Theor Chem Acc (2000) 104:317–322
DOI 10.1007/s002140000137

Theoretical
Chemistry Accounts

*Regular article*

# A first principles study of Pd deposition on the $TiO_2(1\,1\,0)$ surface

**Javier Fdez Sanz, Norge Cruz Hernández, Antonio Márquez**

Departamento de Química Física, Facultad de Química, 41012, Seville, Spain

Received: 14 September 1999 / Accepted: 3 February 2000 /

**Abstract.** The adsorption of isolated Pd atoms on the (1 1 0) surface of rutile $TiO_2$ was investigated through ab initio embedded-cluster calculations performed at the Hartree–Fock, second-order Møller–Plesset and Becke's three parameter hybrid method with the Lee–Yang–Parr correlation functional levels. The role played by the magnitude of the surrounding charges used in the embedding procedure was carefully analyzed. The most stable site for adsorption consisted of a fourfold hollow site in which the Pd atom was coordinated to a fivefold Ti atom, two basal oxygens, and a protruding oxygen atom. However, the adsorption energies computed after basis set superposition error corrections seemed to favor a bridge site in which the Pd atom binds two protruding oxygen atoms. A periodic slab calculation using gradient-corrected functionals and plane-wave basis sets confirmed that for full coverage, the hollow site was more stable, although Pd displacement along the fivefold Ti channels was almost free. These results agree with the experimental data obtained from scanning tunneling microscopy. Finally, the adsorption energy computed from the periodic calculations was found to be 1.88 eV.

**Key words:** Embedded clusters – $TiO_2$ surface – Periodic calculation – Pd absorption

## 1 Introduction

Metal deposition on surfaces constitutes one of the most useful techniques to produce modified supports with a wide variety of properties [1]. This aspect is especially true for the activation of metal oxide surfaces, which, although they are relatively inactive, can be easily promoted by deposition of, for instance, alkali metals. This procedure gives rise to partially reduced surfaces with increased activity towards potential adsorbates [2]. Alternatively, deposition of transition metals leads to materials exhibiting modified surface properties of undoubted interest in heterogeneous catalysis.

Among a wide variety of metal oxides used as supports, the $TiO_2(1\,1\,0)$ rutile face has been the subject of considerable experimental work concerning the deposition of transition metals [3–7]. In particular, the adsorption of Pd on this surface has been carefully studied by Xu et al. [6]. Using scanning tunneling microscopy (STM), these authors reported that Pd dimers and tetramers are present on the surface, adsorbed on fivefold titanium rows (see Fig. 1 for a general view of the surface). Also, and significantly, images corresponding to isolated Pd atoms adsorbed on the surface were not observed.

From a theoretical point of view and because of the complexity of this surface, the number of theoretical studies addressing the metal deposition on rutile is relatively low and these studies have mainly been devoted to the surface reduction by an alkali metal [8–14]. Recently, Bredow and Pacchioni [15] reported a quantum mechanical study of the interaction of Pd atoms and dimers on the $TiO_2(1\,1\,0)$ surface. Using embedded-cluster models and density functional calculations based on Becke's three parameter hybrid method with the Lee–Yang–Parr correlation functional (B3LYP) these authors found that the preferred sites for Pd atoms were the protruding oxygen atoms, with adsorption energies of about 1.0 eV; however, test periodic supercell calculations carried out in the same work seemed to show a slight preference for the fivefold titanium rows. These contradictory results make it clear that the question is far from being well understood and that more theoretical work is desirable. In particular, one of the key aspects in embedded-cluster calculations deals with both the way in which the cluster boundary is represented and the value of the point charges used to simulate the Madelung potential on the surface.

