Ab initio calculations of H$_2$O and O$_2$ adsorption on Al$_2$O$_3$ substrates

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Abstract

We present and discuss the results of *ab initio* calculations for the adsorption of H$_2$O and O$_2$ on different Al$_2$O$_3$ substrates, namely the Al terminated (0001) surface of corundum, and amorphous-like (Al$_2$O$_3$)$_n$ clusters with $n = 2$–7 formula units. We employ two types of first-principles computer codes, CRYSTAL and SIESTA, which are based on the Hartree–Fock and Kohn–Sham equations, respectively. The former is used for the adsorption calculations on the α-Al$_2$O$_3$(0001) surface, and the latter is used for the study of adsorption and dissociation of H$_2$O and O$_2$ on both kinds of substrates allowing internal relaxation. We have also performed complementary research of adsorption and dissociation of water on (Al$_2$O$_3$)$_n$ amorphous-like clusters with $n = 2$–7. As a next point, we have calculated the binding energy of an O$_2$ molecule on α-Al$_2$O$_3$(0001). Using Hartree–Fock (Kohn–Sham) approximation, the adsorption energy of O$_2$ is 0.12 (0.38) eV at the equilibrium position 2.46 (1.81) Å. Allowing internal relaxation, the Kohn–Sham binding energy of O$_2$ calculated within the generalized gradient approximation to exchange and correlation effects is 0.58 eV at the equilibrium position 1.98 Å. Our results point to a large contribution of Coulomb correlations and relaxation effects in the adsorption processes on alumina surfaces and clusters.
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1. Introduction

Aluminium oxide in its various allotropical forms plays an important role for numerous applications, like thermal barriers, corrosion protection, and catalyst support, among others. During the last years an increasing number of work has been published studying the influence of the size and preparation of the support [1,2], presence of water [3] and other parameters, on the reactivity of metal-oxide surfaces. Various theoretical works predict that the aluminium terminated (0001) surface of α-alumina (corundum) is the most stable [4]. However, Tepesch et al. [5] and Eng and co-workers [6] have shown that the hydrated (0001)

surface is terminated by OH. Recent AFM images of the single-crystal corundum (0001) surface in water are not enough atomically resolved to decide definitely among Al or oxygen termination [7]. When the corundum (0001) surface is in aqueous solution or in humid air (where most applications occur), the dominant surface species are surface hydroxyl groups [8].

There are also several theoretical works dealing with water adsorption on alumina. Hass et al. [4] have studied the adsorption and dissociation of H$_2$O on the α-Al$_2$O$_3$(0001) by means of a density-functional theory (DFT) plane-wave pseudo-potential method, and found that dissociation is energetically more favourable than adsorption. In the dissociation process the H$_2$O splits in HO$^-$ and H$^+$, with the hydroxyl on top of an Al surface atom and the proton transferred to the first (dissociation 1–2) or second (dissociation 1–4) neighbour surface

oxygen. In these calculations [4], dissociation 1–2 is energetically favourable but the barrier for dissociation 1–4 is smaller. Similar results were obtained by Wittbrodt et al. [9] in their study of the adsorption of water on $(Al_2O_3)_n$ clusters of different size ($n = 2$–4), but H^+ is transferred to the first or second neighbour oxygen depending on the cluster size. These authors employed both, Hartree–Fock and DFT methods. Shapovalov and Truong [10] also study the water adsorption on the corundum (0 0 0 1) surface by means of the embedded cluster model. They found, that dissociation is preferred over adsorption, and that the water adsorption has noticeable effect on the geometry and the electronic structure of the crystal.

In this paper we have performed complementary Hartree–Fock and DFT calculations for the adsorption of a single H_2O molecule on the corundum (0 0 0 1) surface. We will compare our results with those from earlier studies [4]. However, our main interest is to study separately the contributions from Coulomb correlation beyond Hartree–Fock and from surface relaxation to the adsorption energy. Next we extend a previous study about the adsorption and dissociation of water on fully relaxed $(Al_2O_3)_n$ clusters for $n = 2$–7 [11]. Here, we also analyze the adsorption and dissociation energy dependence with cluster size, as well as the H–O and OH–Al distances in adsorbed and dissociated water, which lead to a clear manner to distinguish these processes. Finally, we study the oxygen molecular adsorption on the corundum (0 0 1) surface, as a first step in the study of the co-adsorption of O_2 and CO on gold particles supported on alumina and other oxide substrates, leading to CO oxidation [12]. We have studied recently the adsorption of CO on Au/alumina supports [13], and we will study the simultaneous adsorption of O_2 and CO on these substrates in the near future. Conclusions and summary are given in the last section.

