

Formation of a High Coverage (3×3) NO Phase on Pd(111) at Elevated Pressures: Interplay between Kinetic and Thermodynamic Accessibility

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Using in situ polarization modulation infrared reflection absorption spectroscopy and density functional theory calculations, a new high-coverage monomeric NO adsorption state on Pd(111) was observed and proposed to have a (3×3)-7NO structure. Formation of this high coverage NO phase was found to take place only at elevated pressure and temperature conditions showing that some of the accessible thermodynamic equilibrium states at elevated temperatures and pressures are thermodynamically unfavorable or kinetically hindered at lower temperatures and pressures. Our results emphasize the danger of extrapolating results from traditional surface science experiments performed under ultrahigh vacuum to elevated temperature and pressure conditions encountered in heterogeneous catalysis.

A great challenge of catalytic science is the design of model systems that mimic the essential features of their corresponding industrial counterparts while providing molecular-level definition and access to their surface properties and function at realistic reaction conditions. Many traditional surface analytical spectroscopic tools can not be used at elevated pressures (~ 1 bar) as they require ultrahigh vacuum (UHV) environments where the state and behavior of the model system of interest can be significantly different than its realistic counterpart. Catalytic activation by bond breaking, dissociative adsorption, recombinative desorption, and simple physisorption/chemisorption phenomena are some of the well-known examples where overcoming a high activation barrier could be crucial for removing kinetic hindrance. Therefore, this type of activated surface phenomena tends to occur at elevated temperatures and/or pressures which may fall outside of the UHV regime.

To overcome this challenge, new in situ surface analysis tools have been developed and employed such as scanning tunneling microscopy (STM),^{1–3} sum-frequency generation (SFG),⁴ inelastic neutron scattering vibrational spectroscopy (INS),⁵ and polarization modulation infrared reflection absorption spectroscopy (PM-IRAS).^{6–10} Only very recently, the use of PM-IRAS for in situ studies of adsorption phenomena and surface reactions at gas/solid interfaces at elevated pressures and temperatures has been fully explored.^{6–10} Its surface sensitivity relies on the fact that IR absorption by an adsorbed species on a metal surface

TABLE 1: Adsorption Site Assignments and Vibrational Frequencies for Monomeric NO Adsorption States on Pd (111) Surface

θ (ML)	structure	Pd (111)*	ν_{NO} (cm^{-1})	ref
0–0.50	disordered	f+h	1525–1620	11, 14
0.50	c(4×2)-2NO	f+h	1620	11, 12, 14, 17
0.625	c(8×2)-5NO	tlt+f+h	1744, 1736, 1605, 1586	11, 12
0.75	p(2×2)-3NO	tlt+f+h	1758, 1548	11, 12, 14, 17
0.778	(3×3)-7NO	tlt+f+h	1766, 1543	this work

*f: fcc (3-fold hollow) sites, h: hcp (3-fold hollow) sites, tlt: tilted atop sites.

shows a strong dependence on the polarization of the incoming IR beam, whereas gas-phase species are isotropic with respect to the polarization.

Due to its relevance to catalytic NO_x reduction originating from automobile exhaust emissions, NO adsorption on Pd single crystals have been studied extensively in the literature.^{11–15} These studies mostly focused on the coverage dependent ordered overlayers of NO that are formed under UHV conditions which are listed in Table 1. In these studies, the high coverage regime of the NO/Pd(111) phase diagram was simulated by lowering the surface temperature of the Pd single crystal under UHV conditions. Therefore, the saturation coverage for monomeric NO overlayers has been reported to be 0.75 monolayers (ML) with the p(2×2)-3NO structure.^{11–15} This previously suggested NO saturation coverage overlayer structure on Pd(111) presents striking similarities to that of CO where it has been shown that the highest CO coverage (θ_{CO}) that can be obtained within $10^{-9} < P_{\text{CO}} < 1$ bar and $90 < T < 650$ K is $\theta_{\text{CO}} = 0.75$ ML. At this coverage, CO has a p(2×2)-3CO structure^{9,16} indicating that

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all of the thermodynamically favorable CO/Pd(111) adsorption states that can be occupied at high temperatures and pressures are also kinetically available at low temperatures and pressures.

In the present letter, we report the formation of a new high-coverage NO adsorption state on Pd(111) at elevated temperature and pressure conditions. Using in situ PM-IRAS and density functional theory (DFT) calculations, we suggest that this phase is an (3×3) -7NO adlayer with a NO coverage of $\theta_{\text{NO}} = 0.778$ ML and we show that it can not be accessed at lower temperatures and pressures.