In the present work we report a theoretical analysis of the adsorption of Pd atoms on the $TiO_2(1\,1\,0)$ surface from ab initio embedded-cluster calculations carried out at the Hartree–Fock (HF), second-order Møller–Plesset perturbation theory (MP2), and density functional theory (DFT) levels. Several sites and cluster models have been considered, and results for two different sets of

*Correspondence to*: J. F. Sanz
e-mail: sanz@cica.es

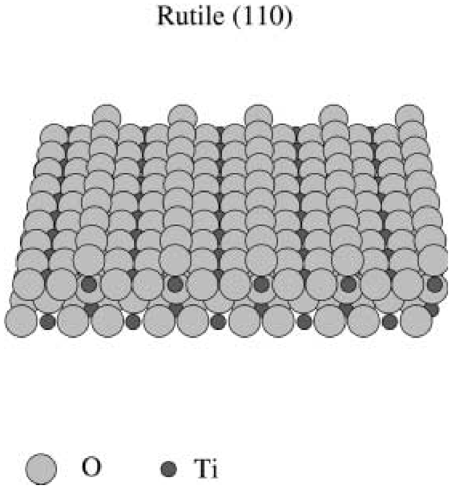

**Fig. 1.** General view of the $TiO_2$(1 1 0) surface

point charges are presented. The article is arranged as follows. In Sect. 2 we describe the cluster models used in the calculations, the details of which are briefly reported in Sect. 3. Section 4 deals with the results, and the main conclusions are summarized in Sect. 5.

## 2 Surface models

To model the different adsorption sites on the $TiO_2$(1 1 0) surface we used the four clusters depicted in Fig. 2. Model A consists of a $(Ti_3O_5)^{2+}$ cluster and is intended to represent the adsorption of Pd on top of a fivefold titanium (Ti5) site ($C_{2v}$). Model B consists of a $(TiO_6)^{8-}$ cluster used to describe the adsorption vertical to a sixfold titanium atom (Ti6), i.e. bridging two protruding oxygen atoms ($C_{2v}$). Model C $(Ti_2O_8)^{8-}$ describes the adsorption on a fourfold hollow site involving two Ti5 and two basal oxygen atoms ($C_{2v}$). Finally, model D consists of a $(Ti_4O_{16})^{16-}$ cluster, which is used to analyze three possible sites: on top of a protruding oxygen, bridging two protruding oxygens, and bridging two basal oxygen atoms as explained later. In order to represent the Madelung field on the surface, the clusters were embedded in an array of positive and negative point charges (about 1440), the values of these charges being discussed later. However, in order to avoid spurious polarization of the outer cluster oxygen atoms, the ions nearest to the clusters were represented by total ion potentials (TIPs) instead of plain point charges (PCs). In accordance with the AIMP method of Barandiarán and Seijo [16, 17], these TIPs were represented through compact model potentials [18] with a residual charge which, beyond the classical interaction between these residual charges and the cluster, introduces Coulomb and exchange HF lattice–cluster interactions. These compact model potentials were first iteratively extracted from HF calculations on bulk $TiO_2$, following a procedure similar to that used for MgO [19]. The fully ionic model potentials were later manipulated to accommodate nonformal charges.

