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NO Dimer and Dinitrosyl Formation on Pd(111): From Ultra-High-Vacuum to Elevated Pressure Conditions

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Abstract: Using in situ polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) and conventional IRAS techniques, the adsorption of NO on Pd(111) was studied from ultra-high-vacuum (UHV) conditions to 400 mbar. New monomeric and non-monomeric high-coverage NO adsorption states were observed at 400 mbar. Initial NO adsorption at 600 K and subsequent cooling in the presence of 400 mbar NO lead to a new high-coverage monomeric adsorption state. For NO adsorption at room temperature, the formation of NO dimer as well as dinitrosyl states was observed, which upon heating transformed into the high-coverage monomeric adsorption state. In contrast, under UHV conditions, NO dimers were stable only at low temperatures up to 60 K, above which they transformed into a monomeric NO adsorption state with a (2×2)-3NO structure. Our results demonstrate that stable NO dimeric and dinitrosyl species can be formed on Pd(111) at elevated pressure conditions, emphasizing their potential role in catalysis.

Introduction

Due to its importance for the understanding of catalytic NO_x reduction originating from automobile exhaust emissions, NO adsorption on Pd single crystals has been studied extensively.[1−6] However, these studies were restricted to the coverage-dependent NO adsorption states formed under ultra-high-vacuum (UHV) conditions listed in Table 1. In a previous communication we have shown that high-pressure conditions, i.e., the presence of 400 mbar of NO, give rise to significant changes in the polarization modulation infrared reflection absorption (PM-IRA) spectra, which have been related to the formation of a new high-coverage phase. For this high-coverage phase, a (3×3)-7NO structure was proposed.[7] Recently, Vang et al. have studied the adsorption of NO on Pd(111) at elevated pressures using scanning tunneling microscopy (STM).[8] Even at high NO pressures up to 720 Torr, the (2×2)-3NO structure was observed. As will be discussed in detail in the following, the initial adsorption temperature strongly influences the resulting NO structure and therefore has to be taken into account. Moreover, in the present article we extend our infrared studies on the adsorption of NO on Pd(111), demonstrating the presence of non-monomeric NO adsorption states under both UHV and elevated pressure conditions.

Table 1. Adsorption Site Assignment and Vibrational Frequencies for Monomeric NO Adsorption States on Pd(111)

Θ (ML)	structure	Pd(111)[33]	ν_{NO} (cm^{-1})	refs
0−0.50	disordered	f + h	1525−1620	1, 4
0.50	c(4×2)-2NO	f + h	1620	1, 2, 4, 5
0.625	c(8×2)-5NO	tlt + f + h	1744, 1736, 1605, 1585	1, 2
0.75	p(2×2)-3NO	tlt + f + h	1758, 1548	1, 2, 4, 5
0.778	(3×3)-7NO	tlt + f + h	1766, 1543	6, this work

Previously, the formation of weakly bound NO dimeric species under UHV conditions was observed using high-resolution electron energy loss spectroscopy (HREELS) after saturation of the Pd(111) surface with NO at lower temperatures such as 20 K.[4] The formation of dimeric NO adsorption states deserves special attention, as it has been demonstrated in the literature that on Ag(111) N_2O formation takes place via a NO dimeric intermediate at low temperatures (∼80 K).[3] NO dimers have been observed on various surfaces, including Cu(100),[9] Cu(110),[10] Cu(111),[11] Ag(111),[12,13] Al_2O_{31},[14] MgO,[15] and

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graphite.[16,17] Recently, NO dimeric species could be observed directly on Ag(111) using STM.[18]

To study the surface properties and function of model systems at elevated pressure, a variety of in situ surface analysis tools have been developed and employed, such as STM,[19−21] sum-frequency generation (SFG),[22] inelastic neutron scattering vibrational spectroscopy (INS),[23] and PM-IRAS.[24] Only very recently has the use of PM-IRAS for in situ studies of adsorption phenomena and surface reactions at gas/solid interfaces at elevated pressures been fully explored.[24−28] Its surface sensitivity relies on the fact that IR absorption by an adsorbate on a metal surface shows a strong dependence on the polarization of the incoming IR beam, while gas-phase species are isotropic with respect to the polarization.

This paper is organized as follows: The first part covers the adsorption of NO at low (10^{-6} mbar), intermediate (13.3 mbar), and elevated (400 mbar) pressures leading to monomeric NO adsorption states. In the second part, the formation of NO dimers under UHV conditions at low temperature (25 K) is discussed. The third part describes the formation of dimeric and dinitrosyl adsorption states of NO on Pd(111) at elevated pressures (400 mbar). As will be shown below, the latter states are accessible only at elevated pressure conditions.

