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Interaction of Pd with α-$Al_2O_3(0001)$: A case study of modeling the metal-oxide interface on complex substrates

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The Pd/α-$Al_2O_3(0001)$ interface at low Pd coverage has been studied by a variety of theoretical methods and models at this metal-oxide interface. All results are consistent and predict a noticeable interaction dominated by the metal polarization in response to the presence of the substrate. A significant contribution of the charge transfer from the transition metal to the surface is also observed. The periodic fully relaxed calculations show that the most favorable adsorption site for the interaction of Pd with corundum involves the anionic surface sites, in particular the on-top oxygen site. It is also shown that adsorption of Pd atoms on the surface induces a significant relaxation of the aluminum oxide substrate, especially for the outermost aluminum layer. The small differences observed in the adsorption energies near the oxygen atoms suggest a high mobility of Pd atoms on the surface.

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I. INTRODUCTION

The interaction of metals with metal-oxide surfaces is at the heart of several relevant technologies. Among others, pertinent examples involve applications to metal-ceramic-based gas sensors, microelectronic devices, and oxide-supported transition-metal catalysts.[1] Therefore, it is not surprising that the physics and chemistry of the metal-oxide interface is being strongly investigated.[2,3] Several experimental studies concerning adsorption of metal atoms on oxide supports have been reported over the past few years.[4–11] Unfortunately, the complexity of these systems makes it difficult to obtain direct, structural or electronic, information even under ultrahigh-vacuum, well-defined, controlled, experimental conditions. In some cases, the oxide-surface structure is rather simple, i.e., MgO(100), although even in this simple case the surface presents a large concentration of vacancies and other point defects.[12] On the other hand, the α-$Al_2O_3(0001)$ surface provides a paradigm of a complex surface whose structure is still a matter of discussion.[13–17]

The interaction of metal atoms with the α-$Al_2O_3(0001)$ surface involves a higher degree of complexity not exempt from contradictory interpretations. An example of such contradictions is the case of the Cu/α-$Al_2O_3(0001)$ interface for which both oxygen- and aluminum-terminated α-Al_2O_3 surfaces have been proposed from experiments.[4–9] The adsorption of palladium on the α-Al_2O_3 surface has been recently studied[10] by means of secondary ion mass spectrometry in a static mode, and thermal programmed desorption. From these studies it is predicted that Pd grows on α-Al_2O_3 following either Stranski-Krastanov (SK) completion of a monolayer plus three-dimensional (3D) crystallite growth, or three-dimensional Volmer-Weber (VW) mechanisms. At low coverage, Pd-Al bonds are first formed whereas Pd-O bonds seem to be formed in a subsequent step. A tiny negative charge during the adsorption stage is observed but palladium atoms remain essentially neutral during deposition. Palladium clusters in the 0.1–0.3-nm thickness range exhibit a work function that remains at a constant value of 6.5 eV on α-Al_2O_3. The very recent experiments of Pang *et al.*[11] using noncontact atomic force microscopy, show Pd clusters of ~30–40 Å in diameter and ~2–3 Å high above the α-$Al_2O_3(0001)$ surface. These authors also suggest that their observations are consistent either with the VW or SK growth modes. Similar findings have been previously reported for experiments that use aluminum-oxide thin films grown on a metal support such as NiAl (Refs. 18–20) instead of corundum single-crystal well-defined surfaces. From the theoretical side, Verdozzi *et al.*[21] recently reported a local-density approximation (LDA) study of the adsorption of Ag and Pt atoms on the Al-terminated α-$Al_2O_3(0001)$ surface. For the $\frac{1}{3}$ ML geometrical coverage (a "geometric" ML has one metal atom per surface oxygen), these authors found that Ag atoms are preferentially adsorbed above surface aluminum atoms while Pt is adsorbed above the outermost oxygen atoms. However, for 1 ML geometrical coverage, the LDA predicts that both metals slightly prefer direct adsorption on surface aluminum atoms. Even more recently, Zhang and Smith[22] used LDA and the generalized gradient approximation (GGA) to study the interaction of Nb also with the α-$Al_2O_3(0001)$ surface. These authors also carried out a thermodynamic study and found that depending on the oxygen partial pressure, the interface formation between Nb and α-Al_2O_3 can reverse the order of stability leading to an O-terminated surface, which in absence of oxygen atmosphere is normally less stable than the Al-terminated surface. This could justify the experimental problems referred to above for the copper interaction with α-alumina.