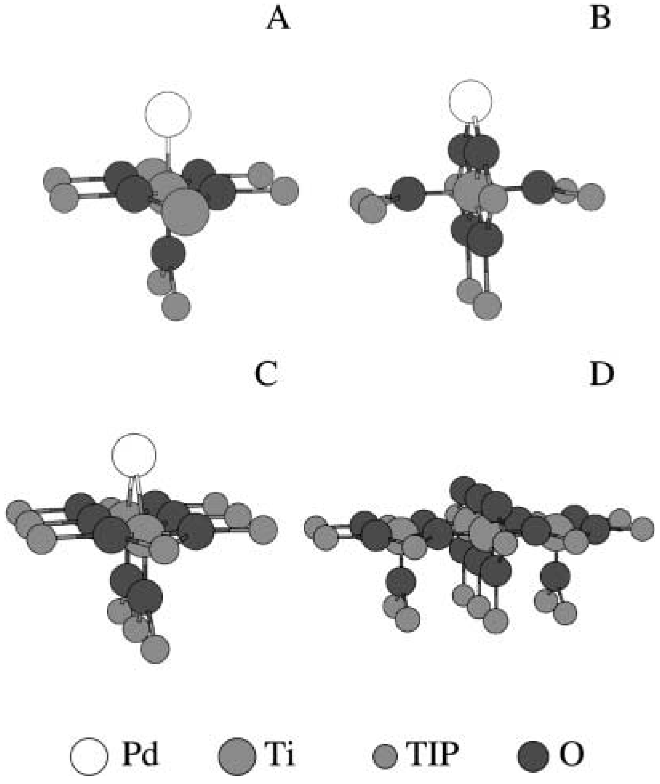

**Fig. 2.** Structure of model clusters used in this work. The Pd atom is not shown in model D

## 3 Computational details

Ab initio HF, MP2, and DFT calculations were performed using a self-modified version of the HONDO98 program [20]. DFT calculations were performed employing the three parameter hybrid Becke functional [21] for the exchange and the Lee–Yang–Parr correlation functional (B3LYP) [22]. The effective core potential approximation of Hay and Wadt [23] (small core) was chosen to describe Pd and Ti atoms. The basis sets for the valence shells were of double-zeta type, and a set of *f* functions ($\alpha = 0.4$) was also added [24] to the Pd atom. For oxygen atoms, the (9*s*5*p*)/[4*s*3*p*] basis set optimized by Broughton and Bagus was used [25]. The surface geometry was that previously obtained from molecular dynamics simulations [10], and in the calculations the ion coordinates were kept fixed. The Pd position was optimized using standard analytical techniques for gradient computation at the HF and MP2 levels, while B3LYP geometries were obtained numerically. All adsorption energies were corrected for the basis set superposition error (BSSE) according to the counterpoise method [26].

## 4 Results

We start this section by considering first the magnitude of the charges (both for TIPs and PCs) employed in the embedding procedure. It has been shown that the use of formal charges +4 and −2 for Ti and O, respectively, gives the best fit in a multipole expansion of the CO/$TiO_2$ system levels [27], these charges having been used in previous work by our group [8–10]; however, on the basis of Ti 3*d* contribution to the O 2*p* valence shell observed in the UV photoelectron spectra, it has been argued that such a fully ionic representation is unrealistic and that half these values would be more consistent

[13, 28]. In order to explore the influence of the charges on the Pd adsorption we performed a set of simple HF calculations using a plain $TiO_4^{4-}$ model embedded in TIPs and PCs with the following values: (+4.0, −2.0), (+3.0, −1.5), (+2.8, −1.4), (+2.5, −1.25), and (+2.0, −1.0). The result is that on decreasing the absolute value of the charges, the Pd–Ti5 distance increases from 2.42 to 2.65 Å and concomitantly the adsorption energy, $E_{ads}$, changes from 2 eV (bound) to −0.19 eV (unbound). This effect is considerably larger than that observed by Bredow and Pacchioni (about 1 eV). The reason resides on the fact that in our calculation the residual charge of the TIPs is also coherently changed; therefore, beyond the effects of the field, we are also altering the Lewis acidity of the Ti centers and, hence, the charge transfer from the Pd atom to the surface. This is illustrated in Fig. 3, where the Mulliken net charges for Ti and Pd are represented as a function of the Pd–Ti distance optimized at the different values of the embedding charges. As can be observed, reducing the values of the charges leads to a clear lowering of the net charge on the Pd atom (0.7 *e*). The effect on Ti appears to be less pronounced since its charge results from the balance between the charge transfer from Pd and the oxygens, which in turn becomes less polarized by the TIPs. Moreover, one can expect that the magnitude of the effect will be dependent on the site as well as on the size of the cluster and, hence, the crucial question dealing with the choice of the charges still persists. In the present work we chose those arising from periodic HF calculations performed on bulk rutile. The Mulliken population analysis gave us +2.76 and −1.38 and these values were also used in modeling the surface [11]. However, because of the evident arbitrariness of this choice, we found it interesting to have another reference and therefore the whole set of calculations using the formal charges +4/−2 was also performed.