Experimental Section

The high-pressure PM-IRAS experiments were performed in a reactor cell attached to a surface analysis chamber equipped with Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD). Details regarding the experimental setup and sample preparation are described elsewhere.[27] The NO gas (C.P. grade) used in the experiments was further purified using a liquid nitrogen/*n*-pentane slurry that was maintained at 143 K during the course of the experiments. To avoid any photoinduced NO_2 formation, both the cleaning procedures and the experiments were conducted with the exclusion of visible light. PM-IRAS data were acquired using a Bruker Equinox 55 IR spectrometer (resolution: 4 cm^{-1}; sampling time: 8 min/spectrum). The experiments were performed with the photoelastic modulator (PEM) set for polarization modulation at 1700 cm^{-1}. The IRAS data were obtained on a Mattson Cygnus 100 spectrometer (resolution: 4 cm^{-1}; sampling time: 4.5 min/spectrum). Details about the instrumentation and data acquisition are described elsewhere.[29,30] The sample was mounted on a modified heating and cooling stage attached to a continuous-flow liquid helium cryostat. The sample could be cooled to 20 K and heated to 1100 K. The temperature was measured using a K-type thermocouple that was calibrated below 80 K using a thermocouple reference junction at liquid nitrogen temperature (77 K). The calibrated temperature was compared to the desorption temperature of multilayer CO (30 K).[31,32]

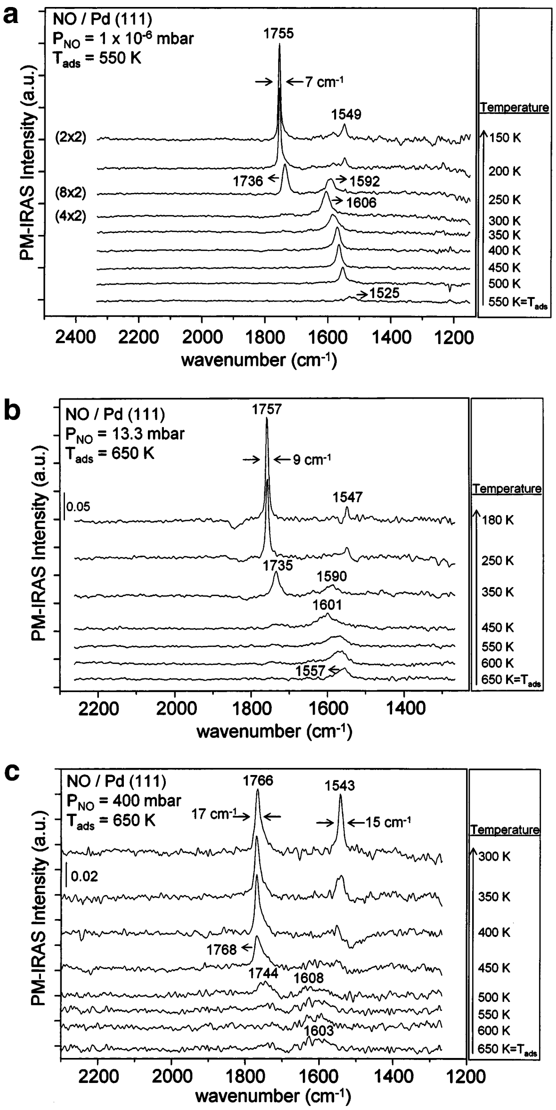

Figure 1. In situ PM-IRAS data for NO adsorption on Pd(111) in the presence of (a) 10^{-6}, (b) 13.3, and (c) 400 mbar NO. Initial adsorption was at (a) 550 and (b,c) 650 K. Spectra are offset for clarity.

Results and Discussion

Figure 1a depicts a series of in situ PM-IRA spectra as a function of sample temperature in the presence of 1×10^{-6} mbar NO. After exposure of the Pd(111) surface to NO at 550 K, the surface temperature was decreased to the given temperatures, thereby increasing the NO coverage. The data show a single vibrational band at $\sim$1525 cm^{-1}, which upon cooling exhibits a continuous blue shift to 1606 cm^{-1}. At 250 K, two bands are observed at 1592 and 1736 cm^{-1}, which shift to their final positions at 1549 and 1755 cm^{-1} upon cooling to 150 K. This behavior is in good agreement with that observed in previous IRAS/LEED studies at low pressures and can be readily explained in the light of the previous IRAS/LEED as well as