From the discussion above it is crystal clear that information coming from theoretical investigations is of extreme importance. This information is necessary to assist the interpretation of data obtained from experimental studies carried out in these complex systems. In spite of this fact, the number of papers devoted to the theoretical study of the metal-oxide interaction is quite limited. For the MgO(100) and $TiO_2(110)$ surfaces (Refs. 23–26, and references therein) several computational methods have been used combined either with the cluster or the periodic approaches. From these works it is concluded that the metal atoms (Ni, Pd, Pt) prefer to bind the oxygen atoms of the oxide surface. A particularly important point concerns the magnitude of the adsorption energies. The calculated values show an unexpected dependence on the choice of computational method.[23,25] This dependence is particularly marked in density-functional-theory (DFT)-based methods. In fact, for Cu on basic sites of MgO(100) it has been shown that the interaction energy obtained from different gradient-corrected exchange-correlation functionals may differ by a factor of 2.[25] Furthermore, the calculated adsorption energies range from moderate to small, $\sim$0.2–1.0 eV, indicating a rather weak interaction that can strongly vary from site to site. On the MgO surface, the computed adsorption energy for Pd adsorbed on the basic sites is almost three times the one calculated for Pd adsorbed on the acidic sites and the same behavior is also followed by different adsorbed metal atoms.[23,27–29] However, the data discussed so far concerning the adsorption of metals on the α-$Al_2O_3(0001)$ surface indicates that even for a clean and nearly perfect surface different surface sites may compete. The order of stability of metal adatoms on the clean α-$Al_2O_3(0001)$ surface may influence the growth mechanism of the metal cluster and has implications for the diffusion of metal atoms on bulk α-Al_2O_3.

In this work we present a detailed systematic study of the interaction of Pd atoms on different sites of the relaxed, clean, α-$Al_2O_3(0001)$ surface using a variety of different models to simulate the system. Both finite cluster models and periodic approaches have been used to represent the corresponding interface. In addition, the surface relaxation induced by the metal deposition has been explored. The paper is organized as follows: In Sec. II the different surface and computational models are described with special attention given to the construction of the embedded-cluster model. Section III presents the whole set of results obtained with the different computational techniques within the cluster model description of the Pd/Al_2O_3 system and compares to experimental results whenever available, whereas results from the periodic approach and a pertinent comparison to cluster results are discussed in Sec. IV. Finally, our conclusions are presented in Sec. V.

II. SURFACE AND COMPUTATIONAL MODELS

The theoretical description of oxide surfaces can make use of either embedded-cluster models or periodic approaches. For a highly ionic material such as MgO it has been shown that the nonpolar surfaces can be equally well represented by means of these two different idealized approaches.[30,31] The highly ionic nature of corundum[32] strongly suggests that this will also be the case for the low index surfaces of this particular form of aluminum oxide, provided relaxation effects are properly taken into account. In principle, the cluster model approach is especially well suited to study surfaces containing point defects, whereas the periodic approach will be the ultimate choice to represent a perfect, infinite surface. In spite of these particularities one must be aware that the properties of adsorbed metal atoms may be largely influenced by the coverage. Hence, embedded-cluster models are representative of low coverage situations whereas different coverages ranging from moderate to large can be described using periodic boundary conditions. In the present work both approaches have been used to represent the interaction of Pd atoms with the relaxed α-$Al_2O_3(0001)$ surface.

A. Embedded-cluster model approach

The low symmetry of corundum together with the existence of a very large relaxation of the Al-terminated surface make it difficult to construct a cluster following the usual procedure employed in representing nonpolar surfaces of simple cubic systems.[23,25–29] The ideal, undefective MgO(100) surface is a prototype of such a simple system.[12] In order to construct a single cluster model representation of the relaxed α-$Al_2O_3(0001)$ surface the following strategy was used. First, we used a special feature of the CRYSTAL 98 code[33] to construct a large sphere of $\sim$9000 atoms that is centered in one aluminum site and has all Al and O atoms in the bulk position. From this large sphere a semisphere with an Al-terminated surface was cut. Next, the radius of the resulting semisphere was varied so that the total charge arising from the Al^{3+} and O^{2-} ions included in the semisphere is zero. Surface relaxation was finally introduced in the model using results from previous all-electron DFT calculations within the Becke-Lee-Yang-Parr (B3LYP) (Refs. 34 and 35) exchange-correlation functional carried out on a two-dimensional periodic model of the α-$Al_2O_3(0001)$ surface containing nine layers equivalent to three Al-O-Al units. The displacements of the four outermost layers thus obtained are first layer (Al) $= -0.72$; second layer (O) $= -0.01$; third layer (Al) $= -0.01$; fourth layer (Al) $= +0.16$ Å. Hence, the first to second layer spacing is reduced by 0.72 Å (-85%), the second to third layer distance is kept constant, the third to fourth layer distance is reduced by 0.17 Å (-35%), and the distance from the fourth to the fifth layer increases by 0.16 Å ($+19\%$). These results remain almost unchanged when going from the nine-layer to a 15-layer slab.[15] Similar results have been reported by Baxter *et al.*[13] and by Verdozzi *et al.*[21] using thicker slabs and either LDA or GGA. In particular, displacements of -87%, $+3\%$, -42%, and $+19\%$ have been reported for a slab model containing up to 18 Al-O-Al units. The final cluster model thus constructed contains a total of 2395 centers distributed in three regions. The first region contains 23 Al and O atoms, which are explicitly treated. The second shell includes 18 total ion potentials[36] (TIP's) that are added to avoid spurious polarization of the outer cluster oxygen atoms.[32] Finally, the third region contains 2354 point charges with values of $+3$ and -2 for cations and anions, respectively. The array of point charges in the third region

