Oxidation of Pd_n ($n = 1-7$, 10) clusters supported on alumina/NiAl(110)

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First-principles theoretical investigations on the oxidation of Pd_n ($n = 1-7$, 10) clusters deposited on alumina/NiAl(110) have been carried out using a gradient-corrected density-functional approach. Our studies indicate that the free Pd_n clusters are compact and maintain their compact structures when deposited on the surface, undergoing only small relaxations of the Pd-Pd distance. The clusters bind to the surface via a pair of Pd atoms and with a binding energy of around 1.0 eV. Studies of oxidation through an O_2 molecule show that O_2 occupies sites closer to the surface for Pd_1, Pd_4, Pd_5, and Pd_6 while, in other cases, the binding is highest to Pd atoms farther from the surface. An analysis of the charge gained by the O_2 molecule upon absorption shows that, while O_2 always gains charge, the amount of charge contributed by the Pd_n cluster or the surface can vary significantly. In particular, in the case of Pd_4, only a small charge is donated by the cluster, thus accounting for the recently observed lack of shift in the x-ray photoelectron spectroscopy levels.

I. INTRODUCTION

Palladium clusters/nanoparticles supported on metal oxides represent an important class of catalyst used in a variety of industrially relevant processes.[1,2] For example, palladium catalysts are the most promising catalyst for methane combustion as they lower the combustion temperature reducing production of pollutants such as CO and NO_x, while providing a high turnover rate.[3] Palladium nanoparticles are also important catalysts for CO oxidation and are widely used in catalytic converters. In practice, the clusters are supported and one of the supports that has drawn considerable attention is a thin layer of alumina on a NiAl(110) surface.[4] The thin layer allows conduction through it, thus preventing excessive charging of the oxide surface while providing a corrosion resistant support. Experimental and theoretical studies indicate that the composition of the Al_2O_3 layer is closer to $Al_{10}O_{13}$.[5] One could thus regard the oxide layer as considerably reduced. A realistic model of atomic positions in the reduced oxide incorporating the atomic structure based on the scanning tunneling microscope (STM) data has been proposed by Kresse *et al.*[5]

In a recent work, Wu *et al.*[6] investigated the size dependence of the oxidation of Pd_n ($n \leq 13$) clusters on alumina/NiAl(110) using x-ray photoelectron spectroscopy (XPS). The size selected clusters were deposited on the oxide layer and they measured the shift in the XPS levels as the deposited clusters were exposed to O_2 at 100 K. Since the XPS lines in PdO are shifted from those in pure Pd, the shift in the spectra was taken as indicative of the oxidation of clusters. The experiments focused on Pd_n clusters containing 1, 4, 7, 10, and 13 atoms and the results indicated that, while a Pd atom and clusters containing 7, 10, and 13 atoms showed appreciable shift, no shift was observed for Pd_4. The peculiar behavior of Pd_4 suggested that, unlike other sizes, the deposited cluster is inert toward oxidation. More interestingly, when the temperature was raised to 300 K and the clusters exposed to O_2 at the elevated temperature, none of the clusters oxidized, implying that the O_2 was probably bound to the cluster surface. These observations raise some puzzling questions. First, why is Pd_4 inert to oxidation while other clusters are oxidized at low temperatures? The ground state of an O_2 molecule is a spin triplet and recent studies in our group indicate that the strength of the O_2 binding can depend on the spin multiplicity of the cluster.[7] Since the small Pd_n clusters as well as Pd monolayers are known to have finite spin magnetic moments,[8] one may wonder if the special behavior is related to its magnetic character. Numerous studies on free clusters have shown that the catalytic properties can change significantly with cluster size. For example, the reactivity of free Fe_n clusters is known to change by orders of magnitude, just by the addition of a single atom.[9] This raises the question if the observed progression is related to intrinsic behavior in free Pd_n clusters. As, there can be charge transfer between the deposited clusters and the substrate, are the deposited clusters closer to charged or free clusters and does the charge transfer modify the structure or the electronic behavior? What happens as the temperature is raised to 300 K since none of the clusters exhibits oxidation? Underlying these observations is the general question about the structure of Pd_n clusters deposited on different surfaces. For example, recent studies on size-selected Pd clusters on TiO_2 surfaces suggest that clusters containing up to ten Pd atoms form a single layer, pointing that the geometries of the clusters are considerably modified from those in free clusters.[10] These studies also reported a strong size dependence of the oxidation of CO with size. Do the Pd_n clusters on alumina/NiAl(110) have the same structure as on TiO_2 and, if so, can the inertness of Pd_4 on alumina/NiAl(110) be related to its special geometrical form?

