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Qualitative Evidence for Lifted Backbond Degeneracy in the Bonding of Edge-Adsorbed NO on Pd/Al_2O_3

Mark R. Albert[1]

Surface Science Center, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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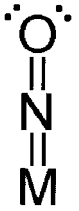
Thermal activation of an NO adsorbate state on Pd/Al_2O_3 is reported. Previously assigned to atop and step sites, these new data allow for its assignment to an edge-bound state displaying lifted backbond degeneracy. As was concluded for an analogous CO state, this NO state arises when electron-deficient edge atoms bond strongly to adsorbed NO molecules to minimize edge metal atom interaction with the edge destabilizing band structure. Published data is reconsidered in the context of this new NO surface-bonding mode.

There has been significant interest in characterizing the nature of NO adsorption on Pd surfaces using vibrational spectroscopy (1–10). On supported Pd, two peaks are detected at 1760 and 1680 cm^{-1} (1, 3–5) and it is generally agreed that the 1760-cm^{-1} peak is associated with atop bound NO (1, 3–6). The peak at 1680 cm^{-1}, however, has been assigned to bridge-bonded NO (4, 5, 8, 9), dimerized NO (2), and a bent NO adsorbate (3, 5). More detailed studies (1, 7) suggest that the peak is associated with NO molecules adsorbed on step sites (7), such as those found on Pd(112), and seem to be atop bound but "more highly backbonded," relative to the 1760-cm^{-1} adsorbate state, with a likely bond order near 2 (1).

Still to be reported, however, is an electronic structure for this NO adsorbate state that can rationalize the atop, step bound conformation (1, 7) and explain how these characteristics could lead to a vibrational peak red shifted relative to the 1760-cm^{-1} peak of "conventional" atop bound NO (1, 3–6). Drawing upon the precedent of applying synthetic chemistry strategies to the study of CO adsorption on Pd/Al_2O_3 (11), this report will offer qualitative arguments to suggest that the NO state associated with the 1680-cm^{-1} peak is atop and step bound since the degeneracy of its backbonds lifts (I) to allow for a strong, localized, multiple bonding interaction with an otherwise electron deficient (12–16) and, therefore, band structure destabilized edge atom on the Pd crystallite. As was done in the CO study (11), this result will be derived through the qualitative interpretation of temperature-dependent transmission infrared data for NO adsorption on the Pd/Al_2O_3 surface in conjunction with literature reports. The ability of a diatomic to lift its backbond degeneracy on the Pd/Al_2O_3 surface has been precedented by the characterization (11) of just such a state for methylisocyanide adsorbed on the same surface.



(I)

Experimental details mirror those of the earlier methylisocyanide and CO adsorption studies (11) including the temperature control that was effected by passing cold or hot nitrogen gas through the hollow sample support tube (17) and the removal of the trace CO remaining after sample preparation by addition of 8.5×10^{13} molecules of O_2 to the sample at 300 K followed by a 60-min hydrogen reduction at 450 K. Nitric oxide was purified before use by passing it over fused KOH until all traces of reddish coloring disappeared. Since the Pd/Al_2O_3 surface preparation includes thermal treatment to 180°C (450 K), no additional sintering of the sample is expected in the thermal processing experiment since that sample temperature is not exceeded during thermal analysis.

Figure 1, consistent with an earlier report (5), shows the evolution of vibrational peaks for the thermal processing of a saturated overlayer of NO adsorbed on Pd/Al_2O_3 at 95 K. At 95 K, only a large peak near 1760 cm^{-1} and a smaller peak near 1695 cm^{-1} is detected. With increasing temperature the 1760-cm^{-1} peak attenuates and shifts to lower frequency. Also, with increasing temperature, a peak at 1680 cm^{-1} grows in and replaces the small peak near 1695 cm^{-1}. As its intensity increases, the peak at 1680 cm^{-1}

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[1] Please send correspondence to Dr. Mark Albert at mralbert@netaxs.com.