2. Details of the calculations

We have used two complementary first-principles computer codes, CRYSTAL 2003 [14] and SIESTA [15]. Within CRYSTAL we performed Hartree–Fock unrelaxed calculations for water adsorption on the Al terminated (0 0 0 1) surface of corundum. For the calculation of O_2 adsorption on Al_2O_3 surface we used the full scale DFT calculations, with Beckes three-parameter exchange-correlation functional (B3PW) [16]. Within SIESTA we performed DFT calculations for the H_2O and O_2 adsorption and dissociation on the alumina surface, and on stoichiometric $(Al_2O_3)_n$ clusters, allowing full relaxation of the adsorbate/substrate complex.

The CRYSTAL code uses a localized Gaussian-type basis set. We performed our cell calculations with $8 \times 8 \times 8 = 512$ k – points in the Brillouin zone. The calculation thresholds N (i.e., the calculation of integrals with an accuracy of 10^{-N}) were chosen as a compromise between the accuracy of the calculations and the large computational time for large cells. They are 7, 8, 7, 7, and 14 for

the Coulomb overlap, Coulomb penetration, exchange overlap, the first-exchange pseudo-overlap, and for the second-exchange pseudo-overlap, respectively. The convergence criteria for the self-consistent field (SCF) energy and eigenvalues were set to 10^{-10} and 10^{-12} a.u., respectively. An additional advantage of the CRYSTAL code is that it treats isolated two-dimensional (2D) slabs, without an artificial periodicity in the z-direction perpendicular to the surface, and thereby is a very convenient tool for modelling of Al_2O_3 surfaces and H_2O and O_2 adsorption therein.

The first-principles code SIESTA [15] solves self-consistently the Kohn–Sham equations [17] of density-functional theory (DFT) using standard norm-conserving scalar-relativistic pseudo-potentials [18] and different approximations for the exchange-correlation functional. Here we use the generalized gradient approximation (GGA) [19], except for the study of H_2O on alumina clusters, which has been performed within the local density approximation (LDA) as parameterized by Perdew and Zunger [20]. The reason for the use of the LDA in these cluster calculations is that we take the cluster geometries optimized in previous calculations [21] by means of the LDA. The core radius of our pseudo-potentials, for both GGA and LDA, are 1.25 a.u. for 1s, 2p and 2d states of H, 1.14 a.u. for 2s, 2p, 3d and 4f states of atomic oxygen, 2.28 a.u. for 3s, 3p, 3d and 4f states of Al. For Al we include non-linear core corrections [22] (with a core correction radius of 1.5 a.u.). Flexible linear combinations of numerical (pseudo) atomic orbitals are used as the basis set, allowing for multiple-zeta and polarization orbitals. In the present calculations we used a double-ζ (s, p) and single d polarization orbital basis. This basis set was tested and used in previous works [11,13,21,23]. In order to limit the range of the basis pseudo-atomic orbitals (PAO), they are slightly excited by a common "energy shift" (here we take 0.001 Ry), and truncated at the resulting radial node (here 4.83 a.u. for H, 3.94 a.u. for O, and 7.10 a.u. for Al). The basis functions and the electron density are projected onto a uniform real space grid in order to calculate the Hartree and exchange-correlation potentials and matrix elements. The grid fineness is controlled by the energy cutoff of the plane waves that can be represented in it without aliasing (here we take 120 Ry). The equilibrium geometries were relaxed by the conjugate gradient method until forces were less than 0.01–0.04 eV/Å.

