Molecular adsorption of NO on PdO(101)

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Abstract

We investigated the adsorption of NO on the PdO(101) surface using temperature programmed desorption (TPD), reflection absorption infrared spectroscopy (RAIRS) and density functional theory (DFT) calculations. From TPD, we find that NO reaches a saturation coverage of ~ 0.54 monolayer (ML) on PdO(101) at 90 K, and that desorption from the saturated layer produces a complex TPD trace with five pronounced maxima between 100 and 550 K. We observe negligible quantities of desorbing products other than NO during TPD, indicating that NO does not react on PdO(101) under the conditions studied. For low coverages, RAIR spectra reveal that NO adsorption at 90 K produces both flat-lying and atop configurations of NO on the coordinatively unsaturated (cus) Pd atoms of PdO(101), but that these configurations are meta-stable and transform to bridge-NO species at higher temperature. RAIRS measurements further show that NO binding on atop-Pd_{cus} sites becomes preferred with increasing coverage above $\sim 25\%$ of the Pd_{cus} density, and provide evidence of a weakly-bound state at coverages above 100% (0.35 ML). Consistent with our experimental findings, DFT predicts that NO preferentially adsorbs on bridge-Pd_{cus} sites at low coverage and that the site preference changes to atop-Pd_{cus} sites with increasing NO coverage, resulting in mixtures of atop-bridge NO configurations as well as an all-atop configuration. DFT also predicts that NO can adopt a flat-lying configuration on the Pd_{cus} row at low coverage, and can also achieve stable bonding on the fourfold Pd sites of PdO(101) at high NO coverages. Both the computational and experimental results show that NO binds on PdO(101) in multiple, local configurations even at low coverage.

Introduction

The surface chemistry of late transition metal oxides plays a central role in many applications of oxidation catalysis. Under sufficiently oxidizing conditions, metal oxide films can develop on metallic catalysts and typically cause significant changes in catalyst performance [1; 2]. Of particular relevance to the present study are applications of NO oxidation in NO_x storage reduction (NSR) systems that are employed for exhaust-gas remediation in lean-burn engines. NSR catalysts are multiple component materials that typically contain a precious metal that acts as both an oxidation and a reduction catalyst. The oxidation of NO by the metal catalyst is a key step in determining the overall performance of the NSR system and occurs under oxygen-rich reaction conditions [3-6]. Prior studies indeed show that Pt and Pd surfaces are covered with high concentrations of oxygen atoms under typical NSR operating conditions [6-9], and that such conditions can lead to the formation of metal-oxide layers. For example, *ab initio* thermodynamics calculations by Jelic et al. [10; 11] predict that single and multilayer PdO(101) structures are thermodynamically preferred on Pd(111) and Pd(100) surfaces and are active toward NO oxidation under catalytically-relevant conditions. These findings suggest that Pd oxide structures may be important in applications of NO oxidation and thereby provide substantial motivation for investigating the interactions of NO with PdO(101) surfaces in detail.

Prior investigations of NO adsorption on the RuO₂(110) surface may aid in developing general insights for understanding how NO interacts with surfaces of late transition-metal oxides. This work shows that NO can adsorb in multiple configurations and binding sites on RuO₂(110) [12-14]. Both experiments and computations indicate that NO preferentially binds in an atop-configuration on the coordinatively unsaturated (cus) Ru sites of RuO₂(110). Experimental measurements show that the atop-NO species reorient beyond a critical NO coverage, with a concomitant reduction in the NO binding energy [12].

Continued adsorption to NO coverages above the Ru_{cus} site density results in the binding of NO molecules to the bridging O-atoms, resulting in $\text{O}_{\text{br}}\text{-NO}$ moieties [12; 14]. Lastly, TPD experiments provide evidence that NO reacts on $\text{RuO}_2(110)$ at high coverage to generate N_2 and N_2O . Indeed, these prior studies show that the adsorption of NO on $\text{RuO}_2(110)$ surfaces can produce rich behavior, involving binding on multiple sites as well as reaction.

In the present study, we investigated the adsorption of NO on $\text{PdO}(101)$ using DFT calculations as well as TPD and RAIRS experiments. We find that NO adsorbs in multiple configurations on the $\text{PdO}(101)$ surface, including different binding sites and molecular orientations. In general, our results show that NO preferentially adsorbs on bridge- Pd_{cus} sites at low coverage, with binding on atop- Pd_{cus} sites becoming favored as the NO coverage increases.

Experimental details

The experiments reported in this study were conducted in an ultrahigh vacuum (UHV) chamber with a typical base pressure below 1×10^{-10} Torr. The UHV chamber is equipped with a four-grid retarding field analyzer for low energy electron diffraction (LEED) and Auger electron spectroscopy (AES), an ion source for Ar^+ sputtering, a quadrupole mass spectrometer (QMS) used for TPD experiments and a Fourier transform infrared spectroscopy (FTIR) system for RAIRS measurements. A single-stage differentially pumped chamber is also attached to the main UHV chamber which houses an inductively coupled RF plasma source that is used to generate atomic oxygen beams [15]. The atomic oxygen beams are collimated by a quartz tube (6 mm in diameter) which separates the beam chamber and the main UHV chamber, and a mechanical shutter is used to control the flow of the beam into the UHV chamber. We use line-of-sight

mass spectrometry to estimate the beam composition and flow rate and thereby ensure reproducibility in the atomic oxygen flux reaching the sample surface.

The FTIR system employed in this study consists of a MIR source (Bruker Tensor 27), a set of mirrors and lenses and an external liquid N₂ cooled HgCdTe (MCT) detector. Outside of the UHV chamber, the MIR beam travels within a sealed box which is purged continuously with carbon dioxide and water-free compressed air. In the purge box, a set of flat mirrors are used to direct the MIR beam onto a parabolic mirror that focuses the beam. The focused MIR beam enters the UHV chamber through a differentially pumped KBr window and then reflects from the sample surface at angle of $\sim 80^\circ$ relative to the surface normal. The reflected MIR beam exits the UHV chamber through another KBr window and is directed onto the MCT detector within a second purge box. We averaged 512 scans at a resolution of 4 cm⁻¹ for all RAIR spectra reported here.

