

Surface model and exchange-correlation functional effects on the description of Pd/ α -Al₂O₃(0001)

Cite as: J. Chem. Phys. **116**, 1684 (2002); <https://doi.org/10.1063/1.1429642>

Submitted: 27 August 2001 . Accepted: 31 October 2001 . Published Online: 10 January 2002

J. R. B. Gomes, F. Illas, N. Cruz Hernández, J. F. Sanz, A. Wander, and N. M. Harrison



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

The structural and electronic properties of nanostructured Ce_{1-x-y}Zr_xTb_yO₂ ternary oxides: Unusual concentration of Tb³⁺ and metal ↔ oxygen ↔ metal interactions

The Journal of Chemical Physics **122**, 154711 (2005); <https://doi.org/10.1063/1.1883631>

Modification of the surface electronic and chemical properties of Pt(111) by subsurface 3d transition metals

The Journal of Chemical Physics **120**, 10240 (2004); <https://doi.org/10.1063/1.1737365>

An all-electron numerical method for solving the local density functional for polyatomic molecules

The Journal of Chemical Physics **92**, 508 (1990); <https://doi.org/10.1063/1.458452>

Lock-in Amplifiers
up to 600 MHz



Surface model and exchange-correlation functional effects on the description of Pd/ α -Al₂O₃(0001)

J. R. B. Gomes and F. Illas^{a)}

Departament de Química Física i Centre de Recerca en Química Teòrica, Universitat de Barcelona, C/ Martí i Franquès 1, E-08028 Barcelona, Spain

N. Cruz Hernández and J. F. Sanz

Departamento de Química Física, Facultad de Química, Universidad de Sevilla E-41012 Sevilla, Spain

A. Wander

CLRC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom

N. M. Harrison

Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, United Kingdom

(Received 27 August 2001; accepted 31 October 2001)

The interaction of Pd with the Al-terminated α -Al₂O₃(0001) surface has been investigated using an embedded cluster model and periodic-supercell approaches. Furthermore, several treatments of electronic exchange and correlation within density functional (DF) theory have been employed including generalized gradient approximation (GGA) and hybrid exchange functionals. In the periodic calculations the influence of pseudopotentials and basis sets have also been investigated by comparing GGA results obtained using all electron basis set and pseudopotential plane-wave approaches. For a given choice of the exchange-correlation functional and for a fixed substrate, the cluster and slab models predict nearly the same structural parameters and adsorption energies. All structural models reproduce the general trend for the interaction of Pd with the α -Al₂O₃(0001) surface, which is that there is a slight preference for adsorption above surface sites sitting directly above oxygen atoms either from the second or fifth layer. However, significantly larger differences exist when comparing different DF methods within a given surface model. The cluster and periodic slab models predict a large adsorbate-induced relaxation with a similar description of the metal-oxide interface provided a minimum number of surface layers is included in the optimization procedure. © 2002 American Institute of Physics. [DOI: 10.1063/1.1429642]

I. INTRODUCTION

Understanding the growth of metal clusters and metal thin films on an oxide substrate is a key issue in a variety of technological applications. The initial steps of the metal atom deposition on the oxide surface are responsible for the resulting morphology of the metal overlayer. This is of considerable interest in many applications ranging from metal-ceramic-based gas sensors to microelectronic devices or oxide-supported transition metal catalysts.¹ Likewise, the affinity of a single metal atom towards a given adsorption site of an oxide surface strongly affects the properties of the supported catalyst and its surface chemistry. Alumina is widely used as a support for ultra-thin metal deposition² and also for metal supported catalysts.¹ Most often, γ -alumina is used as support because of its acid-base properties. However, in some other cases, as in the industrial oxidation reaction of ethylene to produce oxyrane, a virtually inert support is necessary and α -alumina becomes an obvious choice.³

Recently, the adsorption of palladium on the α -Al₂O₃ surface has been studied by means of secondary ion mass

spectrometry in static mode, SSIMS, and by thermal programmed desorption, TPD.⁴ From these studies it is predicted that Pd grows on α -Al₂O₃ following either the Stranski–Krastanov, SK, model, completion of a monolayer plus 3D crystallite growth, or the three-dimensional Volmer–Weber, VW, mechanism. It is suggested that at low coverage Pd–Al bonds are formed first and that Pd–O bonds appear to be formed in a subsequent step. During the adsorption stage, a tiny negatively charged palladium is observed but the Pd atoms remain essentially neutral during deposition. Palladium clusters in the 1–3 Å thickness range exhibit a work function that remains at a constant value of 6.5 eV on α -Al₂O₃. The very recent experiments of Pang *et al.*⁵ using noncontact atomic force microscopy, NC-AFM, show adsorbed Pd clusters which are ~30–40 Å in diameter and ~2–3 Å in height above the α -Al₂O₃(0001) surface. These authors also suggest that their observations are consistent with either SK or VW growth modes. Similar findings have been previously reported for experiments that use aluminum oxide thin films grown on a metal support such as NiAl^{6–8} instead of well-characterized single crystal corundum surfaces.