3. Results and discussion

3.1. Calculation of H_2O adsorption on α-$Al_2O_3(0 0 0 1)$ using the CRYSTAL code

First, considering the periodic slab Al–O–Al–Al–O–Al model and extension of the supercell 1×1, we calculate the total energy for several Al–O distances between the first and second layers in the perpendicular direction to the Al terminated (0 0 0 1) ideal surface of corundum. No relaxation is allowed in the directions parallel to the surface, that is, we neglect surface reconstruction. We obtain the mini-

mum energy when the Al surface layer is shifted 63.0% inward with respect to the Al–O inter-layer separation in the ideal corundum Al_2O_3 crystal. That vertical relaxation is larger than the experimental value ($52.8 \pm 5.0\%$) [24], but smaller than most of the previous first-principles calculations ($\geqslant 86.0\%$; see Table 1 of Ref. [4]), and it is similar to other Hartree–Fock result (68.0%; see Ref. [25]). Then we calculated the adsorption of the H_2O molecule on that Al_2O_3 surface. Thereby our system contained 13 molecules (10 Al_2O_3 and 3 water molecules). We considered the H_2O adsorption perpendicular on the top side of the Al_2O_3 surface Al atom, with the plane of H_2O parallel to the surface. According to our Hartree–Fock calculations, the adsorption energy of the H_2O molecule is 0.79 eV, and the energy minimum occurs when the distance between the H_2O molecule and the Al_2O_3 surface is 2.01 Å. In these calculations, we considered the H_2O molecule as a rigid object, and used the OH length value (0.991 Å) and the H–O–H angle (105.5°) obtained in Ref. [26] using *ab initio* MD calculations. The Al_2O_3 surface was also fixed and only the distance H_2O-surface was optimized.

Next we performed the Mulliken charge analysis for the water molecule and an Al atom, which was located below the water molecule. As a starting point we put the water molecule very far (7.61 Å) from the Al_2O_3 surface, in order to avoid any interaction between the water molecule and surface. At that distance of the surface the water molecule is neutral. The charge on O ion is $-0.94e$, but the charge on each of H ions is $+0.47e$. At this moment the charge on the top Al atom, located directly below the water molecule is $+2.22e$. At the equilibrium distance, 2.01 Å, the charge on each H is $+0.48e$, and the O is charged with $-0.85e$. Thus, the water molecule donates $+0.11e$ to the corundum surface.

Next, we calculated how strongly the rotation of the water molecule around the axis perpendicular to the surface lowers the adsorption energy. The difference between the energy minimum and maximum is 0.009 eV. We do not tested any non vertical orientation of H_2O with respect to the corundum surface, because we are not looking for transition state geometries in the dissociation process of water (see Fig. 7 of Ref. [4]) and our 1×1 cell model is not sufficient for that study. In the next subsection we will calculate the dissociation energy of water, but not the transition state.

3.2. Calculation of H_2O adsorption and dissociation on α-$Al_2O_3(0\,0\,0\,1)$ using the SIESTA code

In a previous work [23] we have studied the Al terminated α-$Al_2O_3(0\,0\,0\,1)$ surface by means of GGA calculations within the SIESTA code for different thick slabs with stacking Al–O–Al–Al–O–Al···, and various sizes of simulation cell, allowing perpendicular and lateral relaxation. In that work we obtained 85% inward relaxation of the first Al layer for a (1×1) 12 layer slab, in good agreement with other first–principles calculations [27,28] for the same slab model. Also in Ref. [23] we have modelled