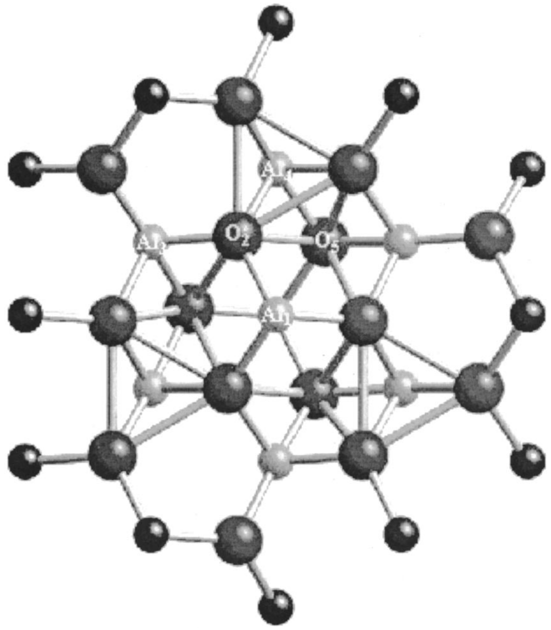

FIG. 1. Schematic representation of the $Al_{26}O_{15}$, TIP's included, cluster model used to represent the various adsorption sites on the Al_2O_3 (0001) surface. Large spheres represent anions and small light spheres the cations that were treated all-electron during the computation procedure. Al^{3+} TIP's are represented as small dark spheres. Notice that the seven Al_5 atoms are not visible in this perspective because they are located exactly below the Al_1 atoms.

provides an adequate representation of the electrostatic or Madelung potential. The Madelung potential on the central Al atom of a complete neutral sphere is −36.7 eV, in good agreement with the exact value of −36.6 eV obtained from the Ewald summation. Similarly, the Madelung potential in O atoms surrounding the cluster central Al atoms is +26.5 eV, which is very close to the exact value of +26.4 eV obtained from the Ewald summation. The Madelung potential on cation and anion surface sites of corundum represented by the semisphere model is reduced to −32.3 and +22.0 eV, respectively, in agreement with the results obtained from slab calculations. It is important to point out that these values of Madelung potential at the surface sites correspond to the ideal unreconstructed surface. Surface relaxation decreases the first to second layer distance considerably and the resulting Madelung potential at Al- and O-surface sites becomes now −34.0 and +28.3 eV, respectively, closer to the bulk value. The TIP is described as a pseudopotential mimicking an Al^{3+} cation. The first and second regions of the α-$Al_2O_3(0001)$ are schematically shown in Fig. 1. The small light spheres represent the eight Al sites included in the cluster, the large spheres represent the anions, and, finally, the small dark spheres correspond to the 18 TIP's.

Using the above-described cluster model, five different sites of the relaxed α-$Al_2O_3(0001)$ surface have been considered for Pd adsorption. These sites are also illustrated in Fig. 1 and labeled with a letter and number indicating the type of atom in the surface and atomic layers, respectively. Because of the very large relaxation of the Al topmost layer, the Al_1 and O_2 can be regarded as top sites while Al_3, Al_4, and O_5 are hollow sites. All electrons of Al and O sites were explicitly treated by means of 6−31G and 6−31+G*—including diffuse and polarization function basis sets, respectively. For the palladium atom, the 28 inner electrons were included in the LANL2 relativistic effective core potential[37] and the LANL2DZ basis set was employed to describe the $4s^2\ 4p^6\ 4d^{10}$ valence electrons. TIP's for Al^{3+} were also described by means of the Hay and Wadt[37] effective core potentials. The perpendicular distance of the palladium atom to each of these adsorption sites was optimized with respect to the B3LYP energy using the GAUSSIAN 98 package.[38] In some cases, a partial geometry optimization involving the substrate atoms near the metal adatom has been carried out. The effect of this partial geometry optimization on the distance of Pd above the surface and on the adsorption energy is further compared to cluster calculations where the substrate is allowed to relax. For comparison purposes, key calculations were also carried out using a different exchange-correlation functional and/or explicitly correlated wave functions (see below). All calculated interaction energies have been corrected for possible basis set superposition errors using the standard counterpoise method.

B. Periodic approach

In order to model the extended nature of the Pd/Al_2O_3 system, periodic 3D DFT calculations were carried out using the VASP 4.4.3 code.[39–41] These periodic calculations were performed for $\frac{1}{3}$ ML Pd coverage. In these series of calculations, the energy has been obtained using the GGA implementation of DFT proposed by Perdew *et al.*[42] Ultrasoft pseudopotentials[43] were employed to remove the core electrons from the calculation and a plane-wave basis set was used opposite the localized Gaussian-type orbital basis functions utilized in the cluster calculations. The cutoff energy for the plane waves was 337 eV and the Monkhorst-Pack set of four k points was used. A rhombic prism unit cell belonging to the hexagonal system was used to represent the Al-terminated surface and a vacuum width of 10 Å was allowed between the slabs. In order to select the thickness of the slab, two different possibilities were considered: 18 and 12 layers (30 and 20 atoms per unit cell). The corresponding slabs were partially optimized allowing the top outermost six layers to relax. The variations in the interplanar distances for the outermost layers are 0.118, 0.876, 0.259, and 1.016 Å for the 18-layer thick slab, and 0.118, 0.870, 0.266, and 1.011 Å for the 12-layer thick slab. In view of these results, and with the aim of speeding up the calculations, the smaller 12-layer thick unit cell was chosen to represent the surface. Notice, on the other hand, that in percentage terms, these values are virtually identical to those obtained from previous DFT calculations and described in Sec. II A: first layer (Al): −86%; second layer (O): +4%; third layer (Al): −48%; fourth layer (Al): +21%. Next, GGA calculations were carried out for the adsorption of palladium above surface sites already described with and without relaxation of up to six substrate layers.