The experimental and technological interest of the alumina-supported catalysts has triggered a number of theo-

^{a)} Author to whom correspondence should be addressed. Electronic mail: f.illas@qf.ub.es

retical studies aimed at understanding the nature of the metal–oxide interaction and predicting the active sites for metal cluster adsorption. Verdozzi *et al.*⁹ recently reported results from a local density approximation (LDA) study of the adsorption of Ag and Pt atoms on the Al-terminated α -Al₂O₃(0001) surface. These authors found that at low coverage, Ag atoms are preferentially adsorbed above surface aluminum atoms while Pt is adsorbed above the outermost oxygen atoms. However, for a 1 ML geometrical coverage, the LDA predicts that both metals have a slight preference for direct adsorption on surface aluminum atoms. Zhang and co-workers¹⁰ used LDA and the generalized gradient approximation, GGA, to study the thermodynamics of the interaction of Nb also with the α -Al₂O₃(0001) surface. Depending on the oxygen partial pressure, they found that the Nb/ α -Al₂O₃ interface formation can reverse the order of stability leading to an O-terminated surface which is normally less stable than the Al-terminated surface. Nevertheless, two recent theoretical studies claim that even under high oxygen partial pressure the Al-terminated surface is stable.^{11,12} One must note that these results contrast with the conclusions of several works summarized in the review by Renaud.¹³ The interaction of Ag with the α -Al₂O₃(0001) surface is currently being studied by Zhukovskii *et al.*¹⁴ using a periodic supercell Hartree–Fock approach including electronic correlation effects by means of a *a posteriori* correlation functional. Similarly, the nature of the interaction between Pd and the α -Al₂O₃(0001) has been investigated by Gomes *et al.*¹⁵ using a cluster model and the constrained space orbital variation method. The cluster results suggest a large adsorbate-induced relaxation that has been confirmed by the same authors through periodic supercell GGA calculations within a plane wave basis set. Using the same periodic supercell GGA approach Hernández and Sanz have analyzed the interaction mechanism of Cu, Ag, and Au with the α -Al₂O₃(0001) surface.¹⁶ Lodziana and Norskov have also used this later approach in recent research involving different terminations and stoichiometries of the α -Al₂O₃(0001) surface.¹⁷ The variety of possible surfaces (Al- or O-terminated), surfaces models (embedded cluster or periodic supercell), and exchange-correlation approximations (Hartree–Fock or various Density Functional treatments) necessitates a systematic investigation of the effects of both material and computational models before reliable conclusions can be drawn. The importance of establishing the influence of these approximations is also manifest in previous studies of the interaction of transition metals on the surface of simple oxides. The previous work of Lopez *et al.*¹⁸ on the interaction of Pd with MgO(100) strongly suggests that in DFT methods the influence of the choice of exchange-correlation functional can be very significant. For the adsorption of Cu on MgO(100) the validity of the cluster model has been demonstrated explicitly. Embedded cluster models of increasing size indicate that, at least for this simple oxide, results converge rather quickly with respect to the number of atoms included.¹⁹ Clearly, α -Al₂O₃(0001) is a much more complicated substrate and it is not obvious that this system could be properly described by means of a cluster model. Establishing the validity of a local description is of great

importance as it facilitates modeling of the ubiquitous surface inhomogeneities and point defects which are believed to be active sites for metal growth.¹ For such problems the cluster model and a localized description are often significantly more convenient than large scale periodic supercell calculations. In comparing various models and making contact with experiment a complete treatment of surface relaxation is important. For this the cluster model must be sufficiently large and periodic supercell models must use large enough supercells and be based on sufficiently thick slabs. In general these questions can only be addressed by systematic studies of the variation of particular results with model size. However, one might expect that the interaction of Pd with α -Al₂O₃(0001), which induces a large substrate relaxation,¹⁵ will converge more slowly with respect to model size than Pd on a simple oxide surface such as MgO.

In this work we present a detailed and systematic study of the interaction of Pd atoms with different sites of the relaxed, clean, Al-terminated, α -Al₂O₃(0001) surface using a variety of structural models. Both finite cluster and periodic supercell models have been used to represent the corresponding interface. In addition, two periodic supercell approaches have been used. In the first, a slab periodic in two dimensions but finite in the third dimension is used, and in the second approach such slabs are also repeated periodically in the third dimension but are separated by a vacuum gap sufficiently large to make slab–slab interactions negligible. This latter approach is particularly convenient when a plane wave basis set is employed and it is very widely used in solid state physics, especially to describe metals and metallic surfaces. In all cases, the surface relaxation induced by the metal deposition has been explicitly taken into account. The article is organized as follows: In Sec. II the different surface models are described. In Sec. III we discuss the various computational approaches. In Sec. IV we present the whole set of results obtained with the different computational techniques within the cluster model or periodic description of the Pd/Al₂O₃ system for a fixed substrate. In Sec. V we describe the adsorbate-induced surface relaxation, and comparison to experimental results, where available, is reported in Sec. VI. Finally, our conclusions are presented in Sec. VII.

II. SURFACE MODELS OF THE Al-TERMINATED α -Al₂O₃(0001) SURFACE

In the present work, the α -Al₂O₃ surface was represented by two extreme ideal models that are also representative of two different ways of thinking about surface phenomena. In the first, one focuses in the local properties such as the interaction of an adsorbate with the surface at very low coverage. Here, the surface is modeled by a finite number of atoms that are quantum mechanically treated. This cluster model is embedded in an environment which accounts for short and long range interactions with the remainder of the crystal. In the second case one imagines a perfect, defect-free, surface infinite and periodic in two dimensions. The resulting model is slab periodic in two dimensions and of limited thickness in the third. As discussed above, the slab may then be subject to vacuum boundary conditions in the

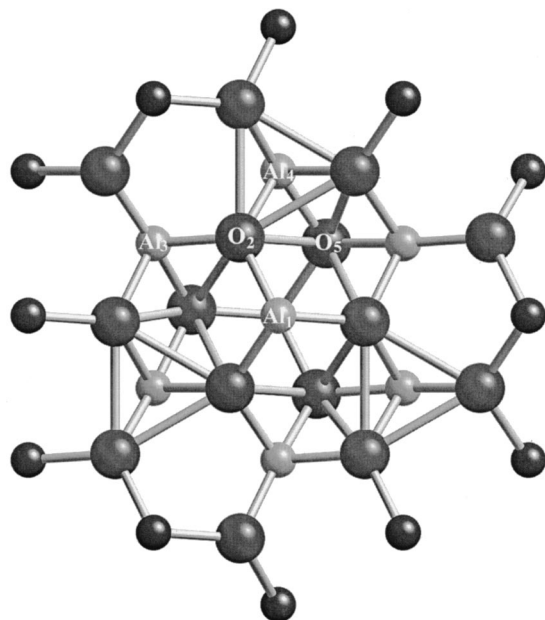


FIG. 1. Schematic representation of the $\text{Al}_{26}\text{O}_{15}$, TIPS included, cluster model used to represent the various adsorption sites on the $\alpha\text{-Al}_2\text{O}_3(0001)$ surface. Large spheres represent anions and small light spheres represent the cations that were treated all-electron during the computation procedure. Al^{3+} TIPS are represented as small dark spheres. Fifth layer aluminum atoms are not shown because they are located exactly below the first layer aluminum atoms.