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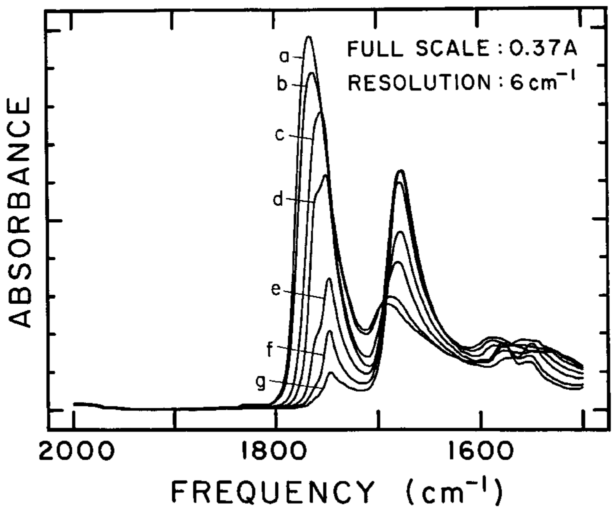

FIG. 1. Change with increasing temperature of the ν(NO) absorption peaks for nitric oxide adsorbed on Pd/Al_2O_3. Annealing temperatures were (a) 95 K, (b) 158 K, (c) 247 K, (d) 286 K, (e) 322 K, (f) 397 K, and (g) 446 K.

shifts slightly to a lower frequency and then remains at constant frequency. Some reports (1, 5) indicate that some of this temperature dependence could be attributable to coverage dependence detected at 300 K. Unlike an earlier report of NO adsorption on Pd/SiO_2 (5), only low-intensity structure is detected below 1600 cm^{-1}.

Since all of the vibrational data was collected under high vacuum conditions, the concerted behavior of the two large peaks in Fig. 1 must indicate that the state associated with the attenuating peak at 1760 cm^{-1} is the precursor to the state associated with the thermally activated peak at 1680 cm^{-1}.

Observation that the 1680-cm^{-1} peak observed for NO adsorption on Pd/Al_2O_3 is thermally activated (Fig. 1) suggests that the associated adsorbate state can be characterized using qualitative arguments similar to those applied to the thermally activated CO adsorption peak on the same surface (11). They can be summarized as follows:

1. Literature reports offering evidence beyond the correlation of red shift to site coordination (18) indicate that the adsorbate state associated with the 1680-cm^{-1} peak is bound to atop sites (1) on steps (7).
2. Since the 1760-cm^{-1} peak shifts to lower energy as it attenuates while the 1680-cm^{-1} peak shifts little as it grows (Fig. 1), the dipole field of the adsorbate state associated with the peak at 1680 cm^{-1} must be much smaller than that of the adsorbate state associated with the peak at 1760 cm^{-1}. A linear arrangement of adsorbate molecules, as might occur along an edge, instead of the two-dimensional arrangement of molecules found on a flat terrace, is consistent with this smaller field. The possibility that the adsorbate state is dispersed within a more prevalent overlayer on a terrace (19, 20) can be rejected since no peak shifting is detected for the 1680-cm^{-1} peak, even after the 1760-cm^{-1} peak attenuates.
3. Edge bonding is also indicated by the thermal activation of the peak at 1680 cm^{-1} (Fig. 1). For CO and methylisocyanide adsorption (11), thermal activation was judged consistent with the need for the bridging precursor to overcome the attenuation of backbonding that must occur while the bridging adsorbate molecule migrates across a region of increasing electron deficiency (12–16) as it moves to the electron-deficient edge to bond with an edge atom. Although the NO precursor state (associated with peak at 1760 cm^{-1}) is atop bound and, therefore, less in need of backbonding electron density relative to a bridging state, the same effect on a smaller scale is still likely. Since the ν(NO) frequency of gas-phase NO is 1876 cm^{-1} (21), a fair amount of backbonding must still be present to cause the detected red shift of 116 cm^{-1}. Consistent with this argument is the less facile growth of the analogous thermally activated CO peak prepared from the bridging CO precursor (11).
4. Also consistent with edge bonding is the coexistence of both the precursor and product NO states on the surface over a wide temperature range (Fig. 1). This indicates that the negative ΔH needed to drive the reaction cannot arise from reacting NO bonds since that would lead to a transformation over a narrow temperature range (11) as is seen for surface ethylidyne formation (22). The only bonds available to drive the conversion reaction, therefore, are those between the surface metal atoms and the only known high-energy surface metal atom bonds on the surface are those associated with the electron-deficient edge metal atoms (12–16). The broad temperature range of conversion would be consistent with the large variety of edges and, therefore, the broad range of electron deficiencies associated with those edges.