TABLE I. Selected properties of Pd adsorbed on the different sites of the cluster model representation of α-Al_2O_3(0001) depicted in Fig. 1. The adsorption energies are calculated with respect to the separated systems and include the counterpoise correction (see text). All properties in this table have been obtained using the hybrid B3LYP or the PW91 form of the GGA exchange-correlation functionals.

	Adsorption site				
	Al_1	O_2	Al_3	Al_4	O_5
B3LYP					
$d_{\text{Pd-surface}}$ (Å)	2.539	2.123	1.961	1.927	2.048
q_{Pd} (e^-)	−0.083	−0.134	0.168	0.140	0.143
$-E_{\text{ads}}$ (eV)	0.44	0.51	0.12	0.30	0.42
PW91					
$d_{\text{Pd-surface}}$ (Å)	2.493	2.063	1.960	1.928	1.960
$-E_{\text{ads}}$ (eV)	0.70	0.86	0.47	0.69	0.77

III. THE EMBEDDED-CLUSTER MODEL APPROACH DESCRIPTION OF THE Pd/Al_2O_3 SYSTEM

In this initial set of calculations only the distance of Pd above each site of the relaxed α-Al_2O_3 has been optimized, leading to R_e, and the adsorption energy computed as

$$E_{\text{ads}}=E(\text{Pd}-\text{cluster})-E(\text{cluster})-E(\text{Pd}). \tag{1}$$

However, we have to remark that an additional complication in the determination of the adsorption energy with quantum-chemical methods based on atomic-orbital basis sets is the occurrence of the so-called basis set superposition error (BSSE). In general the BSSE is important in weak interactions only but in the special case of oxide surfaces the diffuse nature of the oxide anion results in BSSE's of several tenths of an eV.[12,23,25–29] Therefore, only the BSSE corrected adsorption energy computed following the standard Boys-Bernardi counterpoise method[44] is reported in the different tables. This BSSE corrected adsorption energy is computed as

$$E_{\text{ads}}=E(\text{Pd}-\text{cluster})-E(\text{cluster}+\text{Pd basis at } R_e) -E(\text{Pd}+\text{cluster basis at } R_e). \tag{2}$$

A summary of relevant calculated values is reported in Table I.

The first striking result is that computed adsorption energies for cationic and anionic sites are remarkably close. This is at variance of previous results for Pd on MgO (Refs. 23, 27, and 28) and provides a solid indication that the nature of the metal-oxide interface strongly varies with the nature of substrate, consistent with results recently reported for the interaction of Pd on rutile.[24,26] The present results show that there is a preference for adsorption of palladium directly above surface aluminum and oxygen atoms (sites Al_1 and O_2) and also on the hollow site labeled O_5. The calculated adsorption energies for these three sites are in the 0.4–0.5-eV range. Moreover, additional calculations show that the calculated adsorption energies are also rather independent of the basis set, provided a rather extended basis set is used and results properly corrected to avoid basis set superposition errors. Likewise, it is found that the interaction energies do not strongly depend on the choice of a particular cluster model design, i.e., Al- or O-centered cluster models of similar size lead to almost the same adsorption energies. It is worth pointing out that adsorbate-induced surface relaxation may allow Pd to penetrate further below the physical surface and, hence, to increase the interaction energy. The distances from the palladium atom to the top aluminum layer on the substrate surface are close to 2 Å except for the Al_1 site where the Pd-Al_1 distance is about 2.5 Å.