third direction or, for computational convenience, repeated periodically in the third direction with slabs separated by vacuum gaps.

The cluster model used to represent the alumina surface contains 2395 centers that are divided in three different regions as schematically illustrated in Fig. 1. The first region contains 23 atoms, 8 Al and 15 O, which are explicitly treated by a proper quantum mechanical method. The second shell includes 18 total ion potentials,²⁰ TIPs, that are customarily added to avoid spurious polarization of the outer cluster oxygen atoms.^{18,19,21,22} In this case the TIP consists simply of a pseudopotential mimicking an Al^{3+} cation, no basis functions are added to the TIP. Finally, the third region contains 2354 point charges with values of $+3|e|$ and $-2|e|$ for cations and anions, respectively. The array of point charges in the third region provides an adequate representation of the electrostatic potential in the cluster. Surface relaxation was explicitly introduced in this model; the vertical separation between the outermost surface layers was taken from previous work on the reconstruction of the clean and Al-terminated $\alpha\text{-Al}_2\text{O}_3$ surface calculated by periodic all-electron DFT.^{23–25} Further details about the setup of this cluster model can be found elsewhere.¹⁵ For the above-described cluster model, five different sites of the relaxed $\alpha\text{-Al}_2\text{O}_3(0001)$ surface have been considered for Pd adsorption. These sites are labeled as Al_1 , O_2 , Al_3 , Al_4 and O_5 , Al_1 denotes a surface site directly above an Al cation of the outermost atomic layer whereas O_2 denotes a surface site located directly above an oxygen anion in the second layer. The notation for the rest of sites follows the same logic, cf. Fig. 1. Because of the very large inwards relaxation of the Al

outermost layer in the Al-terminated of the clean $\alpha\text{-Al}_2\text{O}_3(0001)$ surface, the Al_1 and O_2 can be regarded as top sites while Al_3 , Al_4 and O_5 are hollow sites.

The periodic supercell calculations were all performed for a $\frac{1}{3}$ ML Pd coverage, i.e., one Pd atom per $(\text{AlO}_3\text{Al})_n$ unit cell, 3^*n being the total number of atomic layers in the slab. In the two-dimensional periodic calculations a nine-layer slab, with the same cell parameters used in our previous work,²⁵ was used to represent the alumina surface. In the three-dimensional periodic calculations, the same unit cell is used in order to facilitate comparison of the models. In this case a vacuum width of 10 Å was introduced between the repeated slabs. The resulting unit cell is a rhombic prism belonging to the hexagonal system. Notice that this structural model is not identical to that used in our previous three-dimensional periodic calculations and, hence, results in the tables are slightly different from those reported in Ref. 15.

III. COMPUTATIONAL MODELS

For the cluster calculations all electrons of Al and O atoms in the local region were explicitly treated by means of 6-31G and 6-31+G* standard Gaussian basis sets, respectively. The latter includes a diffuse and a polarization function of d symmetry. For the palladium atom, the 28 inner electrons were included in a relativistic effective core potential, ECP,²⁶ and the corresponding basis set employed to describe the $4s^24p^64d^{10}$ valence electrons was of double- ζ quality. These ECP and basis sets are usually referred to as LANL2 and LANL2DZ, respectively. The TIPs for Al^{3+} were also described by means of the Hay and Wadt effective core potentials.²⁶ With this cluster model two different sets of calculations were carried out to investigate the Pd/ $\alpha\text{-Al}_2\text{O}_3$ interface. In the first set of calculations only the perpendicular distance of the palladium atom to each of these adsorption sites was optimized and in the second set of calculations a partial geometry optimization involving the substrate atoms near to the metal adatom was carried out for Pd interacting with the Al_1 and O_2 adsorption sites. All cluster calculations were performed with the GAUSSIAN 98 package.²⁷

In order to study the effect of the level of theory in the study of the Pd/ Al_2O_3 interface, several exchange-correlation functionals were used. The density functional methods used in the cluster calculations are the GGA proposed by Perdew and Wang^{28,29} and two different hybrid schemes that follow the ideas of Becke.³⁰ The former is chosen because it is the default approach in many band structure computer codes whereas the hybrid approaches are increasingly used in molecular quantum chemistry. The hybrid methods used are B3LYP and B3PW91. These are very similar to the BLYP and BPW91 pure DFT methods which use the Becke's nonlocal exchange functional³¹ and either the correlation functional given by Lee, Yang, and Parr,³² based on the original work of Colle and Salvetti on the correlation factor,^{33,34} or the correlation functional proposed by Perdew and Wang.^{28,29} However, in the B3LYP and B3PW91 hybrid methods three parameters of the exchange functional are fit to reproduce experimental thermochemical data. The optimum mixing being found for $\sim 20\%$ Fock exchange in the

exchange functional. It is important to note that the B3LYP hybrid functional has found wide applicability in molecular calculation and that in particular it is able to reproduce the thermochemistry of molecules containing transition metal atoms although no transition metal compounds were included in the data set used in its construction.^{35–37} All adsorption energies calculated by means of cluster models have been corrected for possible basis set superposition errors using the standard counterpoise method.