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recent STM and DFT results (see also Table 1).[1,2,33] According to these studies, no well-ordered NO states are formed at low coverages.[34] However, at a NO coverage of $\theta_{NO} = 0.5$ ML, a LEED pattern corresponding to a c(4×2)-2NO structure and an infrared band at 1620 cm^{-1} are obtained. The latter can be assigned to N−O stretching of NO molecules residing on three-fold hollow sites. As the NO coverage is increased, a red shift in the NO band to 1615 cm^{-1} and the appearance of a new high-frequency band around 1734 cm^{-1} are observed. The latter can be attributed to NO bound to atop sites. At a NO coverage of $\theta_{NO} = 0.625$ ML, a LEED pattern suggesting a c(8×2)-5NO phase is obtained. The NO bands around 1740 cm^{-1} correspond to NO species at atop adsorption sites, whereas the low-frequency bands at ∼1586 and 1605 cm^{-1} correspond to adsorption on three-fold hollow sites. As the previous STM studies suggested that the c(8×2)-5NO phase always coexists with the c(4×2)-2NO and p(2×2)-3NO,[1] the IRA spectrum for the (8×2) phase should indeed be a convolution of these three separate domains. At a coverage of $\theta_{NO} = 0.75$ ML, a p(2×2)-3NO overlayer structure is formed, as confirmed by LEED.[2] Two NO adsorption bands were found at 1548 and 1758 cm^{-1}, which result from three-fold hollow and atop site adsorption, respectively. Interestingly, the experimental IR intensity ratio (see Figure 1a) of the NO species corresponding to atop and three-fold hollow sites is ∼4, whereas assuming comparable IR cross sections for atop and hollow sites, the p(2×2)-3NO unit cell structure implies a relative intensity of only 0.5. This suggests that the IRAS cross sections for these two states are considerably different. A similar effect has been reported in a recent DFT study on CO/Pd(111),[35] where it was shown that the IR cross sections for CO molecules on atop and hollow sites may vary by a factor of 4 as a function of the coverage-dependent overlayer structure.

The spectral series shown in Figure 1b was obtained using a preparation method similar to that described above, i.e., by initially introducing the NO gas on the Pd(111) surface at a high temperature (650 K) until an equilibrium NO pressure of 13.3 mbar was maintained inside the high-pressure cell. Next, the sample temperature was gradually decreased, leading to the in situ PM-IRAS data at the lower temperatures given in Figure 1b. At 650 K, NO adsorption gives rise to an N−O stretching feature at 1557 cm^{-1}, indicating adsorption on three-fold hollow sites. At 10^{-6} mbar, a comparable coverage, as indicated by the presence of the band at 1555 cm^{-1} (see Figure 1a), is obtained, yet at a significantly lower temperature (500 K). On the other hand, comparison of parts a and b of Figure 1 clearly indicates that the temperature-dependent adsorption behavior of the NO overlayers on Pd(111) is similar at 1×10^{-6} mbar and 13.3 mbar. The vibrational features suggest the presence of the same set of ordered structures at comparable NO coverages. Thus, there is no indication for a pressure-induced new species or any adsorbate-related reconstruction within this pressure and temperature regime.

Interestingly, experiments performed in the presence of 400 mbar NO reveal a strikingly different NO adsorption behavior. Although a behavior similar to that at lower pressures is also observed at temperatures within the range 650−400 K (see Figure 1c), at higher NO coverages the hollow site band at 1543 cm^{-1} strongly increases in intensity. This intensity growth is indicative of the formation of a new high-coverage NO adsorption state on Pd(111), which has not been observed at lower pressures (see below). Formation of such a high-pressure/high-coverage state was suggested for NO/Rh(111) at 300 K on the basis of in situ STM images showing the evolution of a (3×3)-7NO state at $P_{NO} \geq 0.03$ Torr.[19] As discussed in a previous communication, several high-coverage structures were tested in the DFT calculations, and the most stable one is the (3×3)-7NO structure.[7] The (3×3)-7NO structure presents a slightly lower adsorption energy per NO molecule than the p(2×2)-3NO structure (−1.67 vs −1.76 eV). The vibrational mode analysis of the (3×3)-7NO state yields two strong IR bands at $\nu_1 = 1773$ cm^{-1} (with a normal mode mainly due to atop site NO molecules) and $\nu_2 = 1642$ cm^{-1} (mainly due to in-phase NO stretches of all the hollow sites). Whereas the calculated high-frequency mode (1773 cm^{-1}) is in good agreement with the peak observed at 1766 cm^{-1}, the calculated low-frequency mode (1642 cm^{-1}) allows a less satisfactory assignment with the experimental value (1543 cm^{-1}). However, comparison of the relative integrated IR peak areas for the (3×3)-7NO structure, $(A\nu_1/A\nu_2)_{(3\times3)-7NO}$, indicates a very good correlation between the experimental (1.4) and theoretical (1.6) results. Although the $A\nu_{1,2}$ values for the same unit cell cannot be directly correlated to the populations associated with various adsorption sites in the same unit cell, a comparison of the $(A\nu_1/A\nu_2)$ ratios for different unit cells can be utilized to check the relative populations in different unit cells. We note that, in the ratio $\{(A\nu_1/A\nu_2)_{(2\times2)-3NO}\}/\{(A\nu_1/A\nu_2)_{(3\times3)-7NO}\}$, contributions from different IR cross sections of NO molecules at different adsorption sites tend to cancel each other to effectively yield the ratio:

$$\approx \{(N_{atop}/N_{hollow})_{(2\times2)-3NO}\}/\{(N_{atop}/N_{hollow})_{(3\times3)-7NO}\}$$

where $N_{atop,hollow}$ is the number of NO molecules on atop or hollow adsorption sites. From a purely geometrical point of view, $(N_{atop}/N_{hollow})_{(2\times2)-3NO} = 1/2$ and $(N_{atop}/N_{hollow})_{(3\times3)-7NO} = 1/6$, yielding a relative ratio of $\{(N_{atop}/N_{hollow})_{(2\times2)-3NO}\}/\{(N_{atop}/N_{hollow})_{(3\times3)-7NO}\} = 3$. This ratio is in perfect correlation with the corresponding ratios for the experimental (2.9) and theoretical (3.3) results, which supports the validity of the proposed structure for the novel high-coverage monomeric NO adsorption state on Pd(111).

To check for the existence of highly dense NO adsorption states under UHV conditions, low-temperature IRAS experiments were performed. Figure 2 shows a series of IRA spectra as a function of NO exposure on Pd(111) at 25 K. After an NO exposure of 0.1 L (1 L = 1×10^{-6} Torr s^{-1}), two broad features at 1558 and 1730 cm^{-1} are observed, which upon further exposure (0.5 L) shift to 1593 and 1742 cm^{-1}, respectively. At a NO exposure of 0.5 L, a new band is visible at 1860 cm^{-1}, and a second feature appears at 1778 cm^{-1}. The 1860 cm^{-1} band shifts to 1863 cm^{-1} at NO exposures greater than 1 L. The vibrational bands at 1593 and 1742 cm^{-1} can be assigned to monomeric NO adsorption on three-fold hollow and atop sites, respectively, where the NO coverage is between 0.625 and 0.50 ML (Table 1). The features at 1778 and 1863 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of weakly bound NO dimers, $(NO)_2$, respectively.

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(33) f, fcc (three-fold hollow) sites; h, hcp (three-fold hollow) sites; tlt, tilted atop sites.
(34) The overlayer structure formed at $\theta_{NO} = 0.33$ ML lacks long-range order.
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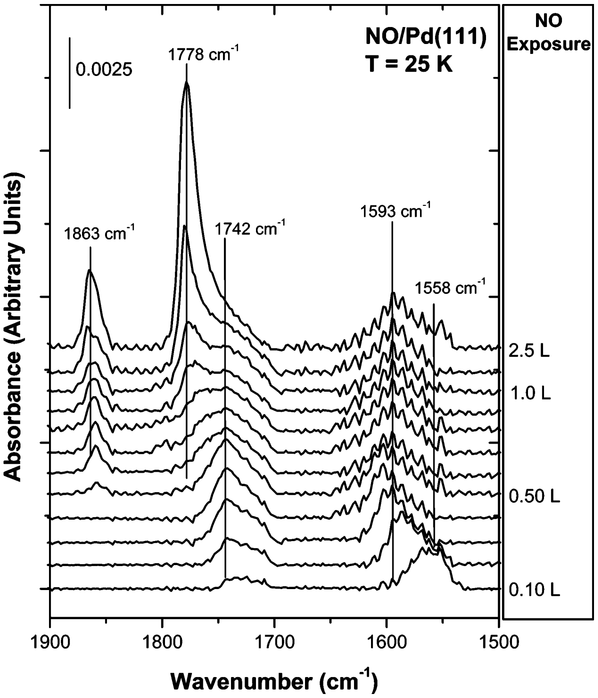

Figure 2. IRAS of NO adsorbed on Pd(111) at the given NO exposures. The initial NO dosing and all data acquisition were performed at 25 K. Spectra are offset for clarity.

The above assignment is consistent with gas-phase NO dimers showing very similar symmetric and asymmetric stretching frequencies of 1788 and 1860 cm^{-1}, respectively,[36] as well as with solid and matrix-isolated $(NO)_2$ showing IR frequencies in the ranges 1768−1776 and 1862−1870 cm^{-1}, respectively.[37−39]