The quite small values of the interaction energy of Pd with the different sites of the corundum surface suggest that chemical bonds are not formed at this metal-oxide interface. Information about the chemical nature of the interaction can be obtained from several theoretical techniques such as the Mulliken population analysis. However, one must caution that this analysis suffers from serious drawbacks in the description of oxides and related systems.[45] In fact, the Mulliken net charge on the substrate atoms strongly varies with respect to the atomic basis set. Using the basis set described above leads to negative charges in the central aluminum atom. This is a clear artifact arising from the rather extended character of the oxygen basis set. Using a rather more contracted basis[46] the charge distribution is much more reasonable and close to those obtained in a periodic B3LYP calculation for the bulk using the same basis and the CRYSTAL code. The calculated charges on Al and O—+2.1 and −1.4, approximately—are still quite far from the full ionic limit. The strong variation of the Mulliken charges with the basis sets prevents using them to extract physical information for these systems. We must insist on the fact that the use of more sophisticated techniques for analysis of the chemical bond point towards a nearly full ionic description of corundum.[32,47,48] Contrary to the situation for the net charges on Al and O just described, the net charge on Pd is almost independent of the atomic basis set. In fact, both basis sets predict an almost negligible net charge on Pd. Consequently, the charge transfer between the palladium atom and the substrate is either negligible or fairly small, in agreement with suggestions from experimental work.[10] Nevertheless, the dependence of the net charges on the atomic basis sets prompted us to carry out more detailed analyses of the interaction between Pd and the corundum surface. First, we rely on the use of a dipole moment curve for the motion of the adsorbate perpendicular to the surface. It has been shown that analyses of dipole moment curves provide unbiased information about the degree of ionicity of a given chemical bond.[49,50] The slope of the dipole moment curve has been found to be independent of the distance from the adsorbate to the oxide substrate near the minimum of energy, and it is very small. Thus, it may be used as other evidence for small charge transfer between the palladium atom and the alumina surface. The picture arising from the dipole moment curve is supported by the constrained space-orbital variation (CSOV) analysis.[51–53] The CSOV technique was initially designed to decompose the Hartree-Fock energy of two interacting units and has been recently extended to analyze B3LYP and other DFT energies as well.[54] Due to technical reasons, the CSOV analysis of the interaction of Pd on the Al_1 and O_2 sites of α-$Al_2O_3(0001)$ has been carried out using a somewhat smaller cluster. Nevertheless, the interaction energies computed for this reduced model are very close to those obtained for the larger cluster. For the interaction above the Al_1 site the initial Pauli repulsion (0.54 eV) between the frozen densities of Pd and the cluster model is offset by the sum of the various bonding contributions. First, we note that the intraunit polarization contribution from the substrate is quite small, $\sim(-0.03$ eV), as expected for an ionic system. As expected, Pd polarization makes a larger contribution, -0.33 eV. Interunit charge transfer from the surface to Pd and from Pd to the surface provides the covalent contributions to the chemical bond. It is important to notice that these contributions are obtained when allowing the orbitals of a given unit to vary in the virtual space of the other unit and, hence, include the BSSE contribution. In general, the BSSE is small enough and can be neglected but in metal-support interactions, removing the BSSE is essential[27] and, therefore, additional analysis is required. In fact, charge transfer from the surface to Pd is -0.23 eV but this comes almost exclusively from the BSSE, i.e., the same energy lowering is found when adding the Pd basis to the substrate. This is at variance with the charge transfer from Pd to the surface energy contribution, which is significantly large, $\sim(-0.60$ eV), and almost unaffected by the BSSE, showing thus that this bonding mechanism is physically meaningful. Summing up the physical contributions results in a total interaction energy of $+0.54-0.33-0.60=-0.39$ eV. This is 20% smaller than the total interaction energy reported in Table I for the larger cluster, which is -0.50 eV. Nevertheless, the CSOV analysis clearly shows that Pd polarization and Pd to substrate charge transfer are the leading contributions to this metal-support interaction. This interpretation of the chemical interaction is quite different from that arising from Mulliken populations and from the analysis of the dipole moment curves. There are two reasons to explain this apparent contradiction. First, the energy contribution from a charge-transfer mechanism is not directly related to the actual extent of the charge transfer. The second reason concerns the magnitude of the total interaction, which is relatively small. The CSOV analysis shows that this picture also holds for the interaction of Pd above the O_2-surface site. Furthermore, this picture of the chemical interaction remains almost unchanged when a Hartree-Fock wave function is used opposite the B3LYP method. The bonding contributions are somewhat smaller but the bonding mechanism is qualitatively the same. This is in agreement with a previous analysis of the chemisorption bond for more conventional systems.[54]

Next, we consider the possible adsorbate-induced relaxation effects for the interaction of Pd above Al_1 and O_2 sites. This has been modeled by allowing some substrate atoms to relax, although in well-defined steps. For adsorption on the Al_1 site it is found that relaxation of the aluminum atom increases the adsorption energy by more than 0.47 eV. When the oxygen atoms nearest the Al_1 adsorption site are also allowed to relax, the adsorption energy increases again but only by 0.06 eV. The present results strongly suggest that adsorbate-induced relaxation effects play a very important role in determining the adsorption site. However, one must realize the cluster model representation of the surface may be inadequate to describe this phenomenon because it does not permit to fully consider the long-range effects of the adsorbate-induced substrate relaxation. Therefore, the effect of induced surface relaxation has been studied by means of a periodic approach including total-energy minimization with respect to the position of all atoms in the unit cell. This is described at length in the next section.

IV. THE PERIODIC APPROACH DESCRIPTION OF THE Pd/Al_2O_3 SYSTEM

Periodic GGA calculations were carried out to investigate in detail the adsorbate-induced relaxation effects that are predicted by the cluster approach. In order to analyze separately the effects of surface relaxation, two series of calculations were performed. In the first series (unrelaxed), the surface atoms were kept frozen at the positions obtained from the surface optimization, and only the Pd-surface distance was minimized. In the second series of calculations (relaxed), both the Pd and the six outermost surface layers were optimized. Results concerning both adsorption energies and distances between the Pd atoms and the surface (defined by the outermost aluminum plane) are reported in Table II for $\frac{1}{3}$ ML coverage.