The periodic calculations were performed by means of the CRYSTAL program,³⁸ for the pure two-dimensional periodic slab calculations, and VASP 4.4.3 code^{39–41} for the three-dimensional periodic calculations. Here, it is important to point out that these calculations use different basis sets and treatments of the core electrons. In the CRYSTAL code the Bloch functions are expanded in terms of Gaussian type orbitals, GTO, that have an identical form to those widely used in molecular quantum chemical calculations. In the VASP calculations the Bloch functions are expanded in a plane wave basis with a discrete set of K -vectors selected to have kinetic energy less than an energy cutoff. Both basis sets are aimed to expand the same Hilbert space and the same results must be obtained with either basis, provided it is extended enough and the same exchange-correlation functional is used. Results in the next section will provide strong evidence that this is indeed the case.

In the CRYSTAL calculations all electrons of the Al, O and Pd atoms are explicitly considered. The GTO basis sets used in the present study are similar but somewhat more extended than those used in the previous studies on the relaxation of the Al-terminated surface.^{24,25} Hence, using Pople's rather standard notation, the O and Al basis sets were of 8-511G and 8-711G quality, respectively. The Pd basis set was a 9-76311-631G quality, i.e., 9 s functions plus 5 sp and 3 d shells constructed from 7+6+3+1+1 and 6+3+1 contraction schemes, respectively.⁴² An auxiliary Gaussian basis set containing 20 even-tempered s -symmetry functions was used to fit the exchange correlation potential while the energy functional was integrated explicitly on an atom centered grid. Finally, the plane wave GGA periodic calculations have been carried out using ultrasoft pseudopotentials to represent the core electrons.⁴³ The cutoff energy for the plane waves was 337 eV and the Monkhorst–Pack set of four k points was used.

In order to have a clear-cut comparison between cluster and periodic calculations, the latter were carried out for a relaxed but fixed substrate and for a surface which was allowed to relax in response to the presence of Pd. In the first case only the distance of Pd perpendicular to the surface above each possible, high symmetry, active site has been considered. Adsorbate-induced surface relaxation was studied by allowing the vertical relaxation of the two outermost atomic layers in the CRYSTAL and VASP calculations, respectively. In the latter case, calculations were repeated by allowing the six outermost substrate layers to relax. However, no significant differences between the two final optimized structures were found. This is important because in the geometry optimizations with the two- and three-dimensional periodic slab models there is a Pd overlayer above each of the two

TABLE I. Effect of the substrate model used to study the interaction of a Pd atom with five different surface sites on the α -Al₂O₃(0001), calculated at the GGA level of theory. The oxide substrate is fixed and only the Pd to surface distance is optimized. The adsorption energies are calculated with respect to the separated systems and include the counterpoise correction. The 2D and 3D slabs refer to the CRYSTAL and VASP calculations, respectively. The last column collects the average between the different models and the standard deviation.

Property	Surface model				Average \pm deviation
	Site	2D slab	Cluster	3D Slab	
d (Pd-Surf)/Å	Al ₁	2.53	2.49	2.43	2.49 \pm 0.05
	O ₂	2.15	2.06	2.06	2.10 \pm 0.05
	Al ₃	2.06	1.96	1.97	2.00 \pm 0.05
	Al ₄	2.06	1.93	2.00	1.97 \pm 0.08
	O ₅	2.05	1.96	1.97	1.99 \pm 0.05
$-E_{\text{ads}}$ /eV	Al ₁	0.83	0.70	0.76	0.76 \pm 0.09
	O ₂	0.98	0.86	1.02	0.95 \pm 0.08
	Al ₃	0.65	0.47	0.66	0.59 \pm 0.11
	Al ₄	0.75	0.69	0.78	0.74 \pm 0.05
	O ₅	0.91	0.77	0.93	0.87 \pm 0.09

Al-terminated surfaces of the slab. The reason for this is to exploit the point group symmetry in the CRYSTAL calculations and at the same time use the same structural model in the three-dimensional periodic calculations. Notice that this implies a symmetric relaxation of the two outermost atomic layers in each of the two surfaces of the slab. The similarity between the optimized structures including just one Pd overlayer with the six outermost atomic layers with no up–down symmetry and those resulting from the symmetric relaxation of the two outermost surfaces indicates that the latter does not introduce any artifact in the model. Finally, we note that for a proper comparison between cluster and periodic approaches it is necessary not only to model the same physical surface but also to use the same approach to density functional theory. Hence, CRYSTAL and VASP calculations have been carried out by means of the GGA model and CRYSTAL calculations were indeed carried out for the B3LYP and B3PW91. The latter is exactly the same for both cluster and periodic calculations, however the LDA part of the correlation functional used in B3LYP cluster and periodic calculations is slightly different. The implementation of the LDA correlation in GAUSSIAN uses the functional defined in Eq. (3) of the paper by Vosko *et al.*⁴⁴ whereas CRYSTAL (and most of the plane wave band structure codes) use the functional defined in Eq. (5) of Ref. 44 (see also the discussion of this point in the papers by Martin and Illas).^{45,46}