The Pd(111) crystal used in the present study is a circular disk (8 mm $\times$ 1 mm) spot-welded to W wires and attached to a copper sample holder that is in thermal contact with a liquid nitrogen cooled reservoir. A type K thermocouple is spot-welded to the backside of the crystal to measure the sample temperature. The sample is resistively heated and the temperature is controlled using a PID controller that adjusts the output of a dc power supply. In this setup, we are able to maintain or linearly ramp the sample temperature from 85 to 1250 K. Initial sample cleaning consisted of cycles of sputtering with 600 eV Ar⁺ ions at a surface temperature of 900 K, followed by annealing at 1100 K for 5 minutes. Subsequent cleaning involved routinely exposing the sample to an atomic oxygen beam for 30 minutes at 856 K, followed by flashing the sample to 923 K to desorb oxygen and carbon oxides. As discussed previously [16], we limited the sample temperature to 923 K in order to maintain saturation of oxygen in the subsurface reservoir, which ensures reproducibility in preparing the PdO(101) thin films. We considered the Pd(111) sample to

be clean when we could not detect contaminants with Auger electron spectroscopy (AES) and did not observe CO production during temperature-programmed desorption after oxygen adsorption.

We generate a PdO(101) thin film by exposing the Pd(111) surface to an ~ 23 ML dose of oxygen atoms at 500 K, where we define 1 ML as equal to the Pd(111) surface atom density of $1.53 \times 10^{15} \text{ cm}^{-2}$. This procedure generates a PdO(101) surface with identical surface structure and chemical properties to those studied previously [16-18]. We provide details of the PdO(101) surface structure in the Computational Details section. During atomic oxygen exposure, the Pd(111) surface is positioned ~ 20 mm from the final collimating aperture and is orientated 70° from the axis of oxygen beam. LEED observations suggest that this preparation procedure generates a PdO(101) that uniformly covers the Pd(111) surface.

After preparing the PdO(101) film, we exposed the sample to various amounts of NO ranging from 0.001 to 20 L (Langmuir) at 90 K. After a NO exposure, we collected TPD spectra by positioning the sample in front of a shielded quadrupole mass spectrometer (Hiden) at a distance of ~ 5 mm. The sample temperature increases to 615 K at 1 K/s as the mass spectrometer monitors NO desorption from the surface. We estimate the NO desorption yields by scaling the NO TPD spectra with that obtained from Pd(111) after saturating with NO at 90 K, assuming that the saturation coverage is 0.625 ML [19]. We collected RAIR spectra at the same temperature at which the NO exposures were conducted.

Computational Details

The periodic plane wave DFT calculations reported in this paper were performed using the Vienna *ab initio* simulation package (VASP) [20; 21] with projector augmented wave (PAW) [22] pseudopotentials provided in the VASP database. The Perdew-Burke-Ernzerhof (PBE) [23] exchange-correlation functional

was used with a plane wave cutoff of 400 eV. We have also tested spin polarization calculations for selected configurations and find that its effect is negligible. It is well-known that PBE underestimates band gaps and DFT-PBE predicts that PdO is a metal when experimentally it is known to be a small band gap semiconductor. The Heyd-Scuseria-Ernzerhof (HSE) [24] hybrid functional has been shown to accurately predict band gaps of oxides such as Cu₂O, FeO, and NiO [25; 26]. Bruska and co-workers have reported that PdO has a band gap of 0.8 eV using the HSE functional [27], which matches the experimental value obtained from optical transmittance measurements [28]. We have recently found that PBE is inaccurate in predicting the stability of CO binding on the bridge versus atop sites on PdO(101) [29]. In that study, we showed that static HSE calculations of relaxed DFT-PBE minima correct this error and provide good agreement between DFT and RAIRS data. Therefore, we also performed single-point HSE calculations on relaxed DFT-PBE minima for selected configurations of NO on PdO(101) to evaluate the accuracy of our PBE results.

Figure 1 illustrates the stoichiometric PdO(101) surface that is investigated in this study. Bulk crystalline PdO has a tetragonal unit cell and consists of square planar units of Pd atoms fourfold coordinated with oxygen atoms. The bulk-terminated PdO(101) surface is defined by a rectangular unit cell, where the a and b lattice vectors coincide with the $[010]$ and $[\bar{1}01]$ directions of the PdO crystal, respectively. The stoichiometric PdO(101) surface consists of alternating rows of threefold or fourfold coordinated Pd or O atoms that run parallel to the a direction shown in Figure 1. Thus, half of the surface O and Pd atoms are coordinatively unsaturated (cus). The areal density of each type of coordinatively-distinct atom of the PdO(101) surface is equal to 35% of the atomic density of the Pd(111) surface. Hence, the coverage of cus-Pd atoms is equal to 0.35 ML, and each PdO(101) layer contains 0.7 ML of Pd atoms and 0.7 ML of O atoms.

Figure 1. Top and side views of the PdO(101) surface. The red and dark blue atoms represent O and Pd atoms, respectively. Rows of coordinatively unsaturated (cus) and fourfold-coordinated (4f) Pd or O atoms are indicated. The vertical and horizontal arrows a and b represent the [010] and $[\bar{1}01]$ crystallographic directions of PdO.

The PdO(101) surface was modeled by a rectangular 4×1 unit cell, with a corresponding $4 \times 2 \times 1$ Monkhorst-Pack k-point mesh [30]. As in our prior studies [2; 29; 31], the PdO(101) film was strained ($a = 3.057 \text{ \AA}$, $b = 6.352 \text{ \AA}$) to match the PdO(101) film structure resolved by Kan and Weaver [17; 18]. The PdO(101) slab was represented by four layers resulting in a $9 \text{ \AA}$ thick slab. The bottom layer is fixed, but other lattice atoms are allowed to relax until the forces are less than $0.03 \text{ eV/\AA}$. As in our previous work the underlying Pd(111) surface is not included since this would require a large unit cell due to the registry of the PdO(101) film with the Pd(111) surface. We use a vacuum spacing of $20 \text{ \AA}$, which is sufficient to eliminate spurious interactions in the surface normal direction. Vibrational frequencies were calculated with only the degrees of freedom associated with the NO molecule included. We performed calculations for selected configurations and find that including the motions of the neighboring Pd and O atoms in the

normal mode analysis has a negligible effect on the computed N-O stretch frequencies. Finally, we define the NO adsorption (or binding) energy as follows $E_{ads} = \left(E_{NO/surf} - (ME_{NO} + E_{surf}) \right) / M$, where E_{NO} is the energy of an isolated NO molecule and $ME_{NO/surf}$ and E_{surf} are the energy of surface slab with M NO molecules adsorbed and the bare surface slab, respectively. With this definition of the adsorption energy, more negative values indicate greater stability.