For the unrelaxed calculations, the interaction of Pd with the O sites appears to be larger than for the different Al sites. The relative energies are in qualitative agreement with those predicted by the cluster calculations although here the O_2 site is found to be clearly preferred. On the other hand, and as expected, adsorption energies increase by allowing the surface to relax. Nevertheless, the order of adsorption site stability found in the unrelaxed calculations is basically preserved; the preferred sites are those labeled as O_2 and O_5. There is also a significant energetic gain in the Al_3 and Al_4 sites, while the adsorption atop the Al_1 surface aluminum atoms is less affected by surface relaxation. The changes in the substrate geometrical parameters caused by adsorbate-induced relaxation of the outermost surface layer are also reported in Table II. The palladium to surface distance decreases slightly for site Al_1 (0.05 Å), and noticeably for the other sites: $\sim$0.3–0.5 Å. This differential behavior can be understood by realizing that this geometrical parameter cor-

TABLE II. Adsorption energy with respect to the noninteracting units, palladium-surface distances, and optimized *z* final position of the Al_1 atom related to their initial positions induced by deposition of the metal as obtained from GGA periodic calculations on a slab model of the α-$Al_2O_3(0001)$ surface.

	Adsorption site				
	Al_1	O_2	Al_3	Al_4	O_5
Unrelaxed					
$d_{\text{Pd-surface}}$ (Å)	2.444	2.081	1.976	1.923	1.958
$-E_{\text{ads}}$ (eV)	0.79	1.10	0.78	0.90	1.02
Relaxed					
$d_{\text{Pd-surface}}$ (Å)	2.396	1.726	1.518	1.414	1.697
$-E_{\text{ads}}$ (eV)	0.88	1.41	1.04	1.22	1.32
$\Delta(Al_1^{\,i}-Al_1^{\,f})$ (Å)[a]	0.170	0.312	0.343	0.373	0.300

responds precisely to the distance between Pd atoms and the outermost layer of aluminum atoms (Al_1). In fact, what is obtained from the calculations is that upon Pd adsorption there is a selective displacement of this surface layer. As shown in Table II this displacement is ~0.30 Å for all sites except for Al_1, where a smaller, 0.17-Å effect is found. The origin of these displacements can be traced with the help of the projected density-of-states (DOS) curves and electron-density maps obtained from the GGA calculations for the most favored site, i.e., the O_2 position, cf. Figs. 2 and 3, respectively. Examination of DOS curves reveals the insulator character of the substrate and the almost neutral character of the adsorbed Pd atom. The calculated valence electron density plotted in Fig. 3 provides further support to the local character of the interaction of Pd with the α-$Al_2O_3(0001)$ surface. This plot suggests that the main interaction involves directly the surface oxygen atom only. The electron density of the aluminum atoms seems to remain practically unperturbed by the presence of Pd atoms near the surface. However, when the electron-density differences are carefully examined, a clear gain of electron density in the region around the surface aluminum atoms appears (middle of Fig. 3). This density comes from the palladium atom as clearly shown at the bottom of Fig. 3, where the regions with a lowering of the electron density are plotted. Variations in electron density around the surface oxygen atoms are also observed. However, it should be noticed that both positive and negative differences are present, and therefore, they correspond mainly to a repolarization of the oxygen cloud induced by the palladium atom. These results are in agreement with the CSOV analysis carried out with the cluster calculations in which a significant component arising from a charge transfer from the transition metal to the surface was found. This charge transfer allows an easy interpretation of the surface

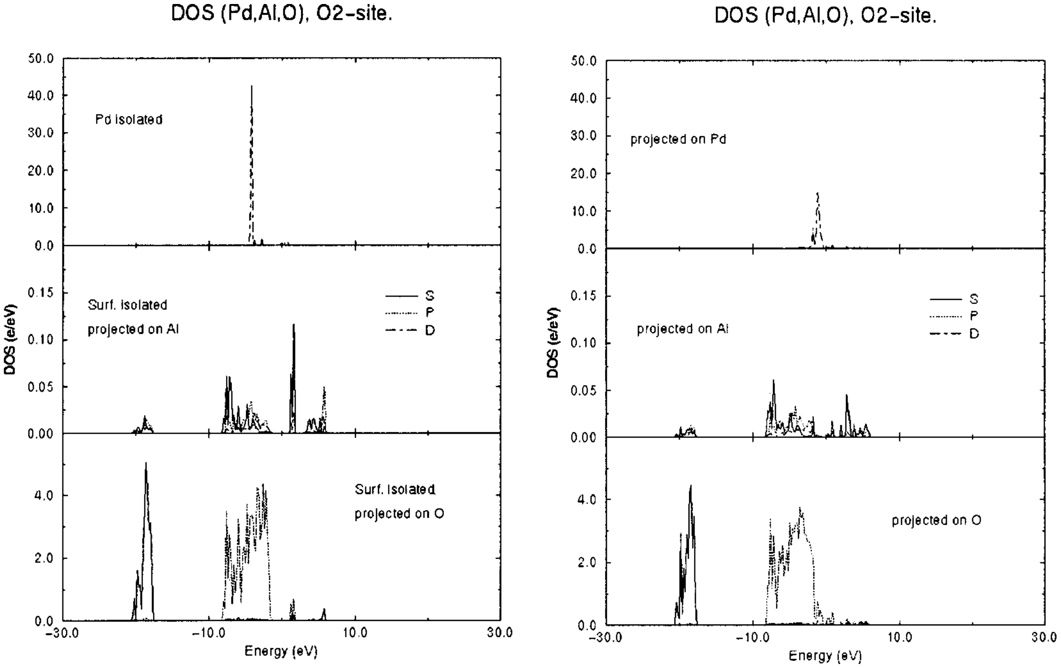

FIG. 2. GGA density of states for $\frac{1}{3}$ ML of palladium adsorbed on O_2 sites of the Al_2O_3 (0001) surface; top: projected on palladium, middle: projected on aluminum, and bottom: projected on oxygen.