initially the $(0\,0\,0\,1)$ surface by a (2×2) nine layer slab (60 atoms), and that is the model that we adopted in the present work. The first six layers were fully relaxed leading to a very large inward relaxation of the first Al layer ($\sim -98\%$), which brings the subsurface O atoms practically at the surface. This strong surface relaxation is similar to the one obtained in Ref. [4] by means of a plane-wave GGA pseudo-potential calculation for a (4×4) nine layer slab model. We used recently the same surface model to study the adsorption of CO on gold deposited on alumina substrates [13], and have been also used by Sorescu and co-workers [29] to study the adsorption of large inorganic molecules on alumina. Starting with this model of $(0\,0\,0\,1)$ corundum surface and different initial positions of the water molecule, we have performed GGA calculations allowing simultaneous relaxation of both, water and the six first layers of the alumina surface. Independent of the initial position of the water molecule (in a plane parallel or not to the surface), we obtained three different equilibrium configurations: (i) H_2O adsorption on a Al ion with the water molecule in a plane parallel to the surface; (ii) H_2O dissociation with OH^- on top of Al and H^+ on top of a first neighbour oxygen atom (1–2 dissociation); (iii) same as (ii) with the proton H^+ on top of a second neighbour oxygen surface atom (1–4 dissociation). For each case, we calculated the adsorption energy as the sum of the total energy of isolated adsorbate and alumina systems minus the total energy of the equilibrium adsorbate/alumina complex. The adsorption energy (binding energy) for processes (i)–(iii), are 1.31 eV, 1.53 eV, and 1.29 eV, respectively. Thus, from the point of view of total energy, the dissociation 1–2 is more favourable than the molecular adsorption process (i) by about 0.22 eV. Possible dissociation barriers are not calculated in this work. On the other hand, the adsorption energy for process (iii) (1–4 dissociation) is slightly smaller (0.02 eV) than the molecular adsorption energy. Comparing the result for molecular adsorption with our unrelaxed Hartree–Fock calculation using the CRYSTAL code, we see that the difference in the molecular adsorption energy is 0.52 eV. This difference can be traced back to the lack of dynamical electron correlation in HF (see below subsection D for the case of O_2 adsorption) and to the effect of relaxation. The effect of interaction between H_2O molecules could also play a role in the CRYSTAL calculations, due to the 1×1 cell used for the simulations. On the other hand, in the first-principles supercell calculation, using the plane-wave pseudo-potential method of Ref. [4], the binding energies 1.01 eV, 1.44 eV, and 1.41 eV for processes (i)–(iii), respectively, are obtained, which predict also a larger binding energy for 1–2 dissociation. Our results for the equilibrium adsorbate–substrate distance O-Al is 1.97 Å, 1.74 Å, and 1.74 Å for cases (i)–(iii), respectively, to be compared with the values 1.95 Å, 1.73 Å, and 1.74 Å obtained in Ref. [4]. On the other hand, our result for the O–H distance in the adsorbed H_2O or dissociated hydroxyl OH^- is slightly larger than in free water.

The molecular adsorption process (i) occurs for different orientations of the plane H_2O with respect to the surface with a variation in binding energy $\sim$0.01 eV, as in the case of CRYSTAL results. The Al–O distance for these configurations is in the range 1.97–2.00 Å, and small changes occur in the H–O distance (0.98–1.01 Å) with respect to the free water molecule (0.98 Å). The molecular H_2O adsorption affects mainly the first Al surface layer, which is pushed down below the O layer, except the Al atom bonded to the water molecule, which is pulled out the surface (composed now of oxygen O_s) up to a Al–O_s distance only half the Al–O layer separation in the ideal crystal surface (as compared to the $\sim$−98% initial surface relaxation). On the other hand, for 1–2 and 1–4 dissociation in the equilibrium configuration, the distance Al–O_s largely increases, and the Al which binds the hydroxyl OH^- is pulled out the O_s surface up to −6.9% and −11.4% for 1–2 and 1–4 dissociation, respectively (measured in % with respect to the separation of Al–O layers in (0001) direction of the ideal α-Al_2O_3 crystal).

By performing Mulliken population analysis, we can notice electron transfer from the surface Al ion to the OH^- radical in the case of dissociation, while a smaller charge (0.136e) flows from the water molecule to the surface in the case of molecular adsorption, as in the Hartree–Fock calculation of Section 3.1. For water dissociation, on the other hand, the surface oxygen atom which binds the proton H^+ results with less charge than the other surface oxygen atoms, becoming similarly charged as the O atom in the OH^- radical bonded to the surface. In this sense, dissociation of water on alumina surface produce two types of surface hydroxyl OH^- radicals, one bonded to Al ions and the other to O atom sites.