Experimental Results and Discussion

TPD measurements of NO adsorption on PdO(101)

Figure 2a shows NO TPD traces obtained after exposing a PdO(101) film to different amounts of NO at 90 K. We find that the desorption of species other than NO (such as NO₂, N₂O, N₂) occurs negligibly during the TPD experiments, indicating that PdO(101) is unreactive toward NO under the conditions studied. The desorption of NO from PdO(101) gives rise to five main desorption features which are labeled as α_1 , α_2 , α_3 , α_4 , and α_5 in order from high to low temperature. In general, the α_1 and α_2 features grow simultaneously as the NO coverage increases, while the α_3 , α_4 , and α_5 peaks populate nearly sequentially until NO saturates PdO(101) at ~0.55 ML. Below 0.03 ML, NO mainly desorbs in the α_2 and α_1 TPD peaks. The desorption temperature of the α_2 peak remains almost constant at 400 K, while the desorption temperature of the α_1 feature shifts gradually from about 457 K to 470 K as the NO coverage increases to ~0.5 ML. Above 0.06 ML, the α_3 TPD peak grows sharply with increasing NO coverage to about 0.26 ML and the α_3 peak temperature downshifts from about 306 K to 297 K. As the α_3 state populates, the combined desorption yield in the α_1 and α_2 also increases slightly toward a saturation value of ~0.075 ML. The α_4 TPD peak first becomes evident at ~200 K at a total NO coverage of 0.09 ML, but intensifies

rapidly with increasing coverage, developing into a sharp peak at 178 Ks, only after the α_3 state nearly saturates at about 0.26 ML. A broad region of desorption also develops between the α_3 and α_4 peak maxima as the α_4 state develops, suggesting that NO molecules encounter diverse binding environments during the development of the α_4 state. Finally, population of the α_5 state initiates once the total coverage of NO increases above ~ 0.35 ML, and the desorption temperature stays relatively constant at about 113 K until NO saturates the PdO(101) surface at ~ 0.55 ML. A minor feature is also evident at ~ 134 K which grows with the α_5 peak.

Figure 2. (a) NO TPD spectra obtained after adsorbing NO on PdO(101) at 90 K. The initial coverages of NO are listed in the figure. (b) Cumulative desorption yields of NO as a function of the total NO coverage.

Figure 2b shows the cumulative desorption yields of NO as a function of the total NO coverage generated at 90 K. We estimate the cumulative NO desorption yields (α_1 , $\alpha_1 + \alpha_2$, $\alpha_1 + \alpha_2 + \alpha_3$, etc.) by integrating the TPD traces above temperatures of 90, 132, 235, 343 and 435 K, where these temperatures are selected to lie between the various TPD features. The α_1 and α_2 peaks populate simultaneously at low

coverage, reaching saturation at about 0.075 ML. The α_3 peak develops as the total coverage increases above 0.05 ML and nearly saturates once the total NO coverage reaches about 0.26 ML. This behavior suggests that NO occupies $\sim 75\%$ of the Pd_{cus} sites at saturation of the α_3 state. Interestingly, instead of continuing to populate the α_3 state as the NO coverage increases to the Pd_{cus} site density (0.35 ML), NO desorbs in a lower-temperature TPD feature (α_4 peak) at coverages above 0.26 ML. This apparent weakening in the NO binding energy as the coverage increases above $\sim 75\%$ of the Pd_{cus} site density suggests that the NO site preferences or binding configurations change before NO molecules saturate 100% of the Pd_{cus} sites. Lower temperature features develop concurrently with the α_4 peak, but the α_4 peak develops more sharply as the total coverage increases to about 0.42 ML. Above ~ 0.42 ML, the α_5 peak and the sharp peak at ~ 134 K grow more steadily with increasing coverage. The NO layer saturates at a total coverage of about 0.55 ML (close to 150% Pd_{cus}), suggesting that NO adsorbs on sites other than the Pd_{cus} sites at high coverage.

We estimated kinetic parameters for NO desorption in the various TPD peaks using the Redhead equation with pre-factors determined from the correlation reported by Campbell and Sellers [32; 33]. This analysis treats each TPD peak as arising from an independent desorption process governed by constant values of the desorption pre-factor and activation energy and is thus approximate. We computed pre-factors by applying the Campbell-Sellers correlation at the TPD peak temperatures. While approximate, the estimated kinetic parameters should provide a reasonable assessment of the NO binding energies associated with the various desorption maxima. Table 1 lists the desorption pre-factors and activation energies estimated for each of the TPD peaks. The activation energies range from about 148 to 31 kJ/mol and the pre-factors span nearly an order of magnitude.

Table 1: Desorption activation energies (E_d) and pre-factors (v_d) estimated for each TPD peak at the TPD peak temperatures (T_p).

TPD peak label	T_p (K)	$\log(v_d)$ (s^{-1})	E_d (kJ/mol)
α_1	475 K	15.2	147.8
α_2	400 K	15.1	123.2
α_3	300 K	14.9	90.8
α_4	180 K	14.6	52.8
α_5	111 K	14.3	31.5

RAIRS measurements after NO adsorption at 90 K

Figure 3a shows RAIR spectra obtained after adsorbing NO on the PdO(101) surface at 90 K to generate the coverages indicated. At low coverage (< 0.11 ML), the RAIR spectra exhibit a feature centered at ~ 1478 cm^{-1} as well as a broad region of intensity between ~ 1650 and 1850 cm^{-1} with distinct peaks evident at 1735 and 1805 cm^{-1} . At 0.07 ML, we estimate that about $2/3$ of the NO desorbs in the α_1 and α_2 TPD peaks, with the remainder desorbing in the α_3 peak. Distinct peaks at 1735 , 1762 and 1805 cm^{-1} develop in the RAIR spectra as the coverage increases to 0.26 ML at 90 K, with a peak at 1762 cm^{-1} emerging as the dominant feature. The intensity of the broad feature at 1478 cm^{-1} diminishes and a small feature at ~ 1867 cm^{-1} becomes evident once the coverage reaches about 0.26 ML.