In this paper, we have carried out a comprehensive study of the free Pd_n clusters, Pd_n clusters deposited on alumina/NiAl(110) ($n = 1-7$, 10), and the oxidation of the deposited clusters to answer some of these questions. All the studies are first principles and are carried out within a gradient-corrected density-functional framework. Section II is devoted to a discussion of the method while Sec. III presents and discusses our results. Section IV summarizes the main conclusions.

II. THEORETICAL METHOD

First-principles electronic-structure calculations within a density-functional framework were carried out using the projector augmented wave method[11] as implemented in the Vienna *ab initio* simulation package (VASP).[12,13] The exchange and correlation contributions were included using the generalized gradient approximation proposed by Perdew *et al.*[14] To determine the electronic structure, the wave functions were expanded using a plane-wave basis set using a cutoff energy of 250 eV. The Brillouin zone was sampled at the Gamma point. This simulation package, capable of studying infinite solids, surfaces, and clusters deposited on surfaces, uses a periodic cell with a unit cell determined by the surface/solid. For free clusters, the same methodology can be used by choosing a larger unit cell to avoid any interaction between the repeating motifs. In the present work, the calculations on free clusters were carried out using a cubic unit cell with a lattice constant of 20 Å and placing the cluster at the center. For the calculations on supported clusters, the alumina/NiAl(110) support was modeled via a supercell containing 316 atoms. As mentioned before, the alumina/NiAl(110) surface has been a subject of several earlier investigations and an atomic structure based on the experimental STM data has been proposed by Kresse *et al.*[5] In this work, we were guided by this structural study and have used a model which corresponds to two layers of alumina on the NiAl(110) modeled by 66 unit cells. The NiAl lattice constant was theoretically calculated to be 4.094 Å. The same model has been successfully used previously to study the properties of Au chains on the same surface.[15] For deposited clusters, each cluster was placed at several possible positions and the most stable state was determined by calculating the forces at the cluster sites and the neighboring surface atoms in the vicinity of the deposited cluster. These atoms were allowed to relax along the path of steepest descent till the forces dropped below a threshold value of 0.02 eV/Å. Since free Pd_n clusters have finite spin moments, different initial spin moments were tried to find the ground state. Any charge transfers between the cluster and the surface were determined through a Bader charge analysis.[16]

III. RESULTS AND DISCUSSION

A. Free Pd_n clusters

Figure 1 shows the ground-state structures of Pd_n clusters containing 2–7, 10 atoms. Also shown are some next higher isomers which are close in energy. Note that the ground-state structures are all compact geometries. The Pd-Pd bond length varies from 2.48 Å in a dimer to 2.76 Å in larger clusters. For the case of Pd_5, while the ground state has a compact triangular bipyramid structure, a square pyramid is only 0.03 eV above the ground state. Pd_{10} also possesses two isomers separated by less than 0.02 eV. Within the accuracy of the calculations, these differences in energy are too small and hence the structures could coexist in free clusters. A rather interesting result is the finite spin magnetic moments. Note that bulk Pd is paramagnetic. However, it has been observed that the introduction of transition-metal impurities
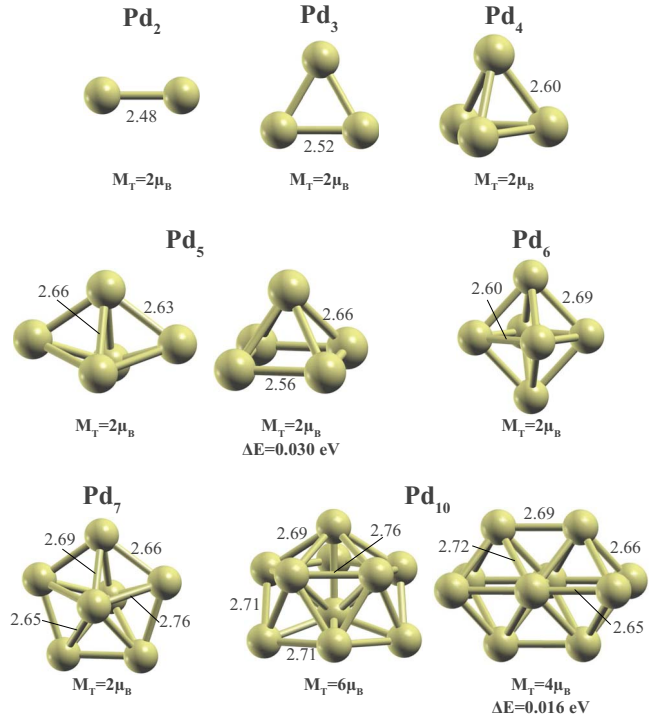

