESDIAD reflects the direction of the chemical bond being ruptured in the ESD process.[20] The observed O$^+$ beam in the ESDIAD study at lower NO coverages on Pd(112) is in the vicinity of the (111) terrace normal direction (Figure 2a,b) indicating that the orientation of the N–O bond is approximately perpendicular to the (111) terrace surface. The small deviation from the exact (111) surface normal direction (+19.5°) is due possibly to final state effects, such as image potential and reneutralization processes which can modify the ion trajectories,[21-23] or to slight tilting of the terrace NO species' N–O bond away from the step edge. Thus, both HREELS and ESDIAD confirm that NO initially occupies (111) terrace sites on the Pd(112) surface.

At high exposures, a new NO adsorption state is observed on Pd(112) with an N–O stretching mode at ~1655 cm^{-1}. Since no such high-frequency NO stretching mode is observed on the flat Pd(111) surface under the same experimental conditions,[14] we assign this NO adsorption state to NO adsorbed on the step sites, which have the (001) surface orientation (Figure 3). Nyberg and Uvdal have observed, on the Pd(100) surface, a $\nu_{(NO)}$ mode at 1640–1664 cm^{-1} for a saturation adsorption of NO at 100 K followed by annealing to 190–250 K.[24] Surface reflection FT-IR studies have also observed this NO adsorption state on Pd(100) with an NO stretching mode at ~1653 cm^{-1}.[19] The surface Pd atoms on Pd(100) have a coordination number of 8. We tentatively assign the NO adsorption state on Pd(112) with $\nu_{(NO)}$ ~ 1655 cm^{-1} to adsorption on site A of the Pd(112) surface as shown in Figure 3. The adsorption site C, though not completely ruled out for NO occupation, is less likely to yield a tilted N–O bond due to steric effects. In addition to the vibrational frequency correlation, suggesting that NO adsorbs on the step sites only at high coverages, our ESDIAD studies show an additional O$^+$ beam oriented in the "downstairs" direction (ca. −16°) at an NO exposure of 6.0 × 10^{14} molecules/cm^2 (Figure 2c,d). This is the direction expected for NO adsorption on step sites (Figure 3), supporting the conclusions of HREELS, that terrace sites are first occupied, followed by step site occupancy.

The stepped Pd(112) surface, with a [3(111) × (001)] surface structure, has a very high percentage of step sites. NO dissociation on Pd(112) is observed after heating adsorbed NO to ~500 K.[14] We do not observe NO dissociation at ~373 K, indicating the incorrectness of an hypothesis where NO dissociation fragments would block the step sites for NO adsorption at low coverages. In fact, experiments using dissociative O_2 adsorption to preferentially block the step sites did not succeed.[14]

Having assigned the adsorption sites, we notice that the NO molecules *bind strongly on terrace sites* and *bind weakly on step sites* as indicated by the N–O bond stretching frequencies observed in HREELS. According to the bonding model involving d–π^* molecular orbitals for metal nitrosyls,[25] the lone pair electrons on nitrogen atoms of the NO(a) molecules donate to the empty d-orbitals of the Pd atoms forming σ bonds. The electrons in the d orbitals of the Pd atoms back-donate to the empty π^* orbitals of the NO(a) molecules. A low N–O stretching frequency observed for terrace NO indicates strong back-donation to the π^* antibonding orbital, weakening the N–O bond and, therefore, enhancing the N–Pd bond strength.

Previous ESDIAD studies of NO adsorption on Pt(112)[9] indicate that NO preferentially chemisorbs on the *Pt step sites.* The current study of NO adsorption on Pd(112) shows an opposite trend: NO preferentially adsorbs on *Pd terrace sites* at low coverage. The difference in behavior of Pd(112) and Pt(112) with respect to NO site occupancy preference and binding energy calls for detailed theoretical considerations.

5. Conclusions

The adsorption of NO on a stepped Pd(112) surface is shown to preferentially involve the (111) terrace sites at low coverage. This conclusion is reached using both HREELS and ESDIAD measurements showing that low coverages of NO exhibit behavior characteristic of NO on Pd(111) sites. At high NO coverage, step sites (of (001) orientation) are also occupied, producing chemisorbed NO with its molecular axis oriented in the downstairs direction. These NO species exhibit HREELS behavior characteristic of adsorption on Pd(100) sites. This order of the NO site occupation sequence on Pd(112) is opposite to that on Pt(112), as well as to the behavior of other adsorbates on stepped transition metal surfaces.

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