As shown in Figure 2, the onset of NO dimer formation is observed at a surface coverage of about 0.625 ML. With increasing NO exposure, there is a strong intensity increase of the dimer-related bands but no phase transition to a (2× 2)-3NO monomeric state observed at $\theta_{NO} = 0.75$ ML at different temperature and pressure conditions (Figure 1). This observation is most likely due to the kinetic limitation of the surface ordering in the adsorbate overlayer; a commonly observed surface phenomenon, particularly at low temperatures.[40] Thus, the results shown in Figure 2 indicate that, at 25 K, NO multilayer domains start to grow well before the completion of a full monolayer on the Pd(111) surface. The current IRAS results, yielding clearly resolved symmetric and asymmetric stretching modes of the NO dimers under UHV conditions, also allow a detailed discussion of orientational changes of the NO dimer on the Pd(111) model catalyst surface. In previous experiments, owing to the lower resolution of HREELS, the symmetric stretching feature of the NO dimer species at ∼1860 cm^{-1} could be only poorly resolved.[4]

Different isomers of NO dimers, including *cis*-ONNO, *trans*-ONNO, *cis*-ONON, and *trans*-ONON, have been previously identified in the literature, and it is generally accepted that the *cis*-ONNO isomer, with a planar configuration, is the most stable isomer.[41] The *cis*-ONNO isomer can assume different adsorption geometries, as shown in Figure 3. Based on the symmetry arguments, *only* the *end-on* structure should lead to *both* symmetric and asymmetric stretch vibrations, while the other geometries should give rise to only *a single symmetric stretching* band.[42] As can be seen in Figure 2, at intermediate exposures (i.e., 0.5 L), the intensity of the symmetric band is greater than that of the asymmetric band, implying that, at the early stages of the multilayer growth, NO dimers can assume any of the possible orientations given in Figure 3 or their combinations. At higher exposures, such as 2.5 L, a significant increase in the asymmetric stretch signal (1778 cm^{-1}) is observed in Figure 2. This indicates an increased preference for the *end-on geometry*; however, the extremely broad and convoluted nitrosyl band between 1700 and 1780 cm^{-1}, as well as the simultaneous increase in the symmetric dimer stretch at 1863 cm^{-1}, still suggests a significant contribution from other adsorption configurations, namely *upright*, *lying down*, and *tilted geometries*.

Figure 4 shows a series of IRAS results acquired after introducing a multilayer dose of NO to the Pd(111) surface at 25 K and subsequently increasing the temperature to the indicated values. At 25 K, three prominent vibrational bands are observed at 1590, 1777, and 1864 cm^{-1}. As discussed above, they are assigned to monomeric NO adsorption on three-fold hollow sites and the asymmetric and symmetric stretching vibrations of $(NO)_2$, respectively. As the surface temperature is increased above 25 K, a significant enhancement of the asymmetric stretching feature at 1788 cm^{-1} is observed, which reaches its maximum intensity at ∼55 K. As the asymmetric stretching feature can originate only from the *end-on geometry*, it can be concluded that the temperature increase induces the NO dimers to line up mostly in the *end-on geometry*, i.e., with the N−N bond aligned perpendicular to the surface. The intensity increase of the *end-on* asymmetric stretch is not accompanied by any pronounced increase in the intensity of the symmetric stretch feature at 1860 cm^{-1}. This behavior can be explained by the surface selection rule of IRAS, which states that only those vibrations with dipole moments perpendicular to the surface are detected. As the overall dipole moment of the symmetric stretch vibration of the *end-on* species is parallel to the Pd(111) surface, this mode is not active.

Consistent with the data given in Figure 2, IRAS data shown in Figure 4 also reveal that, at 25 K, NO dimers can assume all possible geometries. This interpretation of randomly oriented NO dimers, which rearrange into a more ordered layer upon annealing, is supported by the fact that, besides the change in frequency, the full width at half-maximum of the asymmetric stretching band also significantly decreases upon heating to 55 K, suggesting an ordering of the NO multilayer with thermal activation. In contrast, changes of the symmetric stretching band are negligible. This behavior is in agreement with results from matrix isolation experiments, which have shown that the asymmetric stretching mode is more vulnerable toward perturbations resulting from changes in the dimer environment than is the symmetric mode.[39] Also, the intensity ratio of the symmetric and asymmetric bands at 25 K is very close to that

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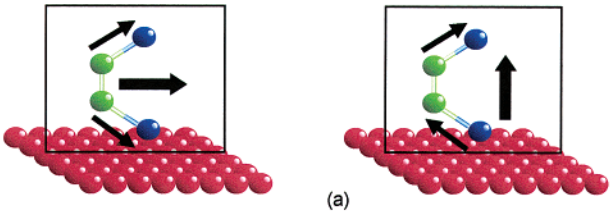
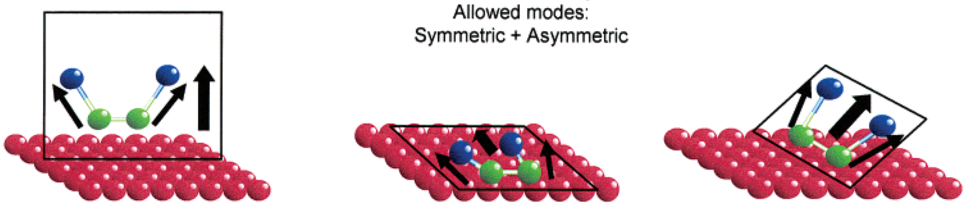


(a)

End-on Geometry:
Allowed modes:
Symmetric + Asymmetric



(b)

Upright Geometry:
Allowed modes:
Only Symmetric

(c)

Lying Down Geometry:
Allowed modes:
Only Symmetric

(d)

Tilted Geometry:
Allowed modes:
Only Symmetric

Figure 3. Possible bonding orientations of the NO dimer on the surface.