FIG. 1. (Color online) Ground-state structures, total spin moment M_T, and some bond lengths (in Å, marked beside the bond) of Pd_n clusters. In some cases, a close higher energy isomer is also shown together with the increment of energy with respect to the ground state ΔE.

in bulk can induce large host polarization on Pd sites that extends up to fourth-nearest neighbors.[17–20] For pure Pd_n clusters, previous studies and present findings indicate that they are magnetic.[21–24] What is more interesting is that Pd_n clusters containing 2–7 atoms all have a spin magnetic moment of 2 μ_B. Pd_{10}, on the other hand, has two isomers with moments of 6 μ_B and 4 μ_B, respectively. While all small clusters have compact geometrical shapes, there are significant variations in the binding energy. Using the total energy of the clusters, we calculated the atomization energy, E_b, defined as

$$E_b = nE(Pd) - E(Pd_n),$$

where $E(Pd_n)$ is the total energy of a cluster with n atoms. Upper panel of Fig. 2 shows the binding energy per atom. Significant variations with size can be observed. In particular, there is a significant jump in the binding energy in going from Pd_3 to Pd_4. Note that the variations in energy can be indicative of stability. For example, cluster sizes where there is a large gain in energy in forming the cluster from the preceding size and a lower gain in energy in growing to the next size can be a signature of local stability. To this end, we also plot in the lower panel of Fig. 2, the gain in energy ΔE in forming the cluster from the preceding size, namely,

$$\Delta E_n = E(Pd_{n-1}) + E(Pd) - E(Pd_n).$$

Note that Pd_4 has the highest peak, followed by Pd_6. These findings are in general agreement with previous studies on pure Pd_n clusters.[21–24] Are these stabilities and compact ge-
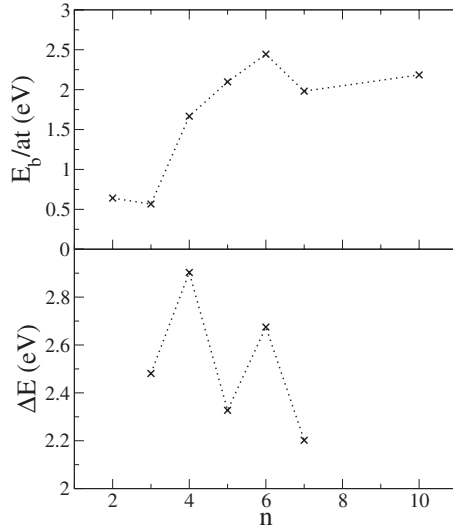
FIG. 2. Binding energy per atom E_b/at (upper panel) and gain in energy in forming the cluster from the preceding size ΔE (lower panel, as defined in the text) of Pd$_n$ clusters.

ometries maintained as the clusters are deposited on alumina?