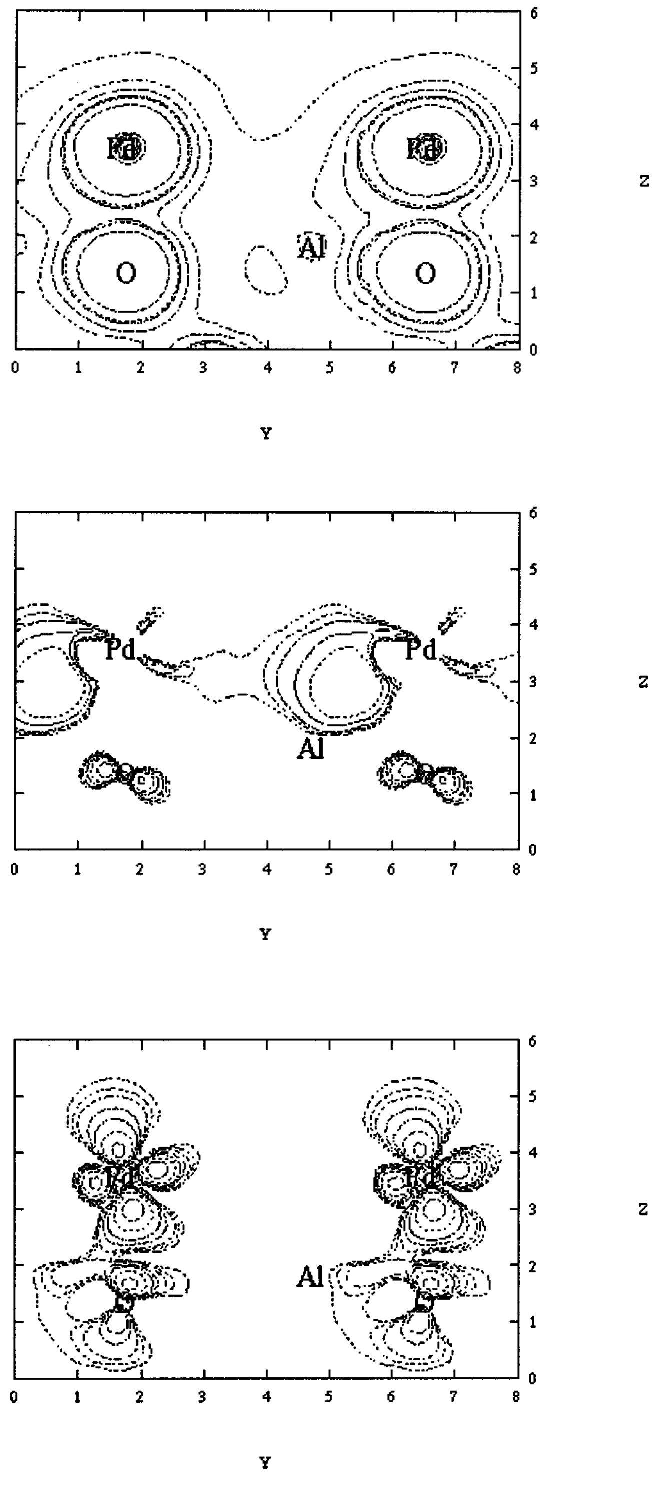

FIG. 3. Calculated GGA valence electron density for $\frac{1}{3}$ ML of palladium interacting with the O_2 sites of the Al_2O_3 (0001) surface. Top: total densities. The difference between the total and isolated surfaces and Pd atom densities are reported in the middle (positive, increased density) and the bottom (negative, decreased density) of the figure. Isodensity lines are 15, 100, 200, 350, 400, and 800 for the total and 6, 10, 15, 30, 50, 100, and 200 for the differences.

relaxation observed in the GGA periodic calculations. In fact, bearing in mind the strong ionic character of α-Al_2O_3, a decrease of the positive charge in the surface aluminum atoms decreases the electrostatic interaction and necessarily involves a relaxation of the Al-O distances just as predicted by the present calculations.

An important point concerns the magnitude of the adsorption energies, which for a fixed surface model fall in the 0.78–1.10-eV range. These are considerably larger than those computed using the cluster approach. This difference can be due to the use of a different exchange-correlation functional and to a different coverage situation. In order to understand the origin of these differences the cluster calculations were repeated but using the same GGA exchange-correlation functional. Technically, these correspond to the use of Perdew-Wang (PW91PW91) in the GAUSSIAN code. The GGA cluster calculations agree with the unrelaxed periodic ones, the adsorption energies being in the 0.5–0.9-eV range, systematically 0.2–0.3-eV smaller than the ones obtained from the periodic calculations. The origin of this difference reflects either a deficiency of the cluster model or a coverage effect. In order to rule out the first possibility, calculations for the interaction of Pd with the O_2 site were carried out for an embedded $O_{22}Al_7$ cluster model centered precisely at the O_2 site. The GGA and B3LYP adsorption energies for Pd on the O_2 site of this cluster differ by as much as 0.05 eV from those obtained using the Al_1-centered cluster. Clearly, the systematic differences between periodic and cluster calculations have to be attributed to the different coverage situation. However, an additional factor concerns the fact that the structure of isolated surfaces of these models is not strictly the same. Both of them are relaxed surfaces, but coherently, obtained with different approaches (CRYSTAL and VASP). These small differences result in the fact that a fully meaningful comparison cannot be performed.