Experiments were performed in a surface analysis chamber equipped with Auger electron spectroscopy (AES), low energy electron diffraction (LEED), temperature-programmed desorption (TPD), and PM-IRAS. Details regarding the experimental setup and sample preparation are described elsewhere.⁹ The NO gas used in the experiments was C.P. grade and was further purified using liquid nitrogen/*n*-pentane slurry that was maintained at 143 K during the course of the experiments. To avoid any photoinduced NO₂ formation, both the cleaning procedures and the experiments were conducted with the exclusion of visible light. PM-IRAS data were acquired⁹ using a Bruker Equinox 55 IR spectrometer with 4 cm⁻¹ resolution (sampling time: 8 min/spectrum).

Details of the DFT calculations and the relevant literature can be found in ref 17. The DFT calculations were performed using the Vienna Ab initio Simulation Program (VASP).¹⁸ The Perdew and Wang 91 generalized gradient approximation (GGA) exchange-correlation functional was used¹⁹ together with the projector-augmented-wave (PAW) method.²⁰ To ensure a tight electronic convergence, the plane-wave cutoff was set to 400 eV. The 2D Brillouin zone integrations have been performed on dense $9 \times 9 \times 1$ and $7 \times 7 \times 1$ grids for the (2×2) -3NO and (3×3) -7NO structures respectively for the adsorption energy calculations and on $5 \times 5 \times 1$ and $3 \times 3 \times 1$ grids respectively for the vibrational analysis. The numeric error due to the size of the basis set (<1.5 meV Å⁻² for the free energy and ~ 10 meV for the adsorption energy) has been estimated by increasing the cutoff up to 500 eV for the dense k-point meshes ($9 \times 9 \times 1$ and $7 \times 7 \times 1$).

The surface was modeled by a supercell consisting of four layers of Pd(111) where the NO molecules were adsorbed on one side of the slab. The systematic error due to the supercell approach (<2 meV Å⁻² for the free energy and ~ 20 meV for the adsorption energy) has been calculated by considering six-layer thick slabs. The vibrational analysis was performed at the harmonic level with the numerical calculation and diagonalization of the force constant matrix by considering all molecular NO degrees of freedom. The first derivatives of the dynamic dipole moment were calculated to estimate the infrared intensities for each normal mode of the adsorption structures.²¹

NO adsorption experiments were performed by introducing the NO gas into the analysis chamber until the desired NO pressure was reached while keeping the temperature of the Pd(111) crystal at 650 K (Figure 1). Subsequently, the temperature of the Pd(111) surface was lowered to control the NO coverage. This procedure was found to be crucial for achieving highly dense and ordered overlayer states.^{9,12,22} PM-IRAS data for NO adsorption at 13.3 mbar is shown in Figure 1a. There is an excellent correlation between Figure 1a and that of similar experiments performed at 1×10^{-6} mbar (not shown) and the previous UHV results.¹² Within 650–450 K where the NO coverage is relatively low ($\theta_{\text{NO}} < 0.5$ ML), NO molecules occupy 3-fold hollow sites²³ and lead to a single major vibrational band around 1557–1601 cm⁻¹ which shows a blue

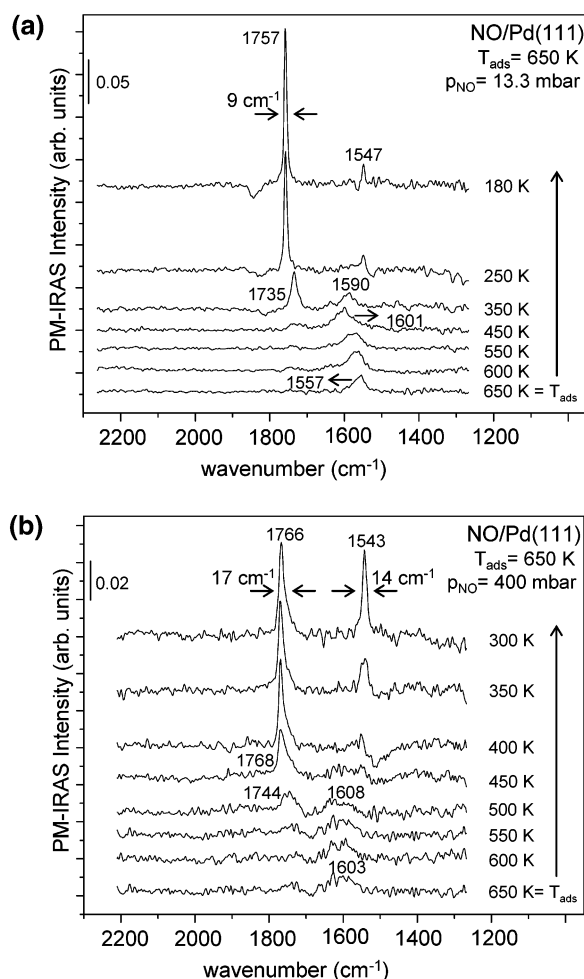


Figure 1. In situ PM-IRAS data for (a) 13.3 mbar and (b) 400 mbar NO adsorption on Pd(111). Spectra were obtained in the presence of NO gas phase. Initial adsorption was at 650 K.