B. Pd$_n$ clusters supported on alumina/NiAl(110)

As we mentioned before, the thin alumina layer is a reduced aluminum oxide and the first issue is the strength of the binding of the clusters to the surface and how it modifies the structure of the free clusters. We carried out a thorough investigation where a Pd atom and clusters containing 2–7, 10 atoms were deposited on the surface. To find the optimum absorption site, each cluster was initially placed in several locations on the surface and the atoms in the cluster as well surface atoms in the vicinity of the cluster were allowed to relax to find the optimum position. Our optimization included trying different initial spin moments. Figure 3 shows the ground-state structure of the deposited clusters. The red and blue spheres represent, respectively, O and Al atoms in the alumina layers while the Pd atoms are marked by yellow spheres. Also shown in square insets are the structures of the corresponding free clusters. While there were small relaxations of the Pd-Pd bonds, in all cases the clusters maintained their free cluster geometry. In most cases only two lower atoms of the cluster bond to the surface. Note that this is different from the case of clusters supported on TiO$_2$, where recent studies point to a two-dimensional growth up to sizes containing ten atoms.[10]

To further analyze the effect of the support, we calculated the binding energy, $E_{b,surf}$, of the various clusters to the support and the atomization energy per atom, $E_{at,surf}$/at, for the deposited clusters using the equations

$$E_{b,surf} = E(Pd_n) + E(surf) - E(Pd_n/surf)$$

and

$$E_{at,surf}/at = [nE(Pd) + E(surf) - E(Pd_n/surf)]/n,$$

where $E(Pd_n)$, $E(surf)$, and $E(Pd_n/surf)$ are the total energies of the free Pd$_n$ cluster, the free surface, and the total energy
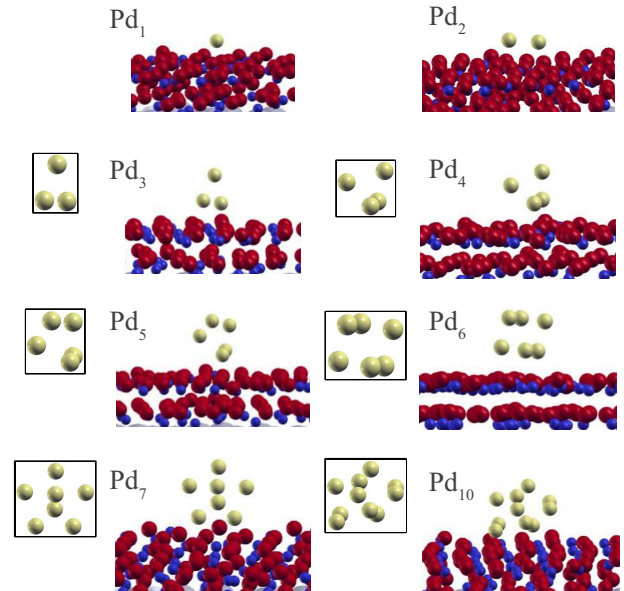

FIG. 3. (Color online) Most stable structures of the deposited Pd$_n$ clusters. Red (dark, big) spheres represent O atoms, blue (dark, small) ones represent Al atoms, and Pd atoms are marked by yellow (light) spheres. Also shown in square insets are the structures of the clusters already presented in Fig. 1, but oriented as in the deposited case.

after the deposition of the Pd$_n$ cluster on the surface. Figure 4 shows the variations in $E_{b,surf}$ and $E_{at,surf}$/at while Table I presents the numerical values. First, note that the binding energy of the clusters to the surface first increases from Pd atom to Pd$_2$ to a value of around 1.1 eV and then remains almost constant around a value of 1.0 eV. This is expected, as the clusters maintain their compact structures and only two atoms in every cluster bond to the surface sites. As to $E_{at,surf}$/at, one notices a rapid increase up until Pd$_4$ and then only a gradual increase with size. A larger increase in $E_{at,surf}$/at in going from Pd$_3$ to Pd$_4$ and then a smaller increase in going from Pd$_4$ to Pd$_5$ again indicate the special stability of Pd$_4$ among deposited clusters (this can also be easily seen through second derivative of the energy that exhibits a maximum). Another important quantity characteriz-
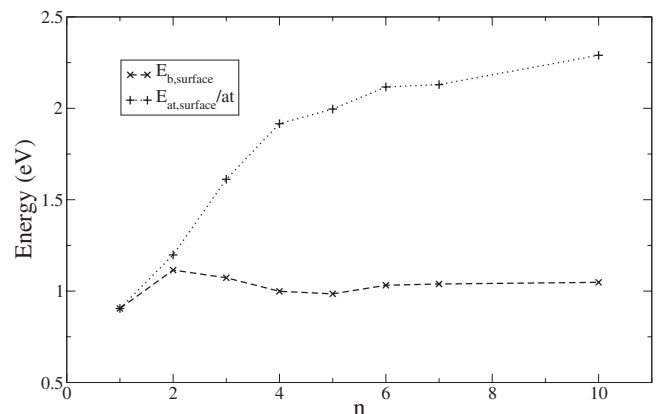

FIG. 4. $E_{b,surf}$ and $E_{at,surf}$/at (as defined in the text) for the supported Pd$_n$ clusters. The lines are just guides for the eyes.