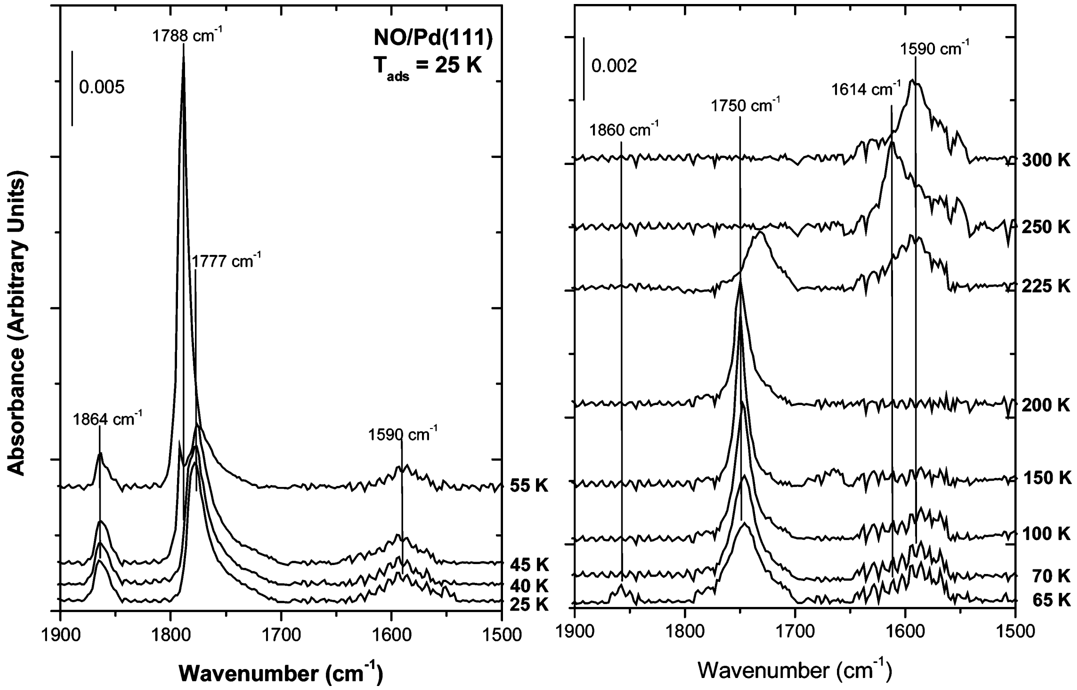


Figure 4. IRAS data for NO adsorption on Pd(111) at the given temperatures. Initial adsorption was at 25 K. Spectra are offset for clarity.

of gas-phase and solid $(NO)_2$, supporting our interpretation that initially the NO dimers adopt a random orientation within the multilayer.[43]

The low-temperature IRAS data also provide insight into the nature and the strength of the N−N dimer bond and the Pd−dimer interaction, respectively. The vibrational bands associated with the NO dimer states almost completely disappear between 65 and 70 K (see Figure 4), implying a weak dimer−surface interaction. Interestingly, at 65 K, a new vibrational band appears at 1750 cm^{-1}, which exhibits a significant red shift (-28 cm^{-1}) from the asymmetric stretch of the dimer and can be assigned to monomeric NO on atop sites. This is indicative of a strong N−N interaction within the dimers, as the scission of the intramolecular N−N linkage and the dissociation of the dimers into monomers has a pronounced influence on the NO stretch frequency. In fact, theoretical studies on NO dimer formation on Ni have shown that the N−N bond in $Ni_2(NO)_2$ is significantly stabilized compared to that of the gas-phase dimer.[44]

The low-temperature IRAS results do not give an indication for the formation of a (3×3)-7NO-like monomeric NO adsorption state. This clearly demonstrates that there are differences in the NO adsorption behavior under UHV and high-pressure conditions. Within the temperature range 65−70 K (Figure 4), a disordered phase containing a small number of dimers besides monomeric NO is observed. Within 100−150 K, the formation of a (2×2)-3NO-like state (θ_{NO} = 0.75 ML) is evident.

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[43] The integrated intensity ratio I_{as}/I_s is 3.6, which is close to the value (2.8) obtained for matrix-isolated $(NO)_2$ (ref 38).