When these qualitative arguments are included with the observation that alternative atop modes for NO such as side-on or through oxygen structures are unlikely (23) and that "bent" NO has already been rejected as an assignment for the 1680-cm^{-1} peak (1), the only remaining assignment for the peak is the one analogous to that of the thermally activated state of CO (11), as shown in Fig. 2, where the NO adsorbate lifts its backbond degeneracy to form a double bond to an unstable edge Pd atom so that the Pd atom can minimize its energy through separation from the destabilizing Pd band structure (12–16) and form a "Pd=N=O" adsorbate complex with the NO molecule. This result is consistent with, but expands upon, an earlier discussion of the atop bound NO adsorbate state (1). Any destabilization of the NO adsorbate in this process would

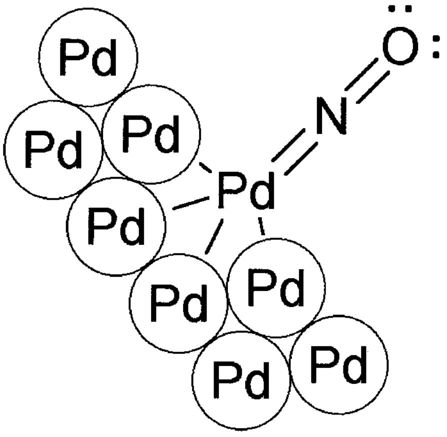

FIG. 2. Illustration of the proposed thermally activated NO bonding mode on the Pd/Al_2O_3 edge sites displaying lifted backbond degeneracy. The absence of a circle around the attached Pd atom represents its likely separation from the surface band structure and transformation into an adsorbate atom. The tilt of the metal atoms is used to represent an edge.

be negated by the greater stabilization of the surface metal atom.

This result explains the larger red shift of the 1680-cm^{-1} peak, therefore, since the shifting is not defined by surface site coordination, as is usually the case (18), but by the vibrational energy of the resulting Pd=N=O asymmetric stretching frequency (Fig. 2) (11), which is defined by the atomic weights of the associated atoms.

Insights as to the validity of the proposed lifted backbond degeneracy adsorbate structure can be gained by reconsideration of published data in the context of the suggested NO adsorbate mode. For instance, vibrational data for NO adsorption on Pd(110) (8, 9) reveals that a peak near 1680 cm^{-1} dominates the spectrum at most NO coverages at both 180 and 300 K and is assigned to NO adsorbed on bridging sites (9). However, given that the rows of Pd atoms on Pd(110) model edges and likely display a similar electron deficiency (12–16), the possibility that this adsorption state of NO displays lifted backbond degeneracy as described above is not unreasonable. Evidence already indicates that CO displays exactly this structure on Pd(110) (11, 24).

The absence of thermal activation, at 180 K or above, associated with the 1680-cm^{-1} peak on Pd(110) (9) does not necessarily preclude this assignment since there would be no need for NO to migrate to the edge sites on Pd(110). The analogous CO state on Pd(110) (11, 24) seems to require less thermal activation relative to the supported metal state since the conversion is reported to be complete by 305 K in IRAS data (25). This assignment could be strengthened by vibrational analysis of this surface system (9) below 180 K.

On low-index Pd planes such as (100) (2, 10) and (111) (6, 7) peaks near 1680 cm^{-1} are also detected. In one IRAS study of NO on Pd(111) (6) thermal processing is shown to cause the conversion of a peak near 1758 cm^{-1} into a peak near 1620 cm^{-1}. This is somewhat similar to the data reported in Fig. 1 but is not consistent because the conversion on Pd(111) (6) is complete at 235 K, a much lower temperature than that seen for the conversion on Pd/Al_2O_3 (Fig. 1). Given that the (111) face predominates on supported Pd (26–28), the reported behaviors of NO on Pd(111) (6) and Pd/Al_2O_3 (Fig. 1) indicate that fundamentally different surfaces are being probed. This may be related to the reported difference of NO adsorbate behavior on the (111) planes of Pd(111) and Pd(112) (7).