3.3. Study of adsorption and dissociation of H_2O on $(Al_2O_3)_n$ clusters using the SIESTA code

We have studied the adsorption and dissociation of a single water molecule on $(Al_2O_3)_n$ clusters with $n = 2$–7. For each alumina cluster size, we have selected the geometry of the lowest energy isomer obtained in a previous work [21] within the LDA for the exchange and correlation energy. For that reason we use in this subsection the LDA instead of the GGA. It is know that, in general, LDA leads to larger binding energies and smaller bond distances than the GGA. However, we are interested in the trend of these magnitudes as the cluster size increases, and we assume that both exchange-correlation functionals will produce a similar trend. We have shown in previous works [21,23] that the atomic structure of these fully relaxed alumina clusters resembles the amorphous alumina phase. To study the water adsorption on $(Al_2O_3)_n$ we try different initial positions of the H_2O molecule on the lower energy isomer for each size n. After fully relaxing all coordinates and atoms of these $H_2O/(Al_2O_3)_n$ complexes, we have obtained minimum energy equilibrium geometries

Table 1
Adsorption and dissociation energy per atom (in eV) of H_2O on $(Al_2O_3)_n$ cluster

n	(i) Molecular adsorption	(ii) Dissociation 1–2	(iii) Dissociation 1–4
2	0.193	0.246	
3	0.145	0.183	0.149
4	0.087	0.102 (0.114[a])	0.123
5	0.110	0.151[b]	0.158
6	0.028		0.059
7	0.130	0.09	0.145

[a] The Al–O_s bond of the cluster substrate is broken after dissociation.
[b] The cluster geometry changes severely after relaxation.

which are analogous cases to the processes (i)–(iii) as in the previous subsection (see Ref. [11] for details).

The results for the adsorption energy, calculated as the difference in the total energy of the $H_2O/(Al_2O_3)_n$ complex and the separated water and cluster molecules, are collected in Table 1. We find that dissociation is favourable for $n \geqslant 2$ and process (iii) predominates for $n \geqslant 4$. The latter result is opposite to the one obtained in Section 3.2 for dissociation on the corundum (0001) surface. This could be due to the different environment of the alumina substrate (ordered versus amorphous-like) and, to a lesser extent, to the different exchange-correlation energy functional.

We have also studied, via Mulliken population analysis, the variation of the charge in the water molecule upon adsorption and dissociation processes on the $(Al_2O_3)_4$ cluster. Similarly to the case of molecular adsorption of water on a corundum (0001) surface, H_2O donates charge to the cluster, whereas for the case of dissociation the charge flows from the alumina cluster to the hydroxyl and proton radicals. Specifically, for the water molecule adsorbed on $(Al_2O_3)_4$ the charge on the O ion is −0.289e and the charge on the H ions is 0.082e and 0.073e respectively. Thus, the total charge transferred from the adsorbed H_2O to the surface is 0.134e. For the dissociation of water on $(Al_2O_3)_4$ in the cases (ii) and (iii), the charge on the ion O (H) of the adsorbed hydroxyl OH^- is −0.07e (0.146e) and −0.105e (0.138e) respectively, while the charge on the dissociated H^+ (and on the O_s ion of the cluster where that H^+ is bonded), is 0.119e (−0.075e) for dissociation case (ii), and 0.069e (+0.029e) for dissociation case (iii).

We have analyzed the different bond distances connecting the water molecule, hydroxyl OH^-, and proton H^+, with the alumina cluster substrate for all the adsorption and dissociation processes and cluster sizes. These distances are shown in Fig. 1. The Al–O distance between adsorbate and substrate is always larger for adsorption than for dissociation at all cluster sizes. The difference in the Al–O bond distance will allow differentiating molecular and dissociative adsorbed species, for example by means of infrared spectroscopy [8]. These distances are $\geqslant$7% larger than the Al–O average bond lengths between Al and O atoms of the stoichiometric alumina cluster [22]. Our results for the adsorbate-cluster Al–O distance for
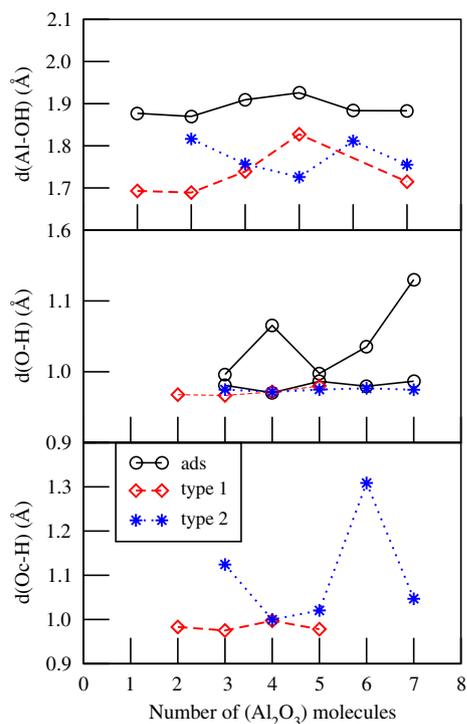
Fig. 1. Al–OH distance (upper panel), O–H⁻ distance (middle panel) and O$_s$–H distance (lower panel) for the adsorption and different dissociation type of a H$_2$O molecule on (Al$_2$O$_3$)$_n$ clusters.