Identifying RAIRS features that arise only from NO which desorbs in the α_1 and α_2 TPD peaks is challenging since these desorption features are difficult to populate at 90 K without obtaining substantial contributions from the α_3 TPD peak as well. In contrast, the changes observed in the RAIR spectra as the coverage increases from 0.07 to 0.26 ML correlate well with the development of the α_3 TPD peak (Figure 2), though a small fraction of the NO molecules does desorb in the α_4 peak in this coverage range. Notably, previous studies report that NO adsorbed on atop, bridge and three-fold hollow sites of metallic Pd surfaces yield N-O stretching vibrations at frequencies between ~ 1700 and 1850 cm^{-1} , 1500 to 1700 cm^{-1} and 1450 to 1600 cm^{-1} , respectively [19; 34-39]. On the basis of prior work, we conclude that the main

RAIRS features observed above 1700 cm^{-1} are characteristic of atop-NO species on PdO(101). We discuss the likely origin of the broad feature at 1478 cm^{-1} in more detail in the Computational Results section. The marked growth of the peak at 1762 cm^{-1} suggests that NO molecules populate atop-Pd_{cus} sites as the coverage increases from ~ 0.07 to 0.26 ML , and that desorption of these species produces the α_3 TPD peak. The nature of the NO binding configurations that develop at low coverages, at which the α_1 and α_2 TPD peaks are dominant, is more difficult to ascertain from the RAIRS data obtained after adsorption at 90 K .

Figure 3: RAIR spectra obtained after adsorbing NO on PdO(101) at 90 K to generate coverages (a) up to 0.26 ML and (b) from 0.26 to 0.54 ML .

Figure 3b shows RAIR spectra obtained after adsorbing NO on PdO(101) at 90 K to generate coverages from ~ 0.26 to 0.54 ML . These RAIR spectra primarily reflect changes in the NO adlayer that give rise to NO desorption in the low-temperature α_4 and α_5 TPD peaks. The main RAIRS peak intensifies slightly and blue shifts from 1762 to 1774 cm^{-1} as the coverage increases from 0.26 to 0.42 ML at 90 K . The peaks at 1735 and 1478 cm^{-1} also diminish as the coverage increases beyond 0.26 ML , with the 1478 cm^{-1} peak dropping into the noise. After generating a coverage of 0.54 ML , the RAIR spectrum exhibits

an intense peak at 1792 cm^{-1} and a feature near 1805 cm^{-1} becomes more evident. Close inspection suggests that the peak at 1792 cm^{-1} is already present in the RAIR spectrum obtained at a coverage of 0.42 ML, and that this peak intensifies relative to the peak at 1774 cm^{-1} when the coverage increases from 0.42 to 0.54 ML. Features at 1675 and 1848 cm^{-1} also grow sharply as the coverage increases above about 0.42 ML.

The appearance of multiple, broad features in the RAIR spectra suggests generally that NO molecules bind in several configurations on PdO(101) at 90 K, even at low coverage, including different binding sites, molecular orientations and local arrangements of adsorbed molecules. These characteristics may indicate that several local minima exist in the NO/PdO(101) potential energy surface, and that kinetic hindrances trap adsorbed NO species in multiple configurations at 90 K. To obtain additional information about the NO binding configurations on PdO(101), we collected RAIRS data after adsorbing NO at temperatures above 90 K and focused mainly on low NO coverages to aid in clarifying the nature of the species which give rise to the α_1 and α_2 TPD peaks.

RAIRS measurements after NO adsorption at different temperatures

Figure 4 shows RAIR spectra obtained after exposing PdO(101) surfaces to a 10 L dose of NO at 343 K and to 0.3 and 0.5 L of NO at temperatures of 90, 132 and 235 K. At 90 K, the 0.3 and 0.5 L exposures generate NO coverages of ~ 0.09 and 0.13 ML and NO desorbs predominantly in the α_1 and α_2 TPD peaks. A 10 L NO exposure is sufficient to saturate the PdO(101) surface at 343 K, with the NO coverage remaining near about 0.08 ML. While the signal-to-noise levels are relatively low in the RAIR spectra obtained at these low coverages, we do observe reproducible changes brought upon by the surface temperature. The RAIR spectra obtained after adsorbing NO at $T \geq 235\text{ K}$ exhibit distinct peaks at 1678,

1649 and 1570 cm^{-1} , whereas such peaks are difficult to discern in the spectra obtained after NO adsorption at lower temperature. Additionally, the broad feature at $\sim 1478 \text{ cm}^{-1}$ and also the intensity above $\sim 1700 \text{ cm}^{-1}$ are lower in the RAIR spectra obtained at $T \geq 235 \text{ K}$ and low NO coverage. Based on previous studies of NO on metallic Pd surfaces [19; 34-39], as well as the DFT results discussed below, the peaks at 1570, 1649 and 1678 cm^{-1} are consistent with bridging NO species adsorbed on the Pd_{cus} rows. The temperature-induced changes in the RAIR spectra thus suggest that the conversion of adsorbed NO molecules to bridging species is mildly activated, and that NO binds in less stable configurations at low temperature ($< \sim 235 \text{ K}$) and low coverage, but transforms to bridge-NO species before desorbing in the α_1 and α_2 TPD peaks. In this case, the RAIR spectra obtained after adsorbing low coverages ($< \sim 0.09 \text{ ML}$) of NO at 90 K depict features from meta-stable NO binding configurations that seem to include atop-NO species ($\nu_{\text{N-O}} > 1700 \text{ cm}^{-1}$) and also a species that yields the broad peak at 1478 cm^{-1} .