On Pd(100) (2) a peak at 208 meV (1677 cm^{-1}) detected at 190 K is replaced by a peak at 185 meV (1491 cm^{-1}) with increasing temperature. In this work, the 1677-cm^{-1} peak is assigned to dimer formation, although (a) dimerization is considered an unlikely process (29), (b) the peak had been previously assigned to an atop bound state on the same Pd(100) surface (10) and (c) the LEED data is consistent with *both* atop bound NO as well as dimerized NO (2). The low-temperature predominance of this peak on Pd(100) might be consistent with its assignment to a lifted backbond degeneracy state since the (100) face is much less prevalent than the (111) face on Pd crystallites (26–28). This observation would be needed to explain why the peak is not detected at low temperature on Pd/Al_2O_3 (Fig. 1).

The possibility of finding the lifted backbond degeneracy NO state on low-index Pd planes is worth consideration since edge bonding is indicated only because that is the location of unstable metal atoms whose high energy can drive the adsorbate to lift its backbond degeneracy. Since terrace atoms are themselves unstable relative to bulk atoms (30), terrace atoms might be unstable enough to prefer strong bonding to NO adsorbate molecules rather than full inclusion in the metal band structure, especially if the energy required to lift NO backbond degeneracy is itself low.

Theoretical calculations (31) do not directly suggest the lifted backbond degeneracy diatomic adsorbate state suggested in this work. They are unlikely to do so, however, unless the possibility of surface metal atom displacement and localization is specifically considered in the calculation.

Also to be assigned is the low-intensity peak detected at low temperature near 1695 cm^{-1} (Fig. 1). In the absence of the temperature-dependent vibrational data (Fig. 1), it is likely that this peak could easily be mistaken for the overlapping 1680-cm^{-1} peak and vice versa. However, based on analogy with CO and methylisocyanide thermal processing data on the same surface (11), as well as earlier assignments (4, 5, 8, 9), the 1695-cm^{-1} peak likely represents the bridging NO adsorbate state. This assignment would offer an interpretation as to why a peak near 1677 cm^{-1}, detected after a 5.0-L exposure of NO to Pd(110) at 180 K, "suddenly" moves to 1688 cm^{-1} after a 6.0-L exposure (9). The higher NO coverage could cause electron donation to the surface that is extensive enough to stabilize the surface Pd atoms within the band structure and suppress their need to lift the backbond degeneracy of the NO adsorbate molecules as could be indicated by the 1677-cm^{-1} peak seen at lower coverages. Bridging NO would then become the more stable structure and likely be associated with the peak at 1688 cm^{-1}.

Although peak structure below 1600 cm^{-1} is not a major component of the data in Fig. 1, its appearance in other reports on both supported Pd (5) and single-crystal surfaces (2, 6, 7, 9, 10) makes it worthwhile to discuss from the standpoint of the "lifted backbond degeneracy" adsorption state reported in this work. While as yet rather little can be concluded, it might indicate the migration of "Pd=N=O" adsorbate complexes over the surface. This sort of migration has already been suggested (11) as a mechanism for the reported reconstruction of Pd(110) by adsorbed CO (32, 33). In addition, harsh thermal processing of a CO overlayer on Pd/SiO_2 (34) has been shown to produce broad vibrational peak structure on the low-frequency side of a peak assignable to CO adsorbates with lifted backbond degeneracy.

The identification of a "lifted backbond degeneracy" adsorption state for NO on Pd/Al_2O_3 indicates the power and versatility of applying synthetic chemistry research methods to the study of surface adsorption well beyond those suggested in earlier discussions of the "cluster-surface analogy" (35–37). The identification of a chemical consequence, i.e., chemical reactivity, of a physics observation, i.e., the electron deficiency of edges (12–16), not only allows for the pursuit and identification of new bonding modes for adsorbates that might likewise be modified by the energy stored in the great variety of edge atoms that are present on metal surfaces but also offers insight into a mechanism that may explain certain types of catalytic reactivity, i.e., the destabilization of ground state adsorbates toward their higher energy transition states by the much greater stabilization, through localization, of attached, otherwise electron-deficient edge atoms. Only to be overcome is acceptance of the greater front end investment in effort required to master the *two* scientific fields necessary to conduct this type of research instead of the usual one. The result of the present work and its predecessor (11), however, indicate that the additional investment ultimately pays off proportionately.

CONCLUSION

Observation of a thermally activated NO state on Pd/Al_2O_3 allows for its assignment to an adsorbate state displaying lifted backbond degeneracy that is attached to an edge metal atom that has localized its electron density away from the destabilizing metal band structure. This result is consistent with that reported for adsorption of both methylisocyanide and CO on the same surface (11).

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