shift with increasing coverage. At 350 K, the NO coverage approaches $\theta_{\text{NO}} = 0.625$ ML where the $c(8 \times 2)$ -5NO structure coexists with $p(2 \times 2)$ -3NO and $c(4 \times 2)$ -2NO domains.^{6,11} This results in complex and broad vibrational features around ~ 1735 and ~ 1590 cm⁻¹ associated with NO molecules residing on atop and 3-fold hollow sites (see Table 1). With increasing coverage, a typical $p(2 \times 2)$ -3NO ordered structure is obtained at 180 K as is evident from the appearance of the sharp (fwhm = 9 cm⁻¹) vibrational features at 1757 and 1547 cm⁻¹, respectively. DFT calculations performed for an optimized $p(2 \times 2)$ -3NO/Pd(111) structure strongly support these observations (Figure 2a). Vibrational mode analysis reveals two strong IR active bands at $\nu_1 = 1770$ cm⁻¹ (with an eigenmode predominantly involving the atop site NO molecules) and $\nu_2 = 1570$ cm⁻¹ (mostly due to an in phase component of the hollow site NO stretches) and an inactive mode at 1520 cm⁻¹ (below experimental resolution), associated with out of phase stretches of the two hollow site NO molecules. Furthermore, there is a quantitative agreement between the DFT calculations and the experimental results in terms of the relative integrated IR peak areas of the two active bands, $(A\nu_1/A\nu_2)_{(2 \times 2)\text{-3NO}}$, which were determined to be 5.3 and 4.1, respectively. It should be noted that, in contrast with usual approximations, the absolute IR intensities do not represent the relative concentrations of NO molecules at different adsorption sites for a given unit cell, as the $p(2 \times 2)$ -3NO unit cell structure contains one atop site NO molecule for every two hollow site NO molecule (Figure 2a). Indeed the normal vibrational modes are coupled and the