Figure 4: RAIR spectra obtained after exposing PdO(101) to (a) 0.3 L and (b) 0.5 L NO exposures at surface temperatures of 90, 132 and 235 K and a saturation NO exposure at 343 K. We estimate that exposures of 0.3 and 0.5 L generate NO coverages of 0.09 and 0.13 ML, respectively, at 90 K.

In summary, the RAIR spectra obtained from NO on PdO(101) exhibit multiple features that are characteristic of several NO binding configurations that change as a function of the coverage. At coverages below about 0.09 ML, the RAIRS data suggests that NO preferentially binds in a bridging configuration on the Pd_{cus} row but that adsorption into this configuration is hindered at temperatures up to at least 132 K, with NO becoming kinetically-trapped in other configurations. Desorption of the bridging-NO species is responsible for the α_1 and α_2 TPD peaks. As the coverage increases from ~0.09 to 0.26 ML, NO appears to adsorb on atop-Pd_{cus} sites, yielding a predominant RAIRS peak at 1762 cm⁻¹, and desorption over this coverage range produces the α_3 TPD peak. Lastly, NO adsorption above 0.26 ML initially causes the RAIRS peak near 1762 cm⁻¹ to blue-shift and intensify which may indicate continued NO adsorption on atop-Pd_{cus} sites as the NO coverage increases toward saturation of the Pd_{cus} sites (0.35 ML). In this case, the corresponding development of the α_4 TPD peak at ~180 K indicates that the binding of NO on PdO(101) weakens above 0.26 ML, and that the preferred NO configurations or binding states might differ at local coverages of 75% (0.26 ML) and 100% (0.35 ML). Finally, at NO coverages greater than the Pd_{cus} site density of 0.35 ML, NO molecules are likely to bind on the Pd_{4f} or O_{cus} sites, and achieve weaker binding compared with adsorption on the Pd_{cus} row. The emergence of the low-temperature α_5 TPD peak is indicative of weakly-bound NO species and the concurrent development of RAIRS peaks at ~1675 and 1848 cm⁻¹ is also consistent with the idea that NO molecules bind on new sites above 0.35 ML.

Computational Results and Discussion

NO configurations at low coverage (0.088 ML)

We used DFT calculations to investigate the binding configurations and energetics as well as the associated N-O stretch frequencies for NO adsorption on the pristine PdO(101) surface. We initially

studied a single NO molecule (0.088 ML) on the 4×1 supercell of pristine PdO(101) adsorbed on top of and in between the Pd_{cus}, O_{cus}, Pd_{4f}, and O_{4f} atoms. The top and side views of the stable configurations found are shown in Figure 5. Among the sites investigated, we find that NO maximizes its binding energy when the N end of the molecule or both N and O atoms interact with the Pd_{cus} row of the PdO(101) surface. Specifically, DFT predicts that the atop and bridge sites along the Pd_{cus} row are both favorable for NO binding at 0.088 ML (Figure 5). It is important to note the coexistence of two adsorption geometries of NO on each type of site (atop and bridge). For both molecular orientations, the NO molecules are tilted with respect to the surface normal, but one is close to the upright position ($\perp$) and leans toward the O_{cus} atom row (Figure 5b, 5d) and the other one is close to the horizontal position ($\parallel$) and leans toward the O_{4f} atom row (Figure 5a, 5c). We use the notation $\parallel$ and $\perp$ to distinguish the two NO orientations on the same site as described above. We also find that the NO molecule can lie down flat along the Pd_{cus} row and interact with two Pd_{cus} atoms (Figure 5e).

Figure 5. Top and side views of the five most stable configurations for a single NO molecule adsorbed on the pristine PdO(101) surface predicted by DFT. We use the notation $\parallel$ and $\perp$ to distinguish two different molecular orientations of NO on given type of site, as described in the text.

Table 2 summarizes the geometry, adsorption energy, and N-O stretch frequencies of the five stable NO configurations that we identified using DFT-PBE calculations (Figure 5). We also show values of the adsorption energy computed using static DFT-HSE. According to DFT-PBE calculations, the energetic stability of the five configurations shown in Figure 5 is $\text{bridge}_{\parallel} > \text{bridge}_{\perp} > \text{flat} > \text{atop}_{\perp} > \text{atop}_{\parallel}$. Thus, the bridge site is preferred at low coverage and the two NO orientations ($\text{bridge}_{\parallel}$ and $\text{bridge}_{\perp}$) are almost energetically equivalent. DFT calculations reported by Jelic et al. [10] also indicate that NO preferentially binds on bridge-Pd_{cus} sites of PdO(101). The N-O stretch frequencies are significantly different for the two bridge-NO species that we identified because the $\text{bridge}_{\parallel}$ configuration has a considerable N-O bond elongation from the gas-phase value of 1.17 Å. The atop site is less stable than the bridge site by ~20 to 30 kJ/mol and the two atop NO orientations have similar adsorption energies. The N-O stretch frequency is slightly lower for the $\text{atop}_{\parallel}$ vs. $\text{atop}_{\perp}$ configuration. The flat-lying NO configuration has the largest N-O bond elongation and the lowest N-O stretch frequency, and is slightly more energetically-favored than the atop-NO species. The flat-lying NO configuration can only exist at low coverage (up to 25%), because one NO molecule occupies two cus-Pd sites and two neighboring flat-lying NO molecules experience strong repulsion. We find that adding a second flat-lying NO molecule to the 4×1 PdO(101) surface is unfavorable such that one of the NO molecules rotates to the $\text{atop}_{\perp}$ configuration during the geometry relaxation.

Table 2. Calculated N-O bond length ($d_{\text{N-O}}$), height from the N atom to its nearest Pd atom ($d_{\text{N-Pd}}$), angle between the NO molecule and the flat PdO surface, adsorption energy computed using PBE (E_{PBE}) and static HSE (E_{HSE}) and N-O stretching frequency (ν) of NO species on PdO(101) at 0.088 ML (25%) coverage.