TABLE I. Total magnetic spin moments M_T (in μ_B), charge transfers ΔN (in e^-), and several energies (in eV) of supported Pd_n clusters. For explanation of each quantity see the text.

n	M_T	ΔN	$E_{b,surf}$	$E_{at,surf}/at$	$E_{def}(surf)$	$E_{def}(clus)$	E_{int}
1	0.00	0.05	0.905	0.905	−0.160		1.065
2	0.00	0.08	1.115	1.198	−0.590	−0.067	1.772
3	0.13	0.20	1.073	1.612	−0.324	−0.023	1.420
4	2.00	0.07	0.999	1.916	−0.311	−0.027	1.337
5	2.01	0.07	0.985	1.996	−0.277	−0.030	1.293
6	2.05	0.07	1.032	2.117	−0.327	−0.021	1.380
7	2.11	0.03	1.039	2.130	−0.264	−0.049	1.352
10	2.23	−0.02	1.048	2.290	−0.226	−0.084	1.358

ing small free clusters is their magnetic moment. Table I lists the spin magnetic moment of the deposited clusters. Note that while the spin moment of a Pd atom, Pd_2, and Pd_3 is quenched or very small, all other clusters have a spin magnetic moment of 2.0 μ_B. These spin moments are almost completely localized around the Pd atoms. While we are here primarily concerned with the oxidation of Pd_n clusters, the finite spin moment indicates that it may be possible to observe these moments in carefully planned superconducting quantum interference device or magnetic force microscopy experiments. Another interesting point is the charge transfer ΔN between clusters and surface. In Table I we also include ΔN as calculated from a Bader analysis.[16] A positive number indicates a gain of electrons, i.e., clusters charging negatively. For the Pd clusters the charge transfer is, in most cases, less than $0.1e^-$, indicating that the supported clusters are not charged. This is in contrast with the situation for gold clusters on the same surface, which get negatively charged.[15]

Table I also includes some deformation and interaction energies to quantify the interaction of clusters and substrate. These quantities are defined as follows:

$$E_{def}(surf) = E(surf) - E'(surf),$$

$$E_{def}(clus) = E(Pd_n) - E'(Pd_n),$$

and

$$E_{int} = E'(Pd_n) + E'(surf) - E(Pd_n/surf),$$

where $E'(surf)$ and $E'(Pd_n)$ are the energies of surface and cluster calculated at the relaxed geometry of the whole system, i.e., the cluster supported on the surface. $E_{def}(surf)$ and $E_{def}(clus)$ give a measure of the deformation energies associated with surface and cluster, respectively, after the cluster deposition. E_{int} gives the interaction energy between cluster and surface. $E_{def}(clus)$ is very small for the deposited clusters (less than 0.1 eV), which is consistent with the lack of deformation visually observed in Fig. 3. The deformation energies for the surface are bigger, but still modest. Thus we can conclude that the nature of the interaction between clusters and surface is mainly electronic with the geometric part playing a minor role.

In Fig. 5 we show the local density of states (LDOS) of the Pd atom and the Al and O atoms in the surface alumina layer. All the Pd states lie in the alumina gap, close to the Fermi energy. There is some hybridization between Pd and the alumina layer, mainly with O atoms. The first unoccupied Pd states have mainly s character with some d component. This is in agreement with the previous suggestion of Nilius *et al.*[25] For the other clusters the situation is similar with most of the states lying in the alumina gap and close to the Fermi energy.

