

## Adsorption and dissociation of water on relaxed alumina clusters: a first principles study

E. M. Fernandez<sup>\*1</sup>, R. Eglitis<sup>2</sup>, G. Borstel<sup>2</sup>, and L. C. Balbás<sup>1</sup>

<sup>1</sup> Dpto. de Física Atómica, Universidad de Valladolid, Prado de la Magdalena, 47011 Valladolid, Spain

<sup>2</sup> Fachbereich Physik, Universität Osnabrück, Barbarastrasse 7, 49069 Osnabrück, Germany

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Using previous results for the equilibrium geometries of stoichiometric  $(\text{Al}_2\text{O}_3)_n$  clusters as models for non ideal alumina surfaces, we obtain, from ab-initio total energy LCAO calculations, the corresponding relaxed structures of the complexes  $\text{H}_2\text{O}-(\text{Al}_2\text{O}_3)_n$  with  $n \leq 7$ . Depending on the initial position of the water molecule relative to the cluster site, the complex evolves to different equilibrium structures, with and without dissociation of  $\text{H}_2\text{O}$ , whose energetic, bond lengths, and charge transfer trends are studied as the morphology and size of the initial cluster change. Dissociation of  $\text{H}_2\text{O}$  with the radical  $\text{OH}^\cdot$  bound on top of an Al atom and the proton  $\text{H}^+$  bound to the second nearest neighbour O, is the dominant process for the reaction  $(\text{Al}_2\text{O}_3)_n + \text{H}_2\text{O}$  with  $n = 4$ , in agreement with the one observed for the adsorption of  $\text{H}_2\text{O}$  on the extended real surface.

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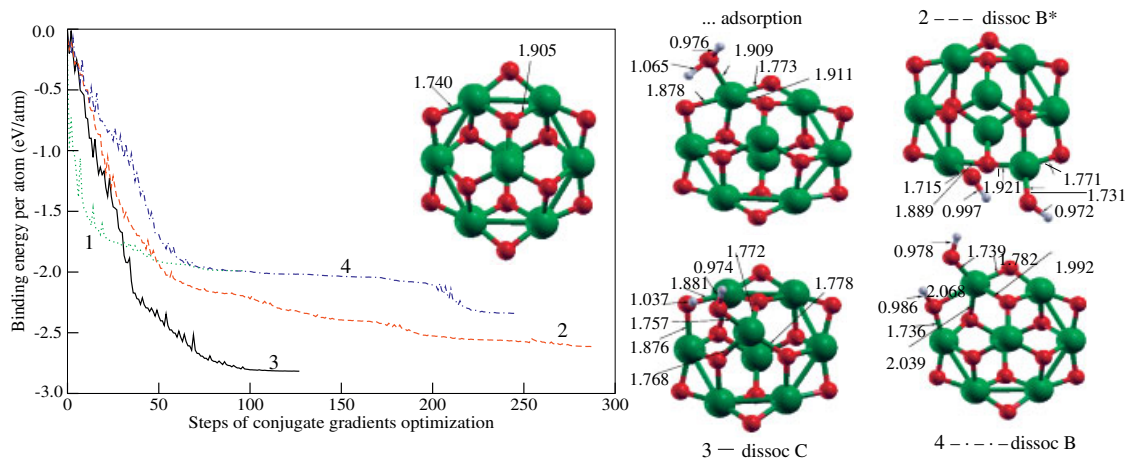
### 1 Introduction