The analysis above permits us to understand the differences in adsorption energy corresponding to the Al_1 and O_2 sites. The B3LYP and GGA cluster calculations for the unrelaxed surface indicate that the preference for the O_2 site is quite small, 0.07 and 0.16 eV, respectively. For the same unrelaxed surface, this difference is doubled when going from the cluster to the periodic calculation, cf. Tables I and II. Since the adsorption energy for Pd on the O_2 site obtained from different clusters (see above) is almost the same, we have to conclude that this enhancement of the adsorption energy is a direct consequence of the coverage. This interpretation is supported by the data reported in Table II that show that the adsorption energy difference between these two sites is doubled again when explicitly including the adsorbate-induced surface relaxation. The reason for this new differential increment of the adsorption energy at the O_2 site lies in the bonding mechanism described in the previous sections. There is a noticeable charge transfer from Pd to the substrate, the charge is mainly transferred to the Al_1 atoms, the decrease in electrostatic interaction is the driving force for the displacement of the Al_1 layer, and this cannot occur when Pd is on top of the Al_1 site. To summarize, since with the exception of Al_1 all sites involve interaction with surface oxygen atoms, it appears clearly that Pd atoms would preferentially occupy O_2 sites, with some mobility around the hollow positions. According to these results, it is expected that upon increasing coverage the Pd atoms will be located mainly on top of the O_2 sites. However, one must consider the fact that increasing coverage can indeed change the order of stability. In fact, recent work by Verdozzi *et al.*[21] has shown that for Pt on α-$Al_2O_3(0001)$ there is indeed such a coverage dependence of the preferred adsorption site. These authors have found that for $\frac{1}{3}$ ML the preferred site is O_2,[21] but that for 1 ML the most stable phase is for Pt atoms on top of Al atoms. Given the chemical similarity between Pd and Pt this possible preferred-site coverage dependence has also been explored. To this end periodic GGA calculations for 1 ML Pd on α-$Al_2O_3(0001)$ have been carried out. Following the strategy used in the previous LDA calculations for Pt on α-$Al_2O_3(0001)$,[21] three different sites have been considered: Al (on top of aluminum atoms), O (on top of oxygen atoms), and H (O_5 hollow sites). The calculations show at this coverage the Al sites are more stable than the O ones by 0.23 eV, and they are in turn also slightly more stable that the hollow sites (0.21 eV). These values agree with those found for Ag on sapphire from LDA calculations: Al sites are favored by 0.07 eV/at. over O, which in turn is favored by 0.03 eV/at. over H sites.[21] Although these results seem to suggest that at this coverage Pd atoms prefer to bind Al centers, it should be noted that only one of the three Pd atoms is directly bound to Al atoms while the remaining two are actually bound to oxygen triads. The relative stabilization of the Al site can be understood taking into account that upon adsorption at 1 ML, the outward relaxation of the outermost Al atom is even larger than for $\frac{1}{3}$ ML: 0.54 Å. This relaxation leads to a significant buckling of the metal overlayer and permits us to better accommodate the Pd-Pd interatomic distances.

V. CONCLUSIONS

The $Pd/Al_2O_3(0001)$ interface at low Pd coverage has been studied by a variety of theoretical methods and approaches. Using different surface models—finite embedded-cluster models versus periodic approaches—and different computational models—hybrid B3LYP versus standard GGA exchange-correlation functionals—has permitted us to reach a quite detailed understanding of the Pd/α-Al_2O_3 interface. Neglecting adsorbate-induced relaxation effects all results are roughly consistent. Moreover, both cluster and periodic approaches predict that a strong relaxation of the substrate is induced by the presence of the palladium atom above the oxide surface. However, qualitatively different results are obtained when the substrate is allowed to relax in response to the presence of the adsorbate. This difference has been attributed to the impossibility to describe a fully relaxed substrate by means of a reasonable finite cluster model. The GGA periodic calculations including substrate relaxation predict that the interaction is stronger on top of the anionic sites. In particular, for $\frac{1}{3}$ ML Pd, metal deposition is predicted to occur at the O_2 sites as computed for Pt interaction with the same surface.[21] This site is only slightly more stable than other hollow sites (in particular the O_5 site), suggesting a certain degree of surface mobility of Pd atoms at low coverage. However, increasing the coverage up to 1 ML results in a change of the preferred site similar to that also predicted for Pt on the same substrate. Finally, it is worth pointing out that the CSOV analysis of the adsorption bond carried out on a surface cluster model suggests that the interaction is dominated by the Pd polarization with a noticeable contribution from the charge transfer from Pd to the surface. This picture is fully consistent with the analysis of the electron-density maps obtained in the periodic calculations

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