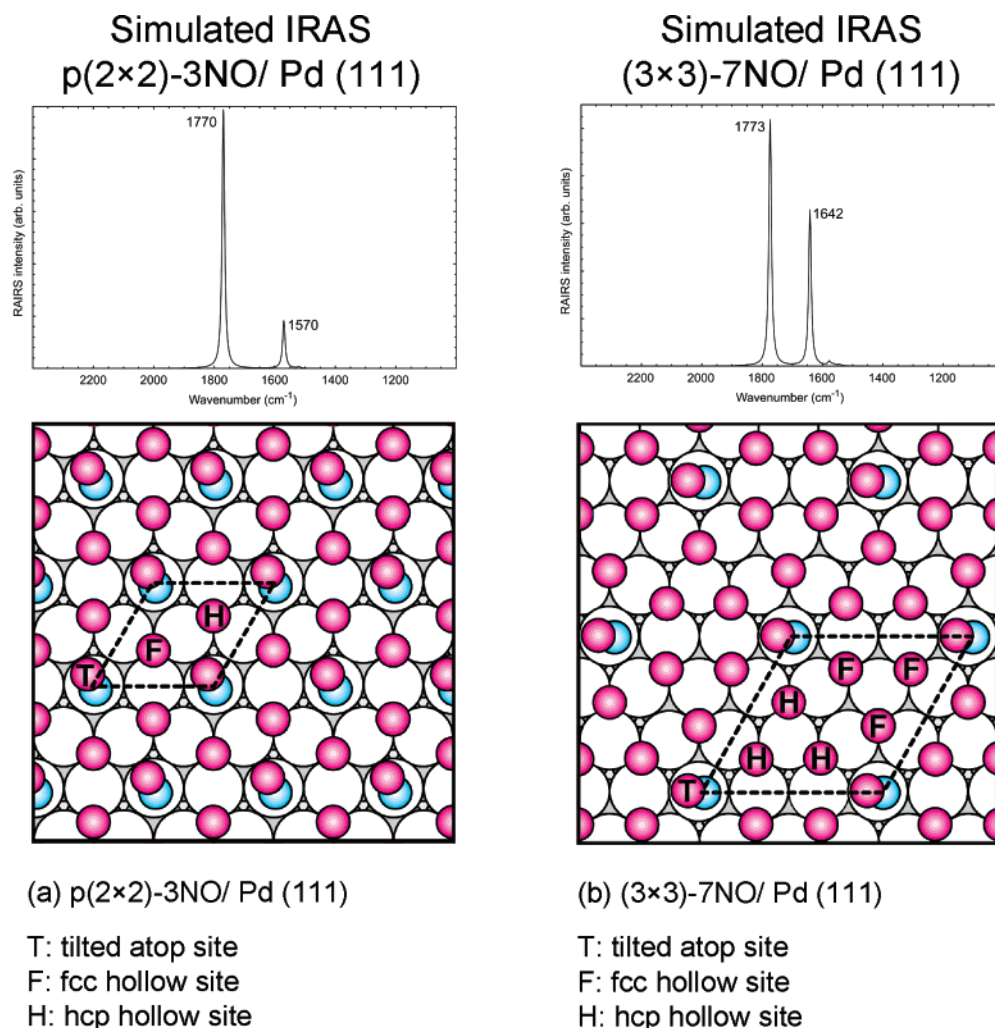


Figure 2. Results of the density functional theory calculations illustrating the calculated IR vibrational spectra and optimized adsorption overlayer structures for (a) p(2 × 2)-3NO and (b) (3 × 3)-7NO phases on Pd(111).

dynamic dipole moment for the NO stretch is strongly site dependent, with a large increase for the atop site.

Interestingly, adsorption experiments performed at 400 mbar reveal a strikingly different NO adsorption behavior. Although similar trends, as seen in Figure 1a leading to a p(2 × 2)-3NO-like state, are also observed within 650–400 K (Figure 1b), as the NO coverage is further increased, an unexpected growth of the hollow site band at 1543 cm⁻¹ becomes clearly visible. Appearance of the 1543 cm⁻¹ feature indicates the formation of a new high coverage NO adsorption state which has not been observed at lower pressures on Pd(111).²⁴ Formation of such a high-pressure/high-coverage state was suggested for NO/Rh(111) at 300 K¹ based on in situ STM images showing the evolution of a (3 × 3)-7NO state at $P_{\text{NO}} \geq 0.03$ Torr as well as in CO+NO reaction on Rh(111) at 300 K ($P_{\text{CO}} = 0.1$ Torr and $P_{\text{NO}} = 0.32$ Torr).²⁵ Several high coverage structures were tested in the DFT calculations and the most stable one is the (3 × 3)-7NO structure shown in Figure 2b and Table 2. This competitive locally stable structure presents a slightly lower adsorption energy per NO molecule than the p(2 × 2)-3NO case (−1.67 vs −1.76 eV). This can be rationalized by considering the similarity between the types of adsorption sites present in both of the unit cells and the small coverage difference between the two adsorption states (0.78 ML vs 0.75 ML). The decrease in NO chemisorption energy due to substrate mediated repulsive interactions¹¹ between the NO molecules on Pd(111) should hence be relatively insignificant. Analogous arguments can also

TABLE 2: Calculated Mean Chemisorption Energies, Surface Free Energies Per Unit Area, Bond Distances, and Bond Angles for p(2 × 2)-3NO vs (3 × 3)-7NO Overlayers on Pd (111)

	p(2 × 2)-3NO	(3 × 3)-7NO
θ_{NO} (ML)	0.75	0.778
$\langle E_{\text{ads}} \rangle$ (eV/NO molecule)	−1.76	−1.67
γ (meV/Å ²)	−195	−192
$d_{\text{N-O}}$ (Å) – atop site	1.17	1.17
$d_{\text{N-O}}$ (Å) – fcc site	1.21	1.20
$d_{\text{N-O}}$ (Å) – hcp site	1.20	1.20
$d_{\text{Pd-N}}$ (Å) – atop site	1.94	1.94
$d_{\text{Pd-N}}$ (Å) – fcc site	2.08	2.07–2.11
$d_{\text{Pd-N}}$ (Å) – hcp site	2.08–2.10	2.07–2.16
$\alpha_{\text{Pd-N-O}}$ (°) – atop site	129	131

be used to account for the similarities between the two unit cells in terms of bond distances and bond angles (Table 2). However, the free adsorption energy shows only a slight difference between the two structures (−195 meV Å⁻² for (2 × 2) and −192 meV Å⁻² for (3 × 3)) in favor of the (2 × 2) phase. Nevertheless, this small energy difference cannot be fully conclusive due to the systematic errors of the model and of the computational approach. 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 developed on the atop site NO molecules) and $\nu_2 = 1642$ cm⁻¹ (mainly due to in phase NO stretches of all the hollow sites) with five additional nonactive modes at 1578, 1572, 1563, 1546, and 1536 cm⁻¹.