Configurations	$d_{\text{N-O}}/\text{\AA}$	$d_{\text{N-Pd}}/\text{\AA}$	NO-PdO angle ($^{\circ}$)	E_{PBE} (kJ/mol)	E_{HSE} (kJ/mol)	ν (cm^{-1})
bridge $_{\parallel}$	1.200	1.352	28.1	-192	-139	1625
bridge $_{\perp}$	1.187	1.457	67.4	-189	-145	1716
atop $_{\parallel}$	1.183	1.851	24.1	-165	-120	1732
atop $_{\perp}$	1.180	1.811	54.8	-172	-134	1756
flat	1.216	1.683	5.1	-175	-149	1490

We also computed the NO adsorption energies at 25% coverage using static DFT-HSE calculations as described in the Computational Details section. A key reason for performing the DFT-HSE calculations is that we have recently found that DFT-PBE incorrectly predicts an equal energetic preference for CO to bind on atop and bridge-Pd_{cus} sites of PdO(101), whereas DFT-HSE calculations predict a strong preference for CO to adsorb on atop-Pd_{cus} sites, in agreement with experimental results [29; 40]. Also, the NO binding energies computed using DFT-PBE are significantly overestimated compared with the values estimated from the TPD traces (Table 1). The DFT-HSE calculations predict that the stability of the NO bonding configurations at 25% coverage decreases in the order, flat > bridge $_{\perp}$ > bridge $_{\parallel}$ > atop $_{\perp}$ > atop $_{\parallel}$. Thus, according to the static DFT-HSE calculations, the bridge-NO species continue to be favored over atop-NO species at low coverage but the difference in energy is only 11 kJ/mol between the preferred atop $_{\perp}$ and bridge $_{\perp}$ configurations (134 vs. 145 kJ/mol). The static DFT-HSE results also suggest that the flat-lying NO configuration is the most stable among the five configurations identified, though its binding energy is only a few kJ/mol higher than that of the bridge $_{\perp}$ configuration. It is also worth noting that DFT-HSE predicts considerably lower NO binding energies compared with DFT-PBE, with values that agree more closely with the experimental estimates.

Comparison of the experimental RAIR spectra with the DFT results suggests an interpretation of the NO configurations that develop at low NO coverage. After adsorption at 90 K, the RAIR spectra exhibit a broad feature at 1478 cm^{-1} as well as peaks at ~ 1735 and 1759 cm^{-1} . These frequencies agree well with the computed N-O stretch frequencies for the flat-lying NO species (1490 cm^{-1}) and the atop ($1732, 1756\text{ cm}^{-1}$) NO species. The origin of the peak at 1805 cm^{-1} in the experimental RAIR spectra obtained at low coverage is unclear. The DFT calculations also support the conclusion that the more prominent peaks (1648 and 1680 cm^{-1}) observed after adsorbing NO at higher temperature arise from bridge-NO species. In this case, the computed N-O stretch frequencies (1625 and 1716 cm^{-1}) appear to differ from the measured values by as much as 36 cm^{-1} . These assignments suggest that NO adsorbs in the flat-lying and atop configurations on the Pd_{cus} row at low temperature and low coverage, and that these configurations transform to bridge-NO species at higher temperature. The low coverage at which the flat-lying NO species is predicted to be stable is also consistent with the experimental observation that only up to 0.075 ML of NO desorbs in the α_1 and α_2 TPD peaks. Overall, the interpretation implies that kinetic hindrances effectively limit NO from binding directly in bridge configurations during adsorption at low temperature, but that NO can more readily access the flat-lying and atop configurations. Determining the origin of such behavior is beyond the scope of the present study. A possibility is that the dynamics of the adsorption process tends to promote NO adsorption into configurations (e.g., flat-lying, atop) that act as intermediates to the formation of bridge-NO species, and that these transformations are activated.

Evolution of NO configurations on PdO(101) with increasing coverage

We also investigated how the adsorbed NO configurations evolve with increasing coverage on the pristine PdO(101) surface. We report only DFT-PBE results in this section and did not apply static HSE

calculations to determine the binding energies of NO on PdO(101) at coverages above 25%. While the static HSE calculations give E_{ads} values that are more in line with experiment, both DFT-PBE and static HSE calculations predict the same relative stability of NO binding on the atop versus bridge sites of PdO(101). It is thus reasonable to expect that DFT-PBE calculations will accurately capture the NO binding site preferences at higher coverage as well. On a 4×1 unit cell, an additional NO molecule is equivalent to increasing the NO coverage by 0.088 ML. In each step, we added one NO molecule to the surface and explored multiple configurations to identify the one which has the highest adsorption energy at each coverage. We investigated NO coverages from 0.088 ML to 0.525 ML (up to six NO molecules on the 4×1 supercell) and show the global minimum structure determined for each coverage in Figure 6. We highlight the energetically preferred pathway with increasing NO coverage using green arrows. Figure 6 also shows representative meta-stable configurations at the lower coverages. For coverages of 75% and below, we find that multiple configurations have binding energies that are only slightly higher than that of the global minimum at a particular coverage. To evaluate the stability of an adlayer configuration at a specific NO coverage, we calculated the energy change (ΔE), which is defined as the energy difference between the final configuration and the initial NO/PdO minimum plus a gas-phase NO molecule. For example, for configuration i at 0.263 ML, its ΔE_i is defined as follows, $\Delta E(i)_{0.263ML} = E(i)_{0.263ML} - E(minimum)_{0.175ML} - E(NO)$, where $E(i)_{0.263ML}$, $E(minimum)_{0.175ML}$, $E(NO)$ are total energies of configuration i at 0.263 ML, the global energy minimum at 0.175 ML, and an isolated NO molecule, respectively. As seen in Figure 6, NO continues to adsorb on the Pd_{cus} row as the coverage increases from 0.088 to 0.35 ML, but the preferred sites change with increasing coverage. After all of the Pd_{cus} sites are occupied at 0.35 ML, additional NO molecules adsorb on the Pd_{4f} row.

Figure 6. Stable configurations of NO on PdO(101) as a function NO coverage from 0.088 ML to 0.525 ML. The global energy minima are connected by green arrows. The energy value shown underneath each configuration is the ΔE defined in the text, and the N-O stretching frequencies are shown for IR active modes.