C. O_2 absorption on Pd_n clusters supported on alumina/NiAl(110)

The main objective of the current work is to understand the behavior of the Pd clusters upon oxidation of the surface. To this end, we examined the binding of an O_2 molecule to the deposited clusters. In each case, an O_2 molecule was allowed to approach the surface from various directions and the geometry was optimized to find the most stable configuration. In Fig. 6 we show the ground-state geometry after the absorption of the O_2 molecule. While the O-O bond was found to stretch after the absorption, there was a barrier to the dissociation of the molecule, and hence the O-O bond
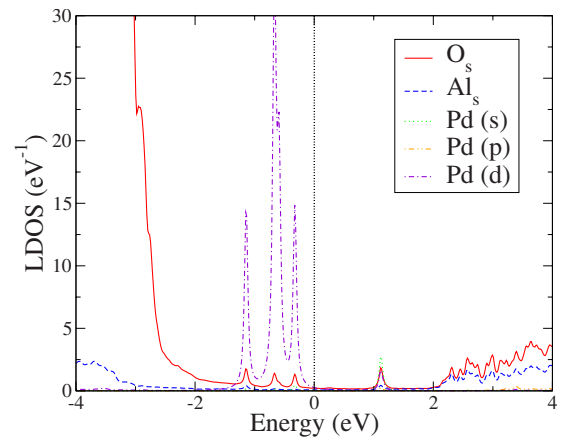

FIG. 5. (Color online) LDOS for the supported Pd atom on the alumina surface. The orbital decomposed LDOS for Pd is presented together with the LDOS for the surface Al and O atoms. A small Gaussian broadening of $\sigma = 0.03$ has been applied.
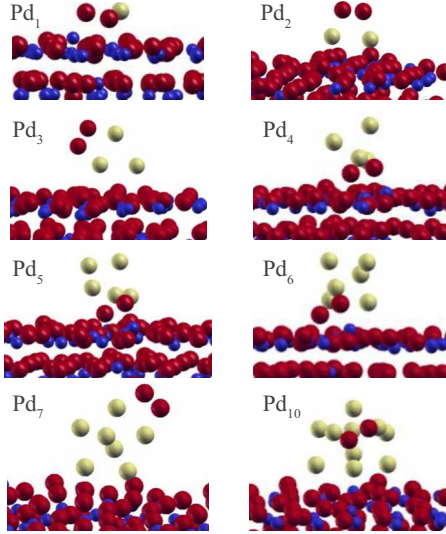
FIG. 6. (Color online) Most stable structures of the O$_2$ molecule adsorbed on the supported Pd$_n$ clusters. Red (dark, big) spheres represent O atoms, blue (dark, small) ones represent Al atoms, and Pd atoms are marked by yellow (light) spheres.

remained intact. More interesting is the nature of binding of O$_2$. While the molecule binds to the cluster sites away from the surface for the case of Pd$_2$, Pd$_3$, Pd$_7$, and Pd$_{10}$ clusters, it binds to sites closer to the surface for other clusters. We also calculated the binding energy of O$_2$ to the supported cluster and to the free surface, $E_b[O_2]$, defined as

$$E_b[O_2] = E_{b,surf} + E[O_2] - E(O_2/Pd_n/surf),$$

where $E(O_2)$ is the energy of a O$_2$ molecule in the gas phase and $E(O_2/Pd_n/surf)$ is the total energy of the system after the O$_2$ absorption. The results are given in Table II. The O$_2$ molecule is bound to a free surface with a binding energy of 2.14 eV, and it is interesting to note that the binding energy varies between 1.78 and 3.01 eV for binding to deposited clusters. For Pd$_4$, the binding energy is 2.71 eV, that is larger than that for many other clusters. Table II also lists the magnetic moment of the cluster after the deposition of O$_2$ and one observes a variation between 0.38 and 2.40 μ_B. Neither

the strength of the binding nor the observed spin multiplicity point to any special behavior for Pd$_4$.