Surfaces of single-crystal alumina are used as substrates for thin-film deposition, and are of interest as catalyst materials. The actual alumina surface may consist of a different oxides from the corundum ( $\alpha$ -phase), and could be the  $\gamma$ -phase or some of the amorphous transition phases. The ideal  $\alpha$ - $\text{Al}_2\text{O}_3$  (0001) surface has been extensively investigated, although many questions remain about the effects of residual hydrogen and adsorbed  $\text{H}_2\text{O}$ . Theoretical studies of this surfaces, based on the 1-Al termination [1] or employing small cluster models [2] have shown that  $\text{H}_2\text{O}$  dissociation is more favourable than molecular adsorption. Comparisons of ideal surface with finite cluster model results raise the question of how large  $(\text{Al}_2\text{O}_3)_n$  cluster one needs to consider in order to achieve accuracies comparable to super cell calculations for ideal  $\alpha$ - $\text{Al}_2\text{O}_3$  surfaces. Small cluster models may be useful for rapidly identifying possible trends, binding modes, and reactions, and for gaining qualitative insights into behaviour of adducts on non ideal surfaces. Here we study, from ab-initio total energy LCAO calculations, the adsorption and dissociation of a single  $\text{H}_2\text{O}$  molecule on relaxed alumina clusters with different sizes, Al environment, and average Al–O bond distances. These clusters, obtained and discussed previously by us [3], are considered here as models for realistic alumina surfaces.

### 2 Results and discussion

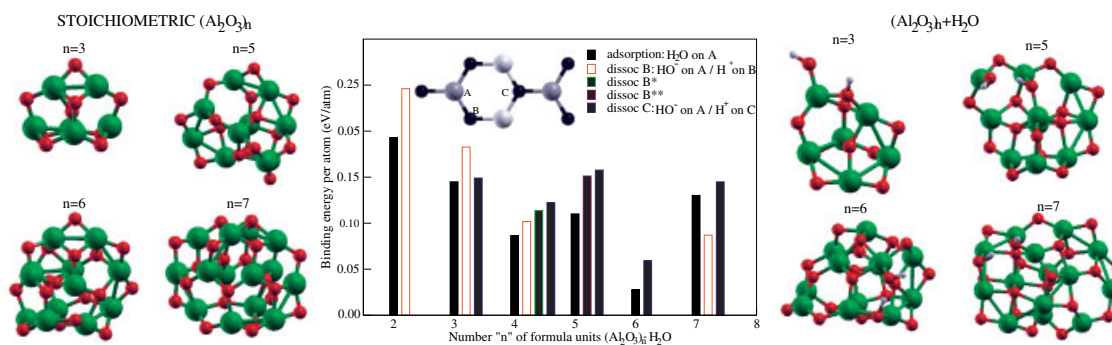
We use the first-principles code SIESTA [4] to solve fully self-consistently the standard Kohn–Sham equations of density-functional theory (DFT) within the generalized-gradients functional for the exchange-correlation potential, and norm conserving pseudo-potentials. For Al we include non-linear core

<sup>\*</sup> Corresponding author: e-mail: [eva@lcb.fam.cie.uva.es](mailto:eva@lcb.fam.cie.uva.es), Phone: +34 983 423 144, Fax: +34 983 423 013



**Fig. 1** (online colour at: [www.pss-b.com](http://www.pss-b.com)) Different intermediate situations of the complex  $(\text{Al}_2\text{O}_3)_4 + \text{H}_2\text{O}$  along steps of conjugate gradients optimization starting with several initial positions of  $\text{H}_2\text{O}$  on the relaxed  $(\text{Al}_2\text{O}_3)_4$  cluster (in the inset). Large (green), small (red), and tiny (blue) spheres represent Al, O, and H atoms respectively. In dissociation process B, the radical  $\text{OH}^-$  binds on top of an Al atom and radical  $\text{H}^+$  binds to the nearest O atom. In process  $\text{B}^*$  the Al–O substrate bond is broken after dissociation. In process C the radical  $\text{OH}^-$  binds on top of an Al atom and radical  $\text{H}^+$  binds to the second nearest neighbour O. This process dominates for  $(\text{Al}_2\text{O}_3)_4 + \text{H}_2\text{O}$  with  $n \geq 4$  (see Fig. 2) and is the one observed for the adsorption of  $\text{H}_2\text{O}$  on the extended real surface.