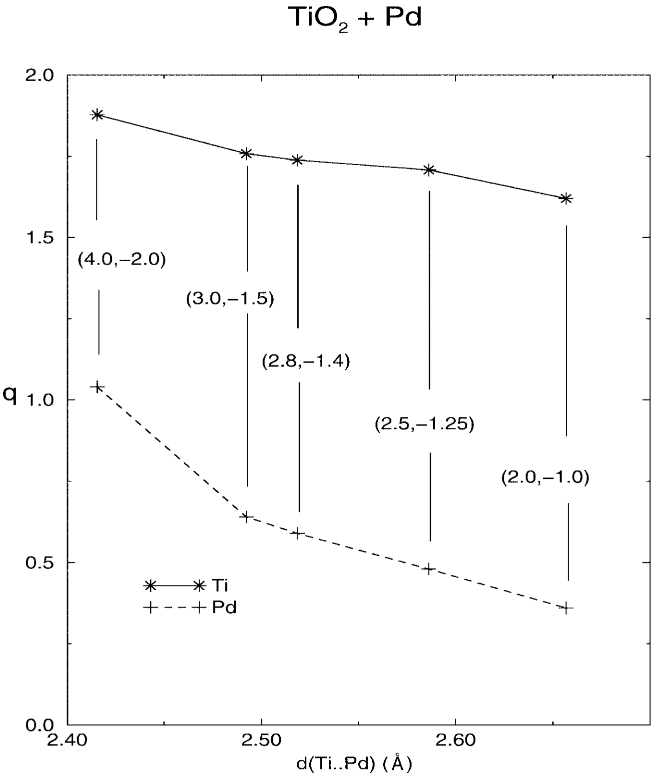

**Fig. 3.** Plots of the Mulliken net atomic charges on Pd and Ti atoms against the optimized Pd–Ti interatomic distances obtained for different sets of point charges

The adsorption energies and relevant structural parameters obtained for models A, B, and C are reported in Table 1. Starting with model A, one can see the large difference found upon changing the charges, the $E_{ads}$ lowering by roughly 1.5 eV, in agreement with the analysis discussed previously. The same trend is also observed in model C; however, in model B the trend is reversed and the fractional charges give rise to larger adsorption energies. This apparently contradictory behavior can be rationalized by taking into account that lowering the charges, and, therefore, lowering the outwards polarization of cluster oxygens, gives rise to a decrease in the Ti6 Lewis acidity, which leads to an increase in the electron density on the protruding oxygens. Also, whatever the set of the charges is, the MP2 and B3LYP values appear to be larger, showing the importance of including electron correlation effects. In fact, in model B the description qualitatively changes from unbound to bound structures. This result confirms the fact that the main contribution to the metal surface bond in model B arises from the interaction between the Pd and oxide closed shells, which is poorly described at the uncorrelated level. Notice how the contribution of the dynamic electron correlation is larger when fractional charges are used, in agreement with the previous discussion. Furthermore, again with the exception of model C, the MP2 adsorption energies are estimated to be larger than those obtained from B3LYP calculations, mainly when formal charges are used.

To decide which is the preferred site is not easy, since it depends on the value of the charges. Thus, for the +4/−2 set, the preferred sites are clearly on top of a fivefold Ti atom (model A), while for the fractional +2.76/−1.38 set, the preferred adsorption would take place on the protruding oxygens (model B). Two difficulties were