IV. Pd ADSORPTION ON A FIXED α -Al₂O₃(0001) SURFACE

The first point to consider concerns the influence of the surface model on structural properties and the energetics of adsorption. To this end we consider the GGA results obtained for the three different structural models of the relaxed Al-terminated α -Al₂O₃ surface which is kept fixed during the interaction with Pd. The use of a fixed substrate and of the same exchange correlation functional isolates the effects of the surface model. From the data reported in Table I it is

clear that the agreement between the cluster and periodic calculations is remarkable, especially between the cluster and the plane wave calculations. Note that these calculations use relativistic pseudopotentials to describe the core electrons. Hence, the small deviation from the results of the purely two-dimensional calculations can be ascribed to the lack of treatment of relativistic effects in the atomic core which are neglected in these all-electron calculations. In fact, the most important relativistic effect is the contraction of the valence shell due to the scalar mass-velocity term. This is indirectly introduced in the pseudopotential either through the fit of the pseudo-orbital to the relativistic all-electron orbital in the formalism of Hay and Wadt²⁶ or by a similar procedure within the ultra-soft approach.⁴⁷ In order to verify that this is the origin of the discrepancy between two-dimensional and cluster and three-dimensional slab calculations we have repeated some of the cluster calculations but using the same all electron basis set for Pd as in the CRYSTAL slab calculations. The final distances are always larger than those obtained from the relativistic ECP by 0.01–0.03 Å. Nevertheless, the three different models predict equilibrium distances that are in agreement within an error bar of roughly ± 0.05 Å.

It is possible to claim that since the adsorbate–surface distance is a local property the agreement between different models described above could be anticipated from previous experience in cluster models of metal, semiconductor, and oxide surfaces.⁴⁸ However, the agreement between the cluster and periodic calculations discussed above is not limited to the equilibrium distance. The summary of adsorption energies reported in Table I shows that the agreement between cluster and periodic calculations also holds for the energetics which are a very sensitive and ultimately the most vital test of the surface model. For the most favorable site (above O₂), the adhesion energy predicted by the cluster and the different slab models differs by 0.13 eV and, in the worst case, the difference does not exceed 0.17 eV. In absolute terms these are quite small values although they do represent a variation of some 15% in the total adsorption energy.

The results of this first part can be summarized in a rather simple way: the use of a cluster or a slab surface model leads to values in the perpendicular equilibrium distance of the Pd atom to the corundum surface that agree to ± 0.05 Å and adsorption energies that agree to ± 0.10 eV. In the forthcoming discussion we will show that the uncertainty caused by the choice of one or another surface model is of the same order as that caused by the choice of a given exchange–correlation functional among those that are believed to be of high accuracy. This statement is supported by the results summarized in Table II for a cluster and a two-dimensional slab model using GGA and two different hybrid functionals to avoid the differences commented above between the two different implementations of B3LYP. Results for the plane wave basis are not included because at present nonlocal Fock contribution to the exchange interaction cannot be conveniently computed within this methodology. Currently, plane wave calculations are limited to LDA and GGA approaches. However, from quantum chemical applications it is known that for molecular systems the thermochemistry and energetics of a given chemical reaction are more accu-

TABLE II. Effect of the exchange–correlation functional in the study of the interaction of a Pd atom with five different surface sites on the α -Al₂O₃(0001), calculated using cluster or purely two-dimensional slab models. The oxide substrate is fixed and only the Pd to surface distance is optimized. The adsorption energies are calculated with respect to the separated systems and include the counterpoise correction.

Property	Site	GGA	B3LYP	B3PW91	Average \pm deviation
Cluster Model					
d (Pd-Surf)/Å	Al ₁	2.49	2.54	2.51	2.51 \pm 0.03
	O ₂	2.06	2.12	2.09	2.09 \pm 0.03
	Al ₃	1.96	1.96	1.90	1.94 \pm 0.03
	Al ₄	1.93	1.93	1.89	1.92 \pm 0.02
	O ₅	1.96	2.05	2.00	2.00 \pm 0.05
$-E_{\text{ads}}$ /eV	Al ₁	0.70	0.44	0.48	0.54 \pm 0.14
	O ₂	0.86	0.51	0.56	0.64 \pm 0.19
	Al ₃	0.47	0.12	0.15	0.25 \pm 0.19
	Al ₄	0.69	0.30	0.32	0.44 \pm 0.22
	O ₅	0.77	0.42	0.49	0.56 \pm 0.19
Two-dimensional model					
d (Pd-Surf)/Å	Al ₁	2.53	2.58	2.54	2.55 \pm 0.03
	O ₂	2.15	2.20	2.16	2.17 \pm 0.03
	Al ₃	2.06	2.19	2.12	2.12 \pm 0.07
	Al ₄	2.06	2.15	2.08	2.10 \pm 0.05
	O ₅	2.05	2.14	2.07	2.09 \pm 0.05
$-E_{\text{ads}}$ /eV	Al ₁	0.83	0.54	0.54	0.64 \pm 0.17
	O ₂	0.98	0.63	0.63	0.75 \pm 0.20
	Al ₃	0.65	0.34	0.33	0.44 \pm 0.18
	Al ₄	0.75	0.44	0.44	0.54 \pm 0.18
	O ₅	0.91	0.55	0.57	0.68 \pm 0.20

rately described using hybrid-type functionals.^{30,35–37} Notice that previous work has clearly shown that GGA has a marked tendency to overestimate the strength of the metal–oxide interaction.^{18,19} This is the main reason for including hybrid functionals in the present systematic study. The analysis of results in Table II reveals that the effect of the exchange–correlation functional is at least of the same order as the effect of the surface model. In fact, even the equilibrium distance that one might expect to be less sensitive to the effect of the functional chosen reflects a non-negligible variation. This effect of the DF method in the distance is accompanied by an even larger effect in the adsorption energy. Nevertheless, all methods predict the same order of stability for the different active sites although one can safely conclude that the accuracy of the adsorption energy does not exceed 0.25 eV. This is somewhat larger than the error introduced by the choice of a surface model.