$n = 2$–4 are about 0.04–0.02 Å lower than the distances obtained by Wittbrodt et al. [9] by means of HF calculations relaxing only the atoms closest to the H$_2$O. After adsorption, the H$_2$O molecule is not symmetric and we obtain two different O–H distances which increase between 0.02 Å and 0.14 Å with respect to the free molecule (see panel 2 of Fig. 1). On the other hand, the distance Oc–H between substrate oxygen atom Oc and the adsorbed proton is larger for the dissociation 1–4 than for the 1–2 one, as can be seen in the lower panel of Fig. 1. In principle, we can discriminate between both dissociation configurations by this distance, which should affect the stretched frequency of Oc–H when measured by infrared spectroscopy. The distance between Al and O atoms of the cluster substrate where the H$_2$O is adsorbed or dissociated, increases ~0.2 Å–0.3 Å. In some cases of 1–2 dissociation, that Al–O bond is broken and the cluster structure becomes heavily modified.

3.4. Results for O$_2$ adsorption on Al$_2$O$_3$ surface using CRYSTAL and SIESTA codes

We calculated, using the HF method implemented in the CRYSTAL code, the adsorption of O$_2$ molecule vertically on Al$_2$O$_3$ surface, using the same periodic slab than in Section 3.1, and an extension of the supercell by 1×1. In our calculations we kept the bond distance in the O$_2$ molecule constant and equal to the experimental value, 1.21 Å. We investigated the case, when the O$_2$ molecule approaches

the top side of Al atom vertically. We found, that the adsorption energy minimum corresponds to a separation of the Al and lower O atom in the O$_2$ molecule by 2.31 Å. The adsorption energy is 0.12 eV. Next we calculated the vertical adsorption of the O$_2$ molecule in the triplet state of the system. Again, similarly as in the singlet state, the O$_2$ molecule approaches the Al atom top side vertically. The adsorption energy of O$_2$ molecule in triplet state was slightly less (0.112 eV), as in singlet state. The minimum adsorption energy at the triplet state was reached for a Al–O separation 2.47 Å, that is, ~6% larger than in the singlet state.

In order to check the importance of dynamical electron correlations (beyond HF) for the binding energy of the molecular adsorption processes, we have studied the vertical adsorption of a O$_2$ molecule using the hybrid method B3PW functional [16] as implemented in the CRYSTAL code. We considered two different initial positions with the O$_2$ molecule, vertical on a top position of Al atoms or with the O$_2$ located between two Al atoms (bridge site). In both cases we fixed the O–O distance and optimized the distance between the O$_2$ molecule and the alumina surface. Thereby the top site adsorption energy by means of B3PW is 0.38 eV at a O$_2$ surface distance of 1.81 Å. For the bridge position the adsorption energy (0.078 eV) is lower with respect to the first site and the Al–O distance increases till 2.91 Å. The difference of binding energy of O$_2$ on corundum (0 0 0 1) calculated with Hartree–Fock and B3PW is 0.26 eV. That means that the dynamical Coulomb correlation energy contributes approx. 68% of the total binding energy.