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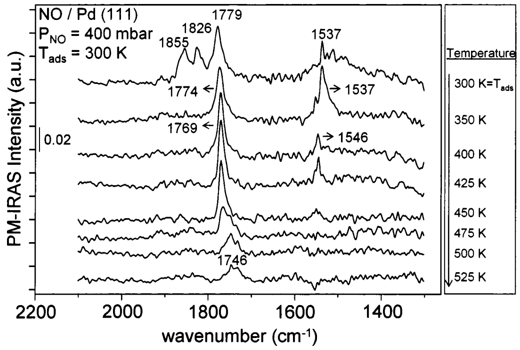

Figure 5. In situ PM-IRAS data for NO adsorption on Pd(111) in the presence of 400 mbar NO. Initial adsorption was at 300 K. Spectra are offset for clarity.

Increasing the temperature (i.e., decreasing the NO coverage) leads to the formation of monomeric (8×2)-5NO ($\theta_{NO} = 0.625$ ML) and (4×2)-2NO ($\theta_{NO} = 0.50$ ML) adsorption states at 225 and 250 K, respectively.

Figure 5 depicts PM-IRA spectra for NO adsorption on Pd(111) in the presence of 400 mbar NO. The initial introduction of the NO gas was at 300 K, and subsequently the catalyst surface was heated to the temperatures indicated in Figure 5. The spectrum at 300 K shows three distinct vibrational features at 1779, 1826, and 1855 cm^{-1}, as well as a broad band around 1500 cm^{-1}. The latter is assigned to NO adsorption on threefold hollow sites. Recently, NO bands with similar position and width have been observed on Pd(111) in the presence of a 240 mbar CO + NO mixture.[26] The bands at 1779 and 1855 cm^{-1} are attributed to the symmetric and asymmetric stretching vibrations of NO dimer species, respectively, in agreement with our[29] and previous[4] UHV results. The frequency values of the symmetric and asymmetric stretching vibrations are close to the values observed in the multilayer regime at 25 K (Figures 2 and 4). The intensity ratio of the stretching bands at 1779 and 1855 cm^{-1} suggests a mixture of NO dimer species with various dimer orientations, including *end-on*, *upright*, *lying down*, and *tilted* species. The additional band at 1826 cm^{-1} has not been observed previously on palladium. However, for NO adsorption on oxidized Mo(110), four vibrational bands at 1550, 1728, 1820, and 1871 cm^{-1} were observed.[45,46] The bands at 1550 and 1728/1871 cm^{-1} were attributed to monomeric NO and strongly perturbed dimer, respectively, whereas the band at 1820 cm^{-1} was assigned to a dinitrosyl species, i.e., a species where two NO molecules are bound to the same metal center, on the basis of isotope labeling studies.[47] Therefore, we attribute the band at 1826 cm^{-1} to the symmetric N=O stretch of a dinitrosyl (ON−Pd−NO) species.

Heating the surface to 350 K results in the disappearance of the dimer and dinitrosyl features and the formation of an ordered adsorption state with a (3×3)-7NO structure ($\theta_{NO} = 0.778$ ML), as evident from the position and relative intensity of the vibrational bands appearing at 1774 and 1537 cm^{-1}. A further increase in surface temperature to 400−450 K leads to the development of (2×2)-3NO-like monomeric adsorption states at ~0.75 ML. Eventually, when the temperature reaches 525 K, the NO coverage drops to a value between 0.75 ML < θ_{NO} < 0.625 ML, as apparent from the presence of the vibrational feature at 1746 cm^{-1}. These observations imply that the non-monomeric NO adsorption state observed at 300 K corresponds to a NO coverage that is higher than the coverage of any of the previously observed monomeric states, i.e., θ_{NO} > 0.778 ML.

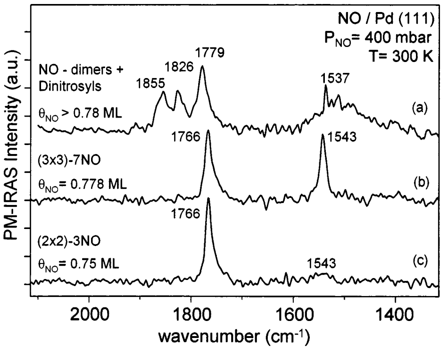

Figure 6. In situ PM-IRAS data for NO adsorption on Pd(111) at P_{NO} = 400 mbar and T = 300 K after various pretreatments. (a) Initial adsorption at 300 K; (b) initial adsorption at 650 K and subsequent cooling to 300 K; (c) initial adsorption at 650 K, cooling back to 300 K, second annealing at 600 K, cooling back to 300 K. All of the spectra were obtained in the presence of P_{NO} = 400 mbar. Spectra are offset for clarity.