V. ADSORBATE-INDUCED RELAXATION EFFECTS FOR Pd ON α -Al₂O₃(0001)

Following previous work,¹⁵ possible adsorbate-induced relaxation effects for the interaction of Pd above the five different adsorption sites were considered by allowing some of substrate atoms to relax. However, for technical reasons, somewhat different optimization procedures were adopted for the different surface models. For the cluster model only the Al₁ and O₂ sites which are sufficiently far away from the cluster edge were relaxed. For Pd adsorption above these two

TABLE III. Effect of the substrate model used to study the interaction of a Pd atom with five different surface sites on the α -Al₂O₃(0001), calculated at the GGA level of theory. Some atomic layers of the oxide substrate are relaxed. The adsorption energies are calculated with respect to the separated systems and include the counterpoise correction.

Surface model	Adsorption site				
	Al ₁	O ₂	Al ₃	Al ₄	O ₅
2D Slab					
d (Pd-surf.)/ \AA	2.37	1.82	1.50	1.44	1.76
d (Al ₁ -O ₂)/ \AA	0.30	0.49	0.53	0.59	0.44
Δ (Al ₁ ⁱ -Al ₁ ^f)/ \AA	0.12	0.40	0.45	0.50	0.40
$-E_{\text{ads}}$ /eV	1.13	1.75	1.44	1.66	1.65
Cluster					
d (Pd-surf.)/ \AA	2.44	1.69			
d (Al ₁ -O ₂)/ \AA	0.53	0.61			
Δ (Al ₁ ⁱ -Al ₁ ^f)/ \AA	0.29	0.37			
$-E_{\text{ads}}$ /eV	1.29	1.60			
3D slab					
d (Pd-surf.)/ \AA	2.39	1.79	1.44	1.42	1.74
d (Al ₁ -O ₂)/ \AA	0.34	0.42	0.52	0.54	0.43
Δ (Al ₁ ⁱ -Al ₁ ^f)/ \AA	0.20	0.29	0.42	0.43	0.28
$-E_{\text{ads}}$ /eV	0.89	1.39	1.04	1.27	1.28

sites we relax the vertical position of the nearest Al₁ atom and the O₂ atoms underneath. This choice is not self-evident, but follows from the results of periodic calculations reported in a previous work.¹⁵ For the two-dimensional slab model we followed a similar approach, the vertical position of the Al₁ and O₂ layers has been optimized and, finally, six layers were fully relaxed in the repeated 3D slabs as commented in Sec. III. In this latter case, the optimization procedure was repeated by allowing only the two outermost, Al₁ and O₂, layers to relax. In this way the two periodic calculations represent exactly the same physical model. The results from the two optimizations with six or two layers relaxed are almost indistinguishable, the latter being the ones included in the tables to allow a more adequate comparison. Results including the relaxation of the six outermost layers have been reported in a previous work although using a slightly different unit cell.¹⁵

Following the strategy of the previous section we divide the discussion of results in two parts. The first one concerns GGA results on different models and the second part is devoted to investigate the effect of the exchange-correlation functional on a given surface model. From the results reported in Table III it appears that all surface models predict a very large adsorbate-induced surface relaxation. Here, the important parameters are the displacement of the Al₁ layer, $\Delta(\text{Al}_1^i - \text{Al}_1^f)$, and the distance of Pd to the Al₁ surface layer. Precisely, $\Delta(\text{Al}_1^i - \text{Al}_1^f)$ is the structural parameter exhibiting the largest variation. The presence of Pd provokes the Al₁ layer to relax outwards. This is easily understood because the adsorption of Pd restores partially the bulk coordination. The O₂ layer does also distort, but because of the lack of C₃ symmetry on the O₂ and O₅ sites there is not a uniform relaxation of this layer. The overall relaxation of the O₂ layer atoms is small for the relaxation of the O₂ layer when the Al₂O₃ surface is cut. The Al-terminated α -alumina surface

cut from an infinite bulk Al₂O₃ crystal exhibits a very large relaxation but only the Al₁ atomic layer is significantly displaced from its initial position and towards the bulk.²³⁻²⁵ Thus, it is not surprising that the presence of any adsorbed species above the α -Al₂O₃ surface affects essentially the top aluminum layer. The qualitative agreement of the various models on the nature of the relaxation is thus to be expected.

An important point emerging from the results on Table III is that the perpendicular distance to the surface predicted by the two- and three-dimensional slabs is the same. We know, however, that for a fixed substrate there were non-negligible differences between the two surface models, cf. Table I, that arise from neglecting scalar relativistic effects on the all electron two-dimensional slab. Therefore, the very close agreement between the two models is somewhat fortuitous. In fact, inspection of Table III reveals that the difference between the two models remains, but now it is almost entirely transferred to $\Delta(\text{Al}_1^i - \text{Al}_1^f)$. Another, important effect of surface-induced relaxation is the change in the order of stability of the different sites, especially for Al₁, that now becomes the least favored site. Nevertheless, the general trends predicted by the three surface models are the same. The only significant difference, apart from that already commented for $\Delta(\text{Al}_1^i - \text{Al}_1^f)$, is the absolute value of the adhesion energy which, as in the case of the fixed substrate, differs by at most 0.3 eV.

The final point to discuss concerns the effect of the exchange-correlation functional for the optimized surface models. The two-dimensional slab model calculations, within the GGA level of theory, produces shorter Pd to surface distances than those calculated by the hybrid method B3LYP, cf. Table IV. The differences between the two functionals are larger than those found for the fixed surface. Similar results are found for the cluster model, but here the effect of the exchange-correlation functional is less pronounced, the differences are of the order of those already found for the fixed surface. The appearance of larger differences in the structural parameters predicted by the GGA and B3LYP periodic calculations must be attributed to the optimization procedure that is based on numerical gradients as opposed to the cluster calculation which makes use of analytical gradients. Hence, the difference in equilibrium geometries is not only due to the effect of the exchange-correlation functional, but also to the relatively flat potential energy for the motion of Pd perpendicular to the surface. With respect to the adhesion energy, it is worth pointing out that the relative energetics of the bonding of Pd on the several adsorption sites on the corundum surface is the same for both computational approaches. The effect of the exchange-correlation functional in the final adhesion energy is again of ~ 0.25 eV, the same that was already found for the fixed substrate with a general trend of GGA to predict larger values of the adhesion energy.