As mentioned before, the experimental investigations probed the shift in the core levels after the absorption of the O$_2$ molecule. Since O$_2$ absorbs by gaining charge, we proceeded to examine the charge on the absorbed O$_2$ molecule to explore if the variations in charge transfer could account for the observed effect. To explore this, we calculated the charge, $\Delta N[O_2]$, gained by the O$_2$ molecule in various cases. Table II lists the value of ΔN for these cases. Note that the charge gained by O$_2$ is much bigger for the cases where O$_2$ is closer to the surface, including Pd$_4$. This is puzzling since one observes no core-level shift in the case of Pd$_4$. We then proceeded to examine whether the charge gained by O$_2$ came from the cluster or from the surface, since O$_2$ occupied locations closer to the surface for the cases with bigger charge transfer. Consequently, we calculated $\Delta N[Pd_n]$ and $\Delta N[Pd_n]/n$, representing the amount of charge on O$_2$ originating in the Pd$_n$ clusters and the charge per atom donated, on average, by each Pd site in the cluster. Table II lists this charge for all the cases. Note that $\Delta N[Pd_n]$ and $\Delta N[Pd_n]/n$ are minimum for the case of Pd$_4$. While there is always substantial charge gained by O$_2$, when O$_2$ is far from the surface a large fraction of this charge is contributed by the cluster. However, when O$_2$ is close to the surface, only a small charge percentage is donated by the cluster, and O$_2$ picks up the remaining charge from the surface. In the case of Pd$_4$ only a small charge is donated by the cluster. Since a charge transfer from the cluster is needed to generate a shift in the XPS levels, the observed inert behavior is a result of the O$_2$ receiving almost negligible charge from the cluster. We believe that this special behavior is rooted in the enhanced stability of Pd$_4$ as seen in free or deposited clusters. We would like to add that $\Delta N[Pd_n]/n$ is also small for Pd$_5$. However, there are no experiments available on this cluster size. We also calculated the relative binding energy of O$_2$ as it bound to sites close or away from the surface. For Pd$_4$, while O$_2$ binds with an energy of 2.71 eV at the site closer to the surface, the binding energy is only 1.34 eV if bound to the Pd atom farthest from the surface. The same variation was observed for Pd$_6$, where the binding energy to a site closer to the surface was 2.24 eV and it reduced to 1.46 eV if O$_2$ was forced to absorb at the Pd atom farthest from the surface.

TABLE II. O$_2$ binding energies $E_b[O_2]$ (in eV), total spin magnetic moments M_T (in μ_B), charge gained by the O$_2$ molecule $\Delta N[O_2]$, or lost by the Pd clusters $\Delta N[Pd_n]$ (in e^-).

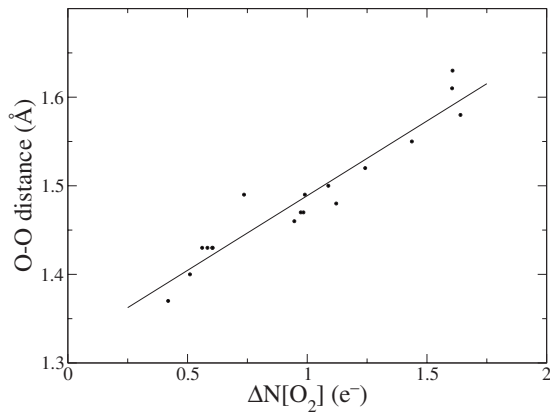| n	$E_b[O_2]$	M_T	$\Delta N[O_2]$	$\Delta N[Pd_n]$	$\Delta N[Pd_n]/n$
1	2.222	0.38	1.34	−0.22	−0.22
2	3.016	1.94	0.51	−0.49	−0.25
3	1.781	1.80	0.56	−0.31	−0.10
4	2.708	2.31	1.44	−0.09	−0.02
5	2.607	2.20	1.61	−0.11	−0.02
6	2.761	2.40	1.62	−0.23	−0.04
7	2.489	2.00	0.61	−0.51	−0.07
10	2.340	2.07	0.74	−0.61	−0.06
Surface	2.138	0.00	1.64		

FIG. 7. O-O distance in the absorbed O_2 molecule (in Å) as a function of the charge transfer $\Delta N[O_2]$ (in e^-). The line shows a linear regression of the data.

As mentioned before, after the absorption the O-O bond stretches. There is some correlation between the O-O distance and the charge the O_2 molecule gets. In Fig. 7 we have plotted the O-O distance versus $\Delta N[O_2]$, for the cases in Table II and some others. In general, the O-O bond gets more stretched as it gets more charge after the O_2 absorption.