**Table 1.** Summary of adsorption energies, $E_{ads}$ (eV), and distances, *R* (Å), between the Pd atom and relevant $TiO_2$(1 1 0) surface atoms computed with model clusters A, B, and C

| Cluster | Formal charges | | | Fractional charges | | |
|---|---|---|---|---|---|---|
| | HF | MP2 | B3LYP | HF | MP2 | B3LYP |
| A | | | | | | |
| $E_{ads}$ | 2.22 | 3.15 | 2.53 | 0.59 | 1.68 | 1.31 |
| *R*(Pd-Ti5) | 2.453 | 2.124 | 2.411 | 2.477 | 2.412 | 2.447 |
| B | | | | | | |
| $E_{ads}$ | −0.44 | 1.93 | 1.01 | −0.21 | 2.23 | 2.07 |
| *R*(Pd-O) | 2.036 | 2.097 | 2.065 | 2.308 | 2.056 | 2.160 |
| *R*(Pd-Ti6) | 2.641 | 2.729 | 2.682 | 3.014 | 2.671 | 2.817 |
| C | | | | | | |
| $E_{ads}$ | 0.91 | 2.16 | 2.21 | −0.18 | 0.29 | 0.53 |
| *R*(Pd-O) | 2.379 | 2.235 | 2.348 | 2.537 | 2.265 | 2.385 |
| *R*(Pd-Ti5) | 2.738 | 2.597 | 2.707 | 2.894 | 2.626 | 2.744 |

encountered in the analysis of these results. The first one refers to the use of different clusters to model the sites, which in addition are computed under the $C_{2v}$ constraint. The second one concerns the fact that in model B only a Ti6 atom is involved. As we have previously shown in the Na/TiO$_2$(1 1 0) system, the reduction in the number of Ti6 atoms is significantly less favored than that of Ti5 centers [8, 9].

In order to overcome both difficulties, model cluster D was considered. In this cluster there are two Ti5 and two Ti6, always keeping a reasonable size and symmetry. As mentioned in Sect. 2, three different approaches of the Pd atom to the cluster were envisaged (Fig. 4). The first one is the adsorption on top of a protruding oxygen ($C_{2v}$ symmetry). The second model consists of a displacement of the Pd atom from the on-top position towards the oxygen rows reaching a site in which it bridges two protruding oxygens ($C_s$). Finally, the third model results from a displacement of the Pd atom from the on-top position towards the Ti5 rows, in such a way that the Pd atom approaches two basal oxygen atoms and one Ti5 center ($C_s$). This site formally corresponds to a fourfold hollow site and is designated as hollow.

**Table 2.** Summary of adsorption energies, $E_{\mathrm{ads}}$ (eV), and distances, $R$ (Å), between the Pd atom and relevant TiO$_2$(1 1 0) surface atoms computed with model cluster D. Relative energies, $E_{\mathrm{rel}}$ (eV), with respect to the most stable hollow site are also included

| Site | Formal charges | | Fractional charges | |
|---|---|---|---|---|
| | HF | MP2 | HF | MP2 |
| On top | | | | |
| $E_{\mathrm{ads}}$ | −0.10 | 3.34 | 0.47 | 2.76 |
| $R$(Pd–O) | 2.153 | 1.832 | 2.214 | 1.991 |
| $E_{\mathrm{rel}}$ | 1.72 | 0.68 | 0.65 | 0.38 |
| Bridge | | | | |
| $E_{\mathrm{ads}}$ | −0.08 | 2.52 | 0.57 | 3.09 |
| $R$(Pd–O)[a] | 2.202 | 2.002 | 2.196 | 1.979 |
| $R$(Pd–Ti6) | 3.439 | 2.986 | 3.227 | 2.979 |
| $E_{\mathrm{rel}}$ | 1.65 | 0.65 | 0.42 | 0.33 |
| Hollow | | | | |
| $E_{\mathrm{ads}}$ | 0.94 | 2.74 | 0.21 | 2.30 |
| $R$(Pd–O) | 2.517 | 2.393 | 2.411 | 2.201 |
| $R$(Pd–Ti5) | 2.491 | 2.339 | 2.707 | 2.578 |