corrections. We use a double zeta plus polarization (DZP) basis, with double  $s$ ,  $p$  orbital and single  $d$  polarization orbital. Conjugate-gradient structural relaxations, using the DFT forces, were performed for several (more than ten) initial positions of the water molecule relative to the equilibrium geometries of stoichiometric alumina clusters [3]. In Fig. 1 are shown different meta-stable situations of the reaction  $\text{H}_2\text{O} + (\text{Al}_2\text{O}_3)_4$  along the conjugate gradients optimization. These different processes occur depending of the initial configuration of the complex, as explained in the caption. The relaxed free  $(\text{Al}_2\text{O}_3)_4$  cluster, shown in the inset, is a model of the  $\alpha\text{-Al}_2\text{O}_3$  (0001) surface. It contains 3-coordinated Al sites at the surface, with average distance to the three O atoms of the second layer (first neighbours) of 1.740 Å, and average distance of these O atoms to the third Al layer of 1.905 Å. These distances are in qualitative



**Fig. 2** (online colour at: [www.pss-b.com](http://www.pss-b.com)) Binding energy per atom for adsorption and dissociation paths of  $\text{H}_2\text{O}$  on alumina clusters of several sizes. The inset shows a top view of a selected portion of the optimized super cell for the (0001) surface of  $\alpha$ -alumina. Small spheres stand for O and larger light (dark) spheres stand for Al in the upper (lower) surface layer. Left and right geometries show, respectively, the initial  $(\text{Al}_2\text{O}_3)_n$  free clusters and the relaxed complexes  $(\text{Al}_2\text{O}_3)_n + \text{H}_2\text{O}$ , for  $n = 3, 5, 6, 7$ . Large (green), small (red), and tiny (blue) spheres represent Al, O, and H atoms, respectively. For  $(\text{Al}_2\text{O}_3)_7$ , which has a structure similar to a piece of corundum crystal, the binding energy for the dissociation process C is about 12.9 kcal/mol larger than for molecular adsorption, to be compared with 9.2 kcal/mol obtained for the ideal  $\alpha\text{-Al}_2\text{O}_3$  (0001) surface by means of plane wave super cell calculations [1].

agreement with previous calculations [1, 2] using constrained relaxations, and, in general, increase when radicals  $\text{OH}^-$  ( $\text{H}^+$ ) binds to surface Al (O) atoms after dissociation of  $\text{H}_2\text{O}$ .

In Fig. 2 we represent the binding energy per atom for adsorption and dissociation processes of  $\text{H}_2\text{O}$  on alumina clusters of different size. We obtain a difference (in kcal/mol) of binding energy between dissociation C and molecular adsorption processes of 19.10, 26.13, 24.03, and 12.9 for  $(\text{Al}_2\text{O}_3)_n$  clusters with  $n = 4, 5, 6,$  and  $7$ , respectively, to be compared with the values 9.2 and 20.8, obtained from a super cell [1], and a  $(\text{Al}_2\text{O}_3)_4$  cluster calculation [1, 2], respectively. In the later, reference [2], the more stable process is dissociation B\* instead of dissociation C. We have performed also a super cell calculation, within the CRISTAL code [5], for the adsorption process, obtaining a binding energy of 17.51 kcal/mol, to be compared with the plane-wave super cell result [1], 23.3 kcal/mol.

In summary, we hope that the stoichiometric clusters of alumina here considered are reasonable models to study the water addition on non-ideal realistic alumina surfaces, with steps and defects. For instance, the  $(\text{Al}_2\text{O}_3)_4$  clusters resembles an oxygen terminated (001) surfaces, whereas  $(\text{Al}_2\text{O}_3)_5$  resembles a surface with a missing Al atom. We obtain that  $(\text{Al}_2\text{O}_3)_n$  clusters with  $n \geq 4$  prefer dissociation of C type (see Fig. 2). The same results obtained by super cell ideal surface calculations, but the binding energy and bond distances vary largely with the environment of the surface Al atoms.

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