The experiments also indicate that the core-level shifts are not observed or highly reduced at higher temperatures. As our results show, the binding energy of O_2 to the free surface is, in most cases, only few percent less than in the presence of clusters. It is then possible that, as the temperature is increased, the increase in entropy associated with the large number of unoccupied positions on the surface makes the free energy for surface absorption lower than for binding to clusters. This would imply that, as the temperature is increased, the O_2 molecules migrate to the free surface.

IV. CONCLUSIONS

To summarize, the present investigations indicate that the observed variations in the oxidation of Pd_n clusters deposited on alumina are related to the nature of binding of the O_2 molecule. While O_2 binds with a binding energy exceeding 2.0 eV in all cases, it occupied different sites depending on the size. For Pd_4, O_2 occupies a location closer to the surface and draws most of its charge from it, leaving the cluster almost neutral and hence without appreciable core shift. Our studies also indicate that the charge transfer is lower for Pd_5. While there are no experiments at this size, we hope that the present studies will stimulate experiments at this size to confirm the present findings. We would like to add that we have here considered the absorption of only a single O_2 molecule. In actual experiments, multiple O_2 molecules are absorbed at the surface and one needs to carry out similar studies with multiple molecules. These attempts are in progress and will be reported in a forthcoming publication.

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[1] D. Ciuparu, M. R. Lyubovsky, E. Altman, L. D. Pfefferle, and A. Datye, Catal. Rev. - Sci. Eng. **44**, 593 (2002).

[2] S. Penner, P. Bera, S. Pedersen, L. T. Ngo, J. J. W. Harris, and C. T. Campbell, J. Phys. Chem. B **110**, 24577 (2006).

[3] C.-Q. Lv, K.-C. Ling, and G.-C. Wang, J. Chem. Phys. **131**, 144704 (2009).

[4] G. Hamm, C. Becker, and C. R. Henry, Nanotechnology **17**, 1943 (2006).

[5] G. Kresse, M. Schmid, E. Napetschnig, M. Shishkin, L. Kohler, and P. Varga, Science **308**, 1440 (2005).

[6] T. Wu, W. E. Kaden, W. A. Kunkel, and S. L. Anderson, Surf. Sci. **603**, 2764 (2009).

[7] A. C. Reber, S. N. Khanna, P. J. Roach, W. H. Woodward, and A. W. Castleman, Jr., J. Am. Chem. Soc. **129**, 16098 (2007).

[8] D. C. Douglass, J. P. Bucher, and L. A. Bloomfield, Phys. Rev. B **45**, 6341 (1992).

[9] R. L. Whetten, D. M. Cox, D. J. Trevor, and A. Kaldor, Phys. Rev. Lett. **54**, 1494 (1985).

[10] W. E. Kaden, T. Wu, W. A. Kunkel, and S. L. Anderson, Science **326**, 826 (2009).

[11] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[12] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).

[13] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[14] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[15] N. Nilius, M. V. Ganduglia-Pirovano, V. Brazdova, M. Kulawik, J. Sauer, and H.-J. Freund, Phys. Rev. Lett. **100**, 096802 (2008).

[16] W. Tang, E. Sanville, and G. Henkelman, J. Phys.: Condens. Matter **21**, 084204 (2009).

[17] G. J. Nieuwenhuys, Adv. Phys. **24**, 515 (1975).

[18] J. W. Cable and L. David, Phys. Rev. B **16**, 297 (1977).

[19] B. H. Verbeek, G. J. Nieuwenhuys, J. A. Mydosh, C. van Dijk, and B. D. Rainford, Phys. Rev. B **22**, 5426 (1980).

[20] B. V. Reddy, S. N. Khanna, and B. I. Dunlap, Phys. Rev. Lett. **70**, 3323 (1993).

[21] F. Aguilera-Granja, J. Ferrer, and A. Vega, Phys. Rev. B **74**, 174416 (2006).

[22] F. Aguilera-Granja, A. Vega, J. Rogan, W. Orellana, and G. García, Eur. Phys. J. D **44**, 125 (2007).

[23] T. Futschek, M. Marsman, and J. Hafner, J. Phys.: Condens. Matter **17**, 5927 (2005).

[24] V. Kumar and Y. Kawazoe, Phys. Rev. B **66**, 144413 (2002).

[25] N. Nilius, T. M. Wallis, and W. Ho, Phys. Rev. Lett. **90**, 046808 (2003).