[a] Distance to the nearest oxygen atom

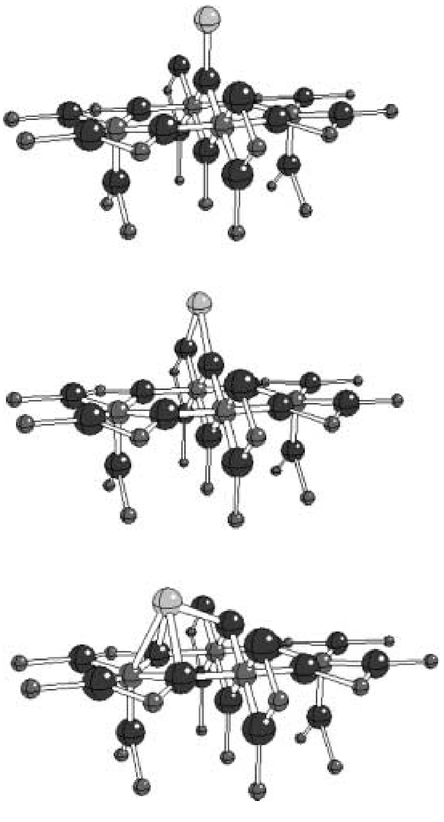

**Fig. 4.** Optimized structures for the three sites of model D obtained from ab initio second-order Møller–Plesset embedded-cluster calculations. *Top*: on-top site; *middle*: bridge site; *bottom*: hollow site

The results obtained for these three models at the HF and MP2 levels are summarized in Table 2. As can be seen, the correlation corrections are large on both geometries and adsorption energies, $E_{\mathrm{ads}}$, which at the correlated level fall in the range 2.30–3.34 eV. Concerning the effect of the charges, it appears that the fractional charges give rise to lower values, again with the exception of the bridge position. Finally, the more favored site still depends on the charges. With the formal ones, the preferred site is the on-top site, while with the fractional charges $E_{\mathrm{ads}}$ is larger for the bridge site. These results do not seem to clarify the situation much; however, the fact that the same cluster has been used for the three sites allows one to compare directly the final energies. Such a comparison shows that, with the two sets of charges, the lowest energy is found for the hollow position. If the relative energies with respect to the hollow site are analyzed (entry $E_{\mathrm{rel}}$ in Table 2), it appears that the on-top and bridge approaches are less stable by 0.33–1.72 eV depending on the charges and the level of calculation. More precisely, at the MP2 level, the hollow position is more stable than the bridge and on-top sites by 0.65 and 0.68 eV using formal charges. With the set of fractional charges, this stabilization is 0.33 and 0.38 eV, respectively. These findings reveal that the relative values of the adsorption energies are determined by BSSE corrections that, on the other hand, are site-dependent. In particular, the BSSE for the hollow site is 0.6–0.9 eV larger than that of the bridge and on-top positions. This result addresses a conspicuous point, since a well-known, the counterpoise method tends to overestimate the BSSE, furnishing only a limiting value. Therefore, assuming an error of 0.6–0.9 eV in the final adsorption energies, the only safe conclusion that can be drawn from the present cluster calculations is that the three sites are equally probable, although based on the final energies, the Ti5 rows seem to be preferred. This would agree with the experiment and with the periodic DFT results reported by Bredow and Pacchioni; however, it should be noted that these authors found an on-top-of-the-Ti5 approach, while in our structure the Pd atom tilts towards the protruding oxygen atom, simultaneously binding one Ti5 and three oxygen atoms. It is also worth noting that our most reasonable adsorption energies (MP2, fractional charges) are more than twice those reported by these authors.