VI. COMPARISON TO AVAILABLE EXPERIMENTAL DATA FOR Pd ON α -Al₂O₃(0001)

From the systematic study presented in the previous sections one can safely conclude that for low Pd coverages or in the initial steps of Pd deposition on the alumina surface, the

TABLE IV. Effect of the exchange-correlation functional in the study of the interaction of a Pd atom with five different surface sites on the α -Al₂O₃(0001), calculated using cluster or two-dimensional models. Some atomic layers of the substrate are relaxed. The adsorption energies are calculated with respect to the separated systems and include the counterpoise correction.

Model	Method	Adsorption site				
		Al ₁	O ₂	Al ₃	Al ₄	O ₅
2D Slab	GGA					
	d (Pd-surf.)/Å	2.37	1.82	1.50	1.44	1.76
	d (Al ₁ -O ₂)/Å	0.30	0.49	0.53	0.59	0.44
	Δ (Al ₁ ⁱ -Al ₁ ^f)/Å	0.12	0.40	0.45	0.50	0.40
	$-E_{\text{ads}}$ /eV	1.13	1.75	1.44	1.66	1.65
	B3LYP					
	d (Pd-surf.)/Å	2.49	1.88	1.77	1.62	1.84
	d (Al ₁ -O ₂)/Å	0.42	0.45	0.45	0.50	0.44
	Δ (Al ₁ ⁱ -Al ₁ ^f)/Å	0.31	0.35	0.36	0.40	0.30
	$-E_{\text{ads}}$ /eV	0.89	1.21	0.94	1.12	1.18
Cluster	GGA					
	d (Pd-surf.)/Å	2.44	1.69			
	d (Al ₁ -O ₂)/Å	0.53	0.61			
	Δ (Al ₁ ⁱ -Al ₁ ^f)/Å	0.29	0.37			
	$-E_{\text{ads}}$ /eV	1.29	1.60			
	B3LYP					
	d (Pd-surf.)/Å	2.47	1.74			
	d (Al ₁ -O ₂)/Å	0.51	0.61			
	Δ (Al ₁ ⁱ -Al ₁ ^f)/Å	0.25	0.36			
	$-E_{\text{ads}}$ /eV	0.97	1.17			

Pd atoms will tend to adsorb above the O₂ sites. This is in full agreement with the suggestions of Ealet and Gillet⁴⁹ who, from the results of several experimental techniques—XPS, LEED, and EELS, proposed that for very low coverages, Pd is weakly bonded to the alumina surface with Pd atoms sitting near the positions that would be occupied by O atoms, i.e., nearly above the O₂ or O₅ sites. Notice that at the GGA level and for a slab model which fully relaxes the outermost six layers the adhesion energy at these two sites differs by 0.1 eV only. Consequently, at room temperature, which is indeed the one used in the experiments of Ealet and Gillet, the Pd atoms are almost free to diffuse from O₂ to O₅ sites. These authors also predict that there is a small charge transfer from this transition metal atom to the Al sites of the α -Al₂O₃(001) surface. This is in full agreement with the analysis of the electronic structure predicted by all theoretical models and surfaces models and discussed at length in a previous study.¹⁵

VII. CONCLUSIONS

In the present work a systematic study of the effects of a given surface model choice have been analyzed together with the influence of the choice of a given density functional approach. From this study two main conclusions emerge that can be judged as positive and negative, respectively. The positive point is that all surface models considered, cluster or periodic, lead to the same conclusions. Moreover, these conclusions do not depend on the choice of the exchange-correlation chosen to solve the Kohn–Sham equations. The negative conclusion is that, from a quantitative point of view,

the accuracy reached by the present state-of-the-art density functional methods in predicting structural geometries and adhesion energies of metals on oxide surfaces is far from that reached in molecular quantum chemical calculations either based on the use of correlated wave functions or of hybrid DF approaches.

ACKNOWLEDGMENTS

This research has been supported by the Spanish DGI-CYT Grant Nos. PB98-1216-C02-01 and PB98-1125 and, in part, by *Generalitat de Catalunya* Grant No. 1999SGR-00040 and the *Junta de Andalucía*, Grant No. FQM132. J.R.B.G. thanks the *Fundação para a Ciência e a Tecnologia* for a post-doc grant (BPD/22098/99), N.C.H. thanks the *Junta de Andalucía* for a predoctoral grant, and N.M.H. acknowledges financial support of the European Community for a stay in Barcelona through the Improving Human Potential Contract No. HPRI-CT-1999-00071 held by the *Center de Supercomputació de Catalunya*, CESCO, and *Center Europeu de Paral·lelisme de Barcelona*, CEPBA. Part of the computer time was provided by the CESCO and CEPBA, through grants from the *Fundació Catalana de la Recerca and from the Universitat de Barcelona*. VASP periodic calculations were carried out at the *Centro de Informática Científica de Andalucía*, CICA, Sevilla.

¹C. R. Henry, Surf. Sci. Rep. **31**, 231 (1998).

²C. T. Campbell, Surf. Sci. Rep. **27**, 3 (1997).

³B. C. Gates, in *Materials Chemistry, an Emerging Discipline*, Advances in Chemistry Series, Vol. 245, edited by L. V. Interrante, L. A. Casper and A. B. Ellis (1992), p. 301.

⁴E. Gillet, M. H. El Yakhlofi, J.-P. Disalvo, and F. Ben Abdelouahab, Surf. Sci. **419**, 216 (1999).

⁵C. L. Pang, H. Raza, S. A. Haycock, and G. Thornton, Surf. Sci. **460**, L510 (2000).