As the coverage increases from 25% to 50%, NO continues to adsorb preferentially on bridge-Pd_{cus} sites and the ΔE remains approximately unchanged at a value of 192 kJ/mol. This behavior demonstrates that bridge-NO molecules interact negligibly with one another when they are separated by two (or more)

lattice constants along the Pd_{cus} row. The associated N-O stretch frequencies of the bridge-NO species blue-shift by about 10 cm^{-1} when the coverage increases from 25% to 50%, most likely due to dipole coupling. According to DFT, the heat of adsorption remains nearly constant when the NO molecules adopt the preferred bridging configurations as the coverage increases to 50%. In contrast, our TPD data suggests that the NO binding energy decreases markedly once the NO coverage increases above 20 to 25% of the Pd_{cus} density; the α_1 and α_2 TPD peaks saturate and the α_3 peak begins to develop once the coverage increases above $\sim 25\%$ (Figure 2). This difference between the computed and experimental behavior may indicate that the NO adlayer does not fully equilibrate during the TPD experiments, and that a fraction of the NO molecules desorbs from meta-stable configurations rather than converting to the preferred bridging configurations that are predicted by DFT.

We find that continued adsorption at bridge sites destabilizes the NO-surface bonding above 50% coverage because adjacent bridge-NO molecules are forced to share Pd_{cus} atoms which weakens the bonding. As a result, DFT predicts that various mixtures of atop and bridge NO species are favored over all-bridge NO species at a coverage of 75%. According to DFT, the four most stable configurations at 75% coverage (Figure 6) are mixtures containing atop $_{\perp}$ and either bridge $_{\perp}$ or bridge $_{\parallel}$ species. The ΔE values for these atop-bridge configurations all lie within about 7 kJ/mol of one another, which suggests that NO molecules can attain appreciable populations in each of the mixed structures. Thus, a distribution of local configurations is likely to constitute the NO adlayer at 0.26 ML, which is consistent with the considerable breadth of the RAIRS features that we observe. We also note that the predicted heat of adsorption (~ 150 kJ/mol) is about 40 kJ/mol lower when the coverage increases from 50% to 75%, compared with the values (~ 190 kJ/mol) predicted for lower coverages. This behavior is generally consistent with the appearance of the α_3 TPD peak as the coverage increases from $\sim 25\%$ to 75%, though the DFT results suggest that the α_3 TPD peak should first appear at 50% coverage. We estimate that the activation energy

for desorption into the α_3 TPD peak is lower than that of the α_2 and α_1 TPD peaks by ~ 32 and 57 kJ/mol, respectively.

Two N-O stretching frequencies are associated with each of the atop-bridge mixtures at 75% coverage, where the low and high values arise from N-O bond stretching of the bridge and atop $_{\perp}$ NO species, respectively. The computed N-O stretch frequency of the atop $_{\perp}$ species ranges from 1765 to 1782 cm^{-1} among the atop-bridge mixtures, and is blue-shifted from the value of 1756 cm^{-1} predicted for this species at 25% coverage (Table 2). The predicted N-O stretch frequencies for the bridge $_{\parallel}$ and bridge $_{\perp}$ species are near 1625 cm^{-1} and 1720 cm^{-1} , respectively, for the atop-bridge mixtures, and are similar to the values predicted for the all-bridge structures at 50% coverage. Using a method reported by Karhanek et al. [41], we predict that the IR absorption strength is larger for the atop species than the bridge species in the mixed structures, by between a factor of 2 to 6 depending on the structure. One would thus expect that the N-O stretch peaks for the atop species (1765 to 1782 cm^{-1}) will exhibit the highest intensity in RAIR spectra obtained after preparing NO coverages near 75%. Consistent with this expectation, the RAIR spectra obtained at 75% coverage exhibit a strong peak at 1762 cm^{-1} as well as less intense peaks near 1735 and 1805 cm^{-1} (Figure 3).

DFT predicts that NO molecules preferentially adsorb in the atop $_{\perp}$ configuration on Pd $_{\text{cus}}$ sites once the coverage reaches 100% (Figure 6). In the all-atop structure, neighboring NO molecules rotate in opposite directions about the surface normal to minimize repulsive interactions with one another. The calculations predict a heat of adsorption of 136 kJ/mol when the preferred atop-bridge structure at 75% coverage transforms to the all-atop structure at 100% via NO adsorption. This energy change is about 19 kJ/mol lower than the energy change which accompanies the conversion of an all-bridge structure at 50% coverage to the preferred atop-bridge structure at 75% coverage, indicating that the binding of NO in the

adlayer further weakens when the coverage increases above 75%. This behavior is consistent with our observation that the α_3 TPD peak saturates at a NO coverage near 75%, and that the lower-temperature α_4 peak begins to develop as the coverage first increases above 75%.

We predict large IR absorption strengths for two N-O stretching modes (1702 and 1802 cm^{-1}) of the all-atop structure. The mode at 1802 cm^{-1} corresponds to in-phase N-O stretching motion of all of the atop-NO molecules, while the mode at 1702 cm^{-1} corresponds to a collective motion wherein alternating NO molecules exhibit in-phase N-O bond stretching while the nearest neighbors vibrate out of phase. The calculations predict that the IR absorption strength is about 33% higher for the mode at 1702 cm^{-1} . In the measured RAIR spectra, the dominant peak blue-shifts from ~ 1765 to 1774 cm^{-1} as the NO coverage increases from 0.26 to 0.42 ML and continues to blue-shift with increasing coverage to 0.54 ML, reaching a value of 1794 cm^{-1} . A broad feature centered at 1675 cm^{-1} also emerges in the RAIR spectra when the NO coverage increases beyond ~ 0.42 ML. The observed blue-shift of the main RAIRS peak toward 1794 cm^{-1} as well as the appearance of a new feature at 1675 cm^{-1} are consistent with the N-O stretching modes at 1702 and 1802 cm^{-1} predicted by DFT. However, the relative intensities of these modes differ between experiment and computation, and the lower frequency peak appears at a higher coverage than is suggested by the DFT calculations ($>\sim 125\%$ vs. 75%). These differences may indicate that a fraction of the NO molecules bind in meta-stable arrangements, and that the all-atop structure develops only gradually with increasing coverage above 75%.