With the aim to go one step further in understanding the problem, it is interesting to reconsider the simplifications made in our approach. First we have the finite size of the clusters. Then, one has to deal with the problem of the surrounding charges. Also, the calculations were performed with fixed surfaces, while some kind of reconstruction is reasonably expected. With the purpose of circumventing these limitations we undertook periodic DFT calculations using a plane-wave basis set. The calculations were performed using the VASP code [29–31], making use of ultrasoft pseudopotentials [32]. The cutoff energy was 400 eV and we used the lowest-order Monkhorst–Pack set of two *k* points [33]. The density functional was the generalized gradient approximation (GGA) of Perdew et al. [34]. The system was described by five-layer-thick slabs separated by a vacuum of 10-Å width. In these preliminary calculations, a 1 × 1 cell was considered, i.e., one Pd atom for each Ti5 surface center. The procedure started by a structural minimization of the isolated surface in which the three outermost layers were allowed to relax. Then, one Pd atom was added to the surface at selected sites and a further relaxation was performed. Four sites were considered as depicted in Fig. 5. Position 1 corresponds to a bridging protruding oxygen adsorption, position 2 on top of Ti5, position three on top of a basal oxygen, and position 4 represents the hollow site between two basal oxygens, a protruding oxygen and a Ti5 atom. The calculations give position 4 as the most stable site, i.e. the hollow site. Site 3 is only 0.1 eV more energetic, while sites 1 and 2 are computed to be 0.38 and 0.33 eV above site 4. This result confirms from a purely first principles approach that the preferred sites are those falling on the Ti5 channels, although not directly on top of Ti atoms but displaced towards the protruding oxygen atoms. Secondly, the differences in the energies are relatively low, suggesting that Pd atoms can move quite freely on the surface and could be the reason for the absence of free Pd atoms on the STM images. Finally, the adsorption energy computed for the hollow site is 1.88 eV, in reasonable agreement with that obtained at the MP2 level using the cluster approach (model D, hollow site) and fractional charges.

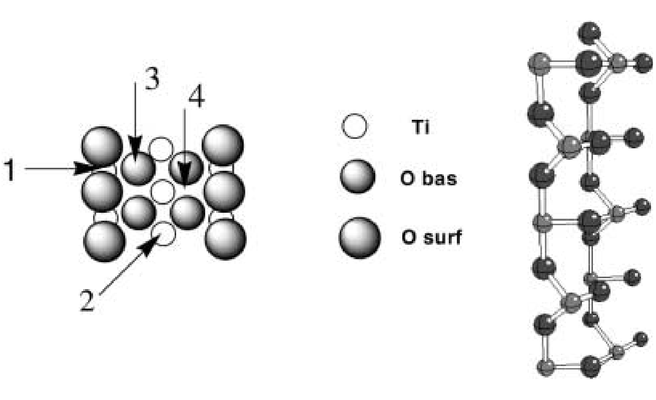

**Fig. 5.** *Right*: side view of the 1 × 1 five-layer cell. *Left*: top view of an expanded cell with the description of the sites considered in the periodic generalized gradient approximation calculations

## 5 Concluding remarks

In this article we reported a first principles study of the adsorption of Pd atoms on the (1 1 0) surface of rutile $TiO_2$. The general method consisted of embedded-cluster calculations carried out at several levels of theory. First, we analyzed the importance of using a proper description of the lattice effects and showed how the charge transfer to the surface depends on the residual charges of the TIPs and PCs. Such an effect is larger for the sites involving Ti5 atoms, while in the O sites, the polarization acts in the opposite sense and there the dynamic electron correlation contributions are prominent. We have also shown how both the preferred sites and the adsorption energies significantly depend on the magnitude of the surrounding charges. The more reliable approach (cluster D, correlated calculations, fractional charges) suggests that the preferred site would be a hollow position in which the Pd atom is coordinated to one Ti5, one protruding oxygen, and two basal oxygens, the adsorption energy being 2.3 eV.

In order to assess these calculations and to overcome some of the technical difficulties we reported a preliminary study in which periodic GGA calculations employing plane-wave basis sets and ultrasoft pseudopotentials were performed. These calculations also show a preference towards that hollow site and also indicate that movement of Pd atoms on the Ti5 channels is almost free. These results agree with the experimental work of Xu et al. in both the site where the Pd dimers are observed and in the fact that isolated Pd atoms are not present in the STM images. Of course, although these findings are encouraging, these studies need to consider lower coverages and work in this direction is currently going on in our laboratory.