We have studied also the O$_2$ vertical adsorption on α-Al$_2$O$_3$(0 0 0 1) using the SIESTA code within the GGA of Ref. [19] for exchange and correlation energy. The surface was modelled by a six layers slab, as in CRYSTAL, but with a 2×2 cell. We allowed relaxation of all atoms in the complex O$_2$/slab. We have obtained for the O$_2$ adsorption on top position of Al atoms the binding energy 0.58 eV and the equilibrium distance 1.98 Å. The distance O^1–O^2 in adsorbed O$_2$ is 1.29 Å and the O^1–O^2–Al is 111.9°. The O^2 is vertically on Al and O^1 is vertically on a subsurface O atom. Thus, the binding energy and bond O^2-surface distance are ~34% and ~9% larger than our calculation using the CRYSTAL code. On the other hand, for the O–O distance in the adsorbed O$_2$, we have obtained 1.29 Å, that is, about 6% larger than the value fixed (1.21 Å) for the CRYSTAL calculation. In order to compare with the CRYSTAL unrelaxed simulation, we performed a further SIESTA calculation of the total energy of a O$_2$/slab complex at different adsorbate–substrate vertical separation without allowing inter-atomic relaxation in the O$_2$ and in the slab. For a slab (0 0 0 1) with six layer and (1×1) cell we obtain 0.43 eV for the binding energy at a distance 2.1 Å. The difference 0.43–0.38 eV (~12%) between CRYSTAL and SIESTA results can be due to the different exchange-correlation energy functional. On the other hand, the difference 0.58–0.43 eV (~26%) between the relaxed

and unrelaxed SIESTA GGA calculations is due to relaxation, and to other effects like the different size of the simulation cell for alumina.

4. Summary and conclusions

We have performed in this work a study of the adsorption and/or dissociation of H_2O and O_2 on two type of alumina substrates: the $(0\,0\,0\,1)$ surface of α-alumina (corundum) and several sizes of fully relaxed amorphous-like $(Al_2O_3)_n$ clusters with $n \leqslant 7$ formula units. The CRYSTAL code was used to study the adsorption on corundum $(0\,0\,0\,1)$ surface within two approaches, the Hartree–Fock (HF) method and the B3PW exchange-correlation functional of DFT. In these calculations the relaxation of the internal structures of adsorbate and substrate is not allowed. On the other hand, we have employed the SIESTA code to perform calculations for adsorption and dissociation processes on both, cluster and surface alumina substrates, allowing relaxation of the initial structures. The Hartree–Fock adsorption energy of H_2O, with the O vertically on top of Al at the α-Al_2O_3 surface and the plane of H_2O parallel to the surface, is 0.79 eV at an equilibrium O-Al distance 2.01 Å. The rotation energy of H_2O around the Al–O axis perpendicular to the surface is 0.009 eV. Our GGA calculations allowing simultaneous relaxation of both, water and alumina surface, leads to three different equilibrium configurations: (i) H_2O adsorption on an Al substrate ion; (ii) H_2O dissociation with OH^- on a surface Al and H^+ on a first neighbour substrate oxygen atom; (iii) same as (ii) with H^+ on a second neighbour oxygen atom. The process (ii) is more favourable energetically than processes (i) and (iii) by about 0.22 eV. The adsorption energy for processes (i) and (iii) is similar. The equilibrium distance O-Al is 1.97 Å, 1.74 Å, and 1.74 Å for cases (i)–(iii) respectively, and the O–H distance after adsorption or dissociation of water is slightly larger than in free water. In the three processes the Al ion is pulled out of the substrate by about 50% with respect to the clean surface.

From the adsorption and dissociation energy of water on $(Al_2O_3)_n$ clusters, calculated within the GGA approximation allowing full relaxation of the $H_2O/(Al_2O_3)_n$ complex, we find that dissociation is favourable for $n \geqslant 2$, and process (iii) predominates for $n \geqslant 4$. By analyzing the different bond distances connecting the water molecule, hydroxyl OH^-, and proton H^+, with the alumina cluster substrate for all the studied cluster sizes, we can distinguish clearly among adsorption and dissociation processes.

For the unrelaxed α-Al_2O_3 surface and O_2 molecule, the adsorption energy of O_2 vertically on Al ions of the substrate is 0.12 (0.38) eV at the equilibrium position 2.31 (1.98) Å, using the CRYSTAL code within HF (B3PW) approximation. On the other hand, using the SIESTA code within GGA, the adsorption energy of O_2 is 0.58 (0.43) eV and the O_2–Al distance is 1.98 (2.1) Å when relaxation is (is not) allowed.

Our results in this paper point to a large contribution of relaxation effects in the adsorption and dissociation processes of water and oxygen on alumina surfaces and clusters.

Acknowledgements

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