According to DFT, NO molecules adsorb between Pd_{4f} and O_{4f} sites as the coverage increases above 100% of the Pd_{cus} density, generating structures that consist of an atop NO molecule on each Pd_{cus} site and additional NO molecules adsorbed on the Pd_{4f} row (Figure 6). The heat of adsorption is about 100 kJ/mol for the addition of an NO molecule to the Pd_{4f} row of the all-atop structure, thereby raising the NO

coverage above 100%, and is about 40 kJ/mol lower than the energy change associated with increasing the coverage from 75% to 100%. The DFT calculations also predict that N-O bond stretching of the NO/Pd_{4f} species occurs at a frequency near 1860 cm⁻¹, in excellent agreement with the position of a peak that appears in the measured RAIR spectra obtained at higher NO coverages (Figure 3b). The RAIR spectra do exhibit a small feature at 1864 cm⁻¹ after preparing NO coverages above about 0.22 ML, but the intensity of this feature remains largely unchanged as the coverage increases toward about 0.42 ML. The peak near 1864 cm⁻¹ intensifies and redshifts to ~1849 cm⁻¹ as the coverage increases above about 0.42 ML, coinciding with the sharp growth of the α_5 TPD peak. The DFT calculations also predict that the in-phase and out-of-phase N-O stretch modes of the atop-Pd_{cus} species redshift after adding NO molecules to the Pd_{4f} row, reaching values of 1744 and 1676 cm⁻¹ at a NO coverage of 150%. The measured RAIRS peak centered at 1675 cm⁻¹ does broaden toward lower frequencies as the coverage increases, but we observe a slight blue-shift (rather than a red-shift) of the main RAIRS peak toward 1792 cm⁻¹ as the coverage increases to 0.54 ML (Figure 3).

Overall, the DFT results suggest a progression of the NO adlayer that agrees reasonably well with the experimental findings. The calculations predict that NO preferentially binds on bridge-Pd_{cus} sites over atop-Pd_{cus} sites at coverages up to 50%, and that further increases in the NO coverage cause NO molecules to bind on atop-Pd_{cus} sites, generating mixtures of atop-bridge configurations at 75% coverage and an all-atop configuration at 100% coverage. DFT also predicts that NO molecules can achieve relatively strong binding by adsorbing on the Pd_{4f} row at coverages above 100% of the Pd_{cus} density. The computed frequencies and IR peak intensities of the various NO species and configurations generally agree well with our experimental observations, though we also find marked differences between the computed and measured behavior, as noted above. Many of the differences are likely attributable to diversity in the NO binding configurations that can be attained, and the formation of meta-stable arrangements during

adsorption at 90 K. Indeed, the considerable breadth of the main RAIRS feature between ~ 1700 and 1800 cm^{-1} is consistent with our prediction that several atop-bridge configurations are nearly energetically degenerate at 75% coverage. Furthermore, our experiments provide evidence that NO adsorption onto bridge-Pd_{cus} sites is kinetically hindered such that NO molecules tend to adsorb into meta-stable configurations (flat-lying and atop) at low temperature and low coverage, with a fraction of these molecules transforming to bridge-NO species when the surface is heated above at least 132 K. The appearance of a RAIRS peak near 1860 cm^{-1} after generating moderate coverages ($< \sim 75\%$) may provide further evidence that a fraction of the NO molecules become trapped in meta-stable arrangements during adsorption at 90 K (e.g., NO-Pd_{4f} species) rather than arranging into fully equilibrated structures. Despite the differences, we consider the agreement between the computed and measured evolution of the NO adlayer on PdO(101) with increasing coverage to be quite good, particularly considering the complexity of this system.

Summary

We investigated the adsorption of NO on PdO(101) using TPD, RAIRS and DFT calculations and find that NO can adsorb in multiple binding configurations on this surface. From TPD, we find that NO saturates the PdO(101) surface at a coverage of $\sim 0.54\text{ ML}$ at 90 K, and that desorption of the saturated NO layer produces a complex TPD trace with five pronounced desorption maxima spanning a temperature range from ~ 100 to 550 K . RAIR spectra obtained after generating low NO coverages on PdO(101) at 90 K exhibit a broad region of intensity between ~ 1700 to 1800 cm^{-1} , with distinct peaks that are characteristic of atop-NO species, as well as a less intense feature at $\sim 1478\text{ cm}^{-1}$ which we attribute to a flat-lying NO species, based on DFT calculations. The considerable breadth of the main RAIRS feature suggests that

NO molecules encounter a diverse set of local binding environments on PdO(101), even at low coverage. Changes in the RAIR spectra suggest that NO molecules preferentially adsorb on atop-Pd_{cus} sites as the NO coverage increases toward 100% of the Pd_{cus} density, and also provide evidence that a more-weakly bound state of NO populates above coverages of 100%. Our RAIRS measurements also provide evidence that NO molecules adsorb in atop and flat-lying configurations at low coverage and low temperature, but that a fraction of these species adopt bridging configurations at temperatures above at least 132 K. This finding suggests that NO molecules become kinetically trapped in meta-stable configurations at low temperature and low coverage, and that conversion to the more favored bridge configurations is mildly activated.

DFT calculations provide a description of the evolution of the NO adlayer on PdO(101) that agrees well with our experimental findings. DFT predicts five stable configurations of an NO molecule on PdO(101), including a flat-lying configuration and two molecular orientations of NO bound at atop and bridge-Pd_{cus} sites. According to DFT-PBE, NO preferentially binds on bridge-Pd_{cus} sites up to a coverage of 50% of the Pd_{cus} density. Binding at atop-Pd_{cus} sites becomes preferred over continued adsorption on bridge-Pd_{cus} sites at coverages above 50%, and results in the development of various mixtures of atop-bridge NO species at 75% coverage and an all atop-NO structure at 100% coverage. The heat of adsorption decreases abruptly when NO molecules shift from bridge to atop-Pd_{cus} sites as the NO coverage increases above 50%. DFT also predicts that NO molecules can achieve stable binding on the Pd_{4f} row at coverages above 100%, producing structures with NO-Pd_{4f} species that co-exist with atop-NO species on each Pd_{cus} site. The diversity in NO binding environments on PdO(101) that are suggested by our RAIRS measurements is consistent with the DFT prediction that NO can bind in multiple configurations on PdO(101) and that several of the predicted NO adlayer structures lie close in energy.

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