*Acknowledgements*. This work was supported financially by the DGES and by the Junta de Andalucía (Spain, projects PB98-1125 and FQM132). We are grateful to G. Pacchioni and D. W. Goodman for fruitful discussions.

## References

1. Henrich VE, Cox PA (1994) The surface science of metal oxides. Cambridge University Press, Cambridge
2. Nerlov J, Christensen SV, Weichel S, Pedersen EH, Möller PJ (1997) Surf Sci 371: 321
3. Schierbaum KD, Fischer S, Torquemada MC, Segovia JL, Roman E, Martín-Gago JA (1996) Surf Sci 345: 261
4. Gao Y, Liang Y, Chambers SA (1996) Surf Sci 365: 638
5. Xu C, Oh WS, Liu G, Kim DY, Goodman DW (1997) J Vac Sci Technol A 15: 1261
6. Xu C, Lai X, Zajac GW, Goodman DW (1997) Phys Rev B 56: 13464
7. Madey TE (1997) In: King DA, Woodruff DP (eds) The chemical physics of solid surfaces, vol 8. Elsevier, Amsterdam
8. Calzado CJ, Oviedo J, San Miguel MA, Sanz JF (1997) J Mol Catal A 119: 135
9. San Miguel MA, Calzado CJ, Sanz JF (1998) Int J Quantum Chem 70: 351
10. San Miguel MA, Calzado CJ, Sanz JF (1998) Surf Sci 409: 92
11. Sanz JF, Zicovich-Wilson CM (1999) Chem Phys Lett 303: 111
12. Calzado CJ, San Miguel MA, Sanz JF (1999) J Phys Chem B 103: 480

13. Bredow T, Apra E, Gatti M, Pacchioni G (1998) Surf Sci 418: 150
14. Thien-Nga L, Paxton AT (1998) Phys Rev B 58: 13233
15. Bredow T, Pacchioni G (1999) Surf Sci 426: 106
16. Barandiarán Z, Seijo L (1988) J Chem Phys 89: 5739
17. Seijo L, Barandiarán Z (1999) In: Leszczynski J (ed) Computational chemistry: reviews of current trends, vol, 4. World Scientific, Singapore
18. Mejias JA, Sanz JF (1995) J Chem Phys 102: 327
19. Mejias JA, Oviedo J, Sanz JF (1995) Chem Phys 191: 133
20. Dupuis M, Chin S, Márquez A (1994) In: Malli GL (ed) Relativistic and electron correlation effects in molecules and clusters. NATO Advanced Study Institute Series B. Plenum, New York, pp 315–338
21. Becke AD (1993) J Chem Phys 98: 5648
22. Lee C, Yang W, Parr RG (1988) Phys Rev B 37: 785
23. Hay PJ, Wadt WR (1985) J Chem Phys 82: 299
24. Balasubramanian K (1988) J Chem Phys 89: 6310
25. (a) Broughton JQ, Bagus PS (1984) Phys Rev B 30: 4761; (b) Broughton JQ, Bagus PS (1987) Phys Rev B 36: 2813
26. Boys SF, Bernardi F (1970) Mol Phys 19: 553
27. Reinhardt P, Causa M, Marian CM, Hess BA (1996) Phys Rev B 54: 14812
28. Pacchioni G, Ferrari AM, Bagus PS (1996) Surf Sci 350: 159
29. Kresse G, Hafner J (1993) Phys Rev B 47: RC558
30. Kresse G, Furthmüller J (1996) Comput Mater Sci 6: 15
31. Kresse G, Furthmüller J (1996) Phys Rev B 54: 11169
32. Vanderbilt D (1990) Phys Rev B 41: 7892
33. Bates SP, Gillan MJ, Kresse G (1998) J Phys Chem B 102: 2017
34. Perdew J, Chevary J, Vosko S, Jackson K, Pederson M, Singh D, Fiolhais C (1992) Phys Rev 46: 6671