⁶D. R. Rainer and D. W. Goodman, in *Chemisorption and Reactivity on Supported Clusters and Thin Films: Towards an Understanding of Microscopic Processes in Catalysis*, edited by R. M. Lambert and G. Pacchioni, NATO ASI Series, Series E: Applied Sciences (Kluwer Academic, Dordrecht, 1997), Vol. 331, p. 27.

⁷M. Bäumer, J. Libuda, and H.-J. Freund, in *Chemisorption and Reactivity on Supported Clusters and Thin Films: Towards an Understanding of Microscopic Processes in Catalysis*, edited by R. M. Lambert and G. Pacchioni, NATO ASI Series, Series E: Applied Sciences (Kluwer Academic, Dordrecht, 1997), Vol. 331, p. 61.

⁸H.-J. Freund, Angew. Chem. Int. Ed. Engl. **36**, 452 (1997).

⁹C. Verdozzi, D. R. Jennison, P. A. Schultz, and M. P. Sears, Phys. Rev. Lett. **82**, 799 (1999).

¹⁰W. Zhang and J. R. Smith, Phys. Rev. B **61**, 16883 (2000).

¹¹P. D. Tepesch and A. A. Quong, Phys. Status Solidi B **217**, 377 (2000).

¹²X. G. Wang, A. Chaka, and M. Scheffler, Phys. Rev. Lett. **84**, 3650 (2000).

¹³G. Renaud, Surf. Sci. Rep. **32**, 5 (1998).

¹⁴Y. F. Zhukovskii, E. A. Kotomin, B. Herschend, K. Hermansson, and P. W. M. Jacobs, preprint and poster presentation at the Eurochem Conference of Molecular Mechanisms of Heterogeneous Catalysis held in San Feliu de Guixols, Spain, 23–28 June 2001.

¹⁵J. R. B. Gomes, F. Illas, N. Cruz Hernández, A. Márquez, and J. F. Sanz, Phys. Rev. B (unpublished).

¹⁶N. C. Hernández and J. F. Sanz, poster and oral presentation at the ESF Conference Density Functional Theory for the study of complex oxides held in London, UK, 14–18 May 2001.

¹⁷Z. Lodziana and J. Norskov, preprint and poster presentation at the Eurochem Conference of Molecular Mechanisms of Heterogeneous Catalysis held in San Feliu de Guixols, Spain, 23–28 June 2001.

¹⁸N. Lopez and F. Illas, J. Phys. Chem. **102**, 1430 (1998).

¹⁹N. Lopez, F. Illas, N. Rösch, and G. Pacchioni, J. Chem. Phys. **110**, 4873 (1999).

- ²⁰N. W. Winter, R. M. Pitzer, and D. K. Temple, *J. Chem. Phys.* **86**, 3549 (1987).
- ²¹M. Fernández-García, J. C. Conesa, P. S. Bagus, J. Rubio, and F. Illas, *J. Chem. Phys.* **101**, 10134 (1994).
- ²²M. Fernández-García, J. C. Conesa, and F. Illas, *Surf. Sci.* **349**, 207 (1996).
- ²³R. Baxter, P. Reinhardt, N. López, and F. Illas, *Surf. Sci.* **445**, 448 (2000).
- ²⁴A. Wander, B. Searle, and N. M. Harrison, *Surf. Sci.* **458**, 25 (2000).
- ²⁵J. R. B. Gomes, I. d. P. R. Moreira, P. Reinhardt, A. Wander, B. Searle, N. M. Harrison, and F. Illas, *Chem. Phys. Lett.* **341**, 412 (2001).
- ²⁶P. J. Hay and W. R. Wadt, *J. Chem. Phys.* **82**, 270 (1985).
- ²⁷M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A. 6 Gaussian, Inc., Pittsburgh, PA, 1998.
- ²⁸J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
- ²⁹J. 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).
- ³⁰A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- ³¹A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- ³²C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1980).
- ³³R. Colle and O. Salvetti, *Theor. Chim. Acta* **37**, 329 (1975); *ibid.* **53**, 55 (1979).
- ³⁴R. Colle and O. Salvetti, *J. Chem. Phys.* **79**, 1404 (1993).
- ³⁵A. Ricca and C. W. Bauschlicher, *J. Phys. Chem.* **98**, 12899 (1994).
- ³⁶T. V. Russo, R. L. Martin, and P. J. Hay, *J. Chem. Phys.* **102**, 8023 (1995).
- ³⁷P. E. M. Siegbahn and R. H. Crabtree, *J. Am. Chem. Soc.* **119**, 3103 (1997).
- ³⁸V. R. Saunders, R. Dovesi, C. Roetti, M. Causà, N. M. Harrison, R. Orlando, and C. M. Zicovich-Wilson, *CRYSTAL 98 User's Manual* (University of Torino, Torino, 1998).
- ³⁹G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993).
- ⁴⁰G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- ⁴¹G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ⁴²Exponents and coefficient for the GTO basis sets are available at the following URL location: <http://www.cse.dl.ac.uk/Activity/CRYSTAL+1129>
- ⁴³D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- ⁴⁴S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).
- ⁴⁵F. Illas and R. L. Martin, *J. Chem. Phys.* **108**, 2519 (1998).
- ⁴⁶R. L. Martin and F. Illas, *Phys. Rev. Lett.* **79**, 1539 (1997).
- ⁴⁷G. Kresse and J. Hafner, *J. Phys.: Condens. Matter* **6**, 8254 (1994).
- ⁴⁸P. S. Bagus and F. Illas, "The Surface Chemical Bond", in *Encyclopedia of Computational Chemistry*, edited by P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, and P. R. Schreiner (Wiley, Chichester, UK, 1998), Vol. 4, p. 2870.
- ⁴⁹B. Ealet and E. Gillet, *Surf. Sci.* **367**, 221 (1996).