Another important feature of the series of elevated pressure PM-IRAS data presented in Figure 5 is the effect of the N−N bond breaking and the transformation of the dimers into monomeric NO adsorption states. Figure 5 indicates that, under elevated pressure conditions, breaking of the N−N intramolecular bond in the dimer structure does not have a significant influence on the nitrosyl band at 1779 cm^{-1}. This observation implies that NO dimers, which exist on Pd(111) at elevated temperatures and pressures (Figure 5), contain a weaker N−N intramolecular bond than that of the NO dimers observed under UHV conditions (Figure 4). A comparison of Figures 4 and 5 reveals that the presence of a high-pressure NO gas phase significantly contributes to the stability of the dimeric states. Although the weakly bound NO dimer states desorb at a surface temperature of ~60−65 K under UHV conditions, in the presence of 400 mbar of NO, NO dimers survive on the Pd(111) surface up to temperatures as high as 300−350 K. These differences in the adsorption energy as well as the intramolecular N−N bond strength indicate that NO dimers can possess different structures at different temperature and pressure regimes. In a previous study on NO dimers on oxidized Mo(110), vibrational spectroscopic results, which are consistent with the series of spectra given in Figure 5, were reported where the weak influence of the intramolecular N−N bond breaking on the remaining nitrosyl stretch and the relatively high adsorption energy of the dimer were attributed to a perturbed NO dimer structure.[45]

Figure 6 shows the influence of pretreatment on the ultimate NO coverage that is accessible on Pd(111) at room temperature and at 400 mbar NO pressure. Spectrum a was recorded after dosing NO at 300 K. These conditions lead to the highest attainable coverage for the NO/Pd(111) adsorption system (θ_{NO} > 0.778 ML) within the pressure and temperature ranges studied. Spectrum b was obtained by initially dosing NO at 650 K and subsequently cooling the surface to 300 K in the presence of 400 mbar NO. This procedure results in the formation of a less dense adsorption overlayer, namely the (3×3)-7NO monomeric state at a NO coverage of 0.778 ML. This noticeable

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decrease in the ultimate obtainable coverage with temperature treatment is most likely due to site blocking, which may take place as a result of NO dissociation at the initially higher dosing temperature of 600 K. In previous TPD studies, it has been shown that dissociation of NO on Pd(111) can take place at temperatures as low as 450 K.[48] Further support for significant dissociation of NO on Pd(111) at elevated temperatures comes also from our work on the CO + NO reaction at elevated pressure.[25,26] It should be mentioned that, at 600 K and in the presence of $P_{NO} = 400$ mbar, the NO surface coverage is still high (0.33 ML $< \theta_{NO} < 0.50$ ML), as evident from the vibrational band at 1603 cm^{-1} (see Figure 1c). Therefore, NO dissociation can lead to the formation of significant amounts of atomic N and O species, which in turn may dictate the ultimate coverage which can be attained after cooling to 300 K. Spectrum c can be interpreted using arguments similar to those outlined above. This surface was prepared first by applying the protocol for the preparation of the surface given in spectrum b, followed by additional annealing to 600 K and subsequent cooling to 300 K. As shown in Figure 6, such a temperature treatment, consisting of successive heating and cooling cycles, results in a (2×2)-3NO-like state at 300 K with an NO surface coverage of only ~0.75 ML, although a constant high-pressure NO gas-phase pressure of 400 mbar was continuously maintained during the entire temperature treatment and data acquisition processes.

Conclusions

In summary, (2×2)-3NO ($\theta_{NO} = 0.75$ ML), (8×2)-5NO ($\theta_{NO} = 0.625$ ML), and (4×2)-2NO ($\theta_{NO} = 0.50$ ML) monomeric adsorption states can be prepared with different temperature pretreatments at any given pressure between 10^{-9} and 400 mbar. NO dimer states were also found under both UHV and elevated pressure (400 mbar) conditions. Whereas in UHV dimer formation requires low temperatures (<60 K), at elevated pressure NO dimers are stable at room temperature. Besides these species, dinitrosyls are formed at $\theta_{NO} > 0.778$ ML. At a slightly lower coverage ($\theta_{NO} = 0.778$ ML), a novel monomeric NO adsorption state is observed which is proposed to have (3×3)-7NO structure. Pretreatment in the presence of 400 mbar NO at 600 K significantly reduces the maximum accessible NO coverage, probably because of thermally activated NO dissociation.

Our results highlight the importance of high-pressure studies on well-defined model catalysts by demonstrating that the formation of NO adsorption states on Pd(111) under high-pressure conditions strongly depends on the initial adsorption temperature a well as surface pretreatment. At the maximum experimental NO coverage, strongly bound NO dimeric and dinitrosyl species were observed, clearly emphasizing their potential role for heterogeneous catalysis.

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