The agreement between PM-IRAS and DFT is partial for the frequency values. The calculated high-frequency mode (1773 cm^{-1}) fully agrees with the peak observed at 1766 cm^{-1} (cf. Figure 1b) whereas the calculated low-frequency mode (1642 cm^{-1}) allows a less satisfactory assignment with the measured value (1543 cm^{-1}). However, the comparison of the relative integrated IR peak areas for the (3×3) -7NO structure or $(Av_1/Av_2)_{(3 \times 3)-7\text{NO}}$, suggests a very good correlation between the experimental (1.4) and theoretical (1.6) results. Although the $Av_{1,2}$ values for the same unit cell can not be directly correlated to the populations associated with various adsorption sites in the same unit cell, a comparison of the (Av_1/Av_2) ratios for different unit cells can be utilized to check the relative populations in different unit cells. We note that in the ratio $\{(Av_1/Av_2)_{(2 \times 2)-3\text{NO}}\}/\{(Av_1/Av_2)_{(3 \times 3)-7\text{NO}}\}$, contributions coming from different IR cross sections of the NO molecules at different adsorption sites tend to cancel each other to effectively yield the ratio

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

where $N_{\text{atop,hollow}}$ is the number of NO molecules on atop or hollow adsorption sites. From a purely geometrical point of view based on the unit cell structures given in Figure 2, $(N_{\text{atop}}/N_{\text{hollow}})_{(2 \times 2)-3\text{NO}} = 1/2$ and $(N_{\text{atop}}/N_{\text{hollow}})_{(3 \times 3)-7\text{NO}} = 1/6$, yielding a relative ratio of $\{(N_{\text{atop}}/N_{\text{hollow}})_{(2 \times 2)-3\text{NO}}\}/\{(N_{\text{atop}}/N_{\text{hollow}})_{(3 \times 3)-7\text{NO}}\} = 3$. This ratio is in perfect correlation with the corresponding ratios for the experimental (2.9) and theoretical (3.3) results, supporting the validity of the proposed model for the novel high coverage monomeric NO adsorption state on Pd(111).²⁶

In summary, by using a combination of in situ vibrational spectroscopy at elevated pressures (PM-IRAS) and DFT calculations, we showed the formation of a new high coverage monomeric NO adsorption state that is only observed under elevated pressure conditions ($P_{\text{NO}} = 400\text{ mbar}$) and have proposed a (3×3) -7NO structure. Although the DFT results, with one frequency slightly shifted, are not fully conclusive in favor of the (3×3) -7NO model, this structure agrees best with the current level of theory. The lack of such a high coverage monomeric NO adsorption state at 25 K under UHV conditions indicates that formation of a (3×3) -7NO phase either requires a high activation barrier which can be overcome only under elevated temperature and pressure conditions or is thermodynamically less favorable. Our results demonstrate that simple extrapolations based on UHV experiments at low temperatures and pressures may be misleading for elucidating the nature of elevated-pressure/temperature systems encountered in heterogeneous catalysis as they are only accurate as long as the thermodynamical equilibrium states are also kinetically available in the relevant regions of the phase space.

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- (23) NO adsorption on Pd(111) takes place mostly in a molecular fashion with a minor contribution from dissociation events (refs 13 and 15) as is evident from the formation of extremely sharp NO vibrational bands showing nominal inhomogeneous broadening.
- (24) Although adsorption site assignments based solely on vibrational spectroscopic data has been criticized in the literature (see ref 13, for example), combination of previous vibrational spectroscopic data with recent atomic resolution STM and DFT results given in refs 11 and 12 and in this work provides unambiguous site assignments for the NO/Pd(111) adsorption system.
- (25) We have also performed NO adsorption experiments under UHV conditions at relatively lower temperatures (25 K) to mimic the effect of high pressure, however (3×3) -7NO monomeric adsorption state was not observed in these studies. Instead, formation of a multilayer NO state consisting of NO-dimers was detected which will be discussed in detail in a forthcoming publication.
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- (27) Possibility of an adsorbate induced surface reconstruction of the Pd(111) single-crystal surface at high NO pressures has also been considered in computational tests. None of the (3×3) structures on these reconstructed Pd surfaces was found to yield a surface energy lower than that of the ideal Pd(111) surface. Narrow experimental fwhm values for the atop and 3-fold/hollow bands (17 and 14 cm^{-1} , respectively) of our high-pressure vibrational data also indicate that such reconstructions are relatively unlikely to take place.