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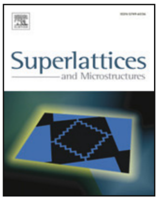

Molecular modelling by DFT of 1,2-diaminoethane adsorbed on the Zn-terminated and O-terminated, anhydrous and hydroxylated ZnO (0001) surface

S. Irrera, D. Costa [*], K. Ogle, P. Marcus

Laboratoire de Physico-Chimie des Surfaces, CNRS-ENSCP (UMR 7045), Ecole Nationale Supérieure de Chimie de Paris, 11 rue P. et M. Curie, 75005 Paris, France

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ABSTRACT

We performed an *ab initio* molecular modelling of diaminoethane (DAE) adsorption on zincite (ZnO). We studied DAE on Zn-terminated and O-terminated polar (0001)-ZnO surfaces, dry and hydroxylated, using a periodic Density Functional Theory based method.

We found that DAE adsorbs tilted on the surface of dry Zn–ZnO, and the interaction consists of the combination of a Zn–N bond between the Lewis acid Zn and the amine base, and additional van der Waals interactions, while adsorption on the O-terminated and hydroxylated surfaces is parallel and occurs through the combination of van der Waals interactions and H bonds. At saturation, the surface coverage is 2.6 diaminoethane/nm^2. The range in the energies of adsorption is Zn–ZnO (-0.52 eV) $>$ O–ZnO (-0.45 eV) $=$ HO–Zn–ZnO (-0.41 eV) $>$ H–O–ZnO (-0.32 eV).

1. Introduction

The understanding of the physics and chemistry of metal oxide surfaces is of general interest due to many technical applications. Various phenomena occurring at liquid or gas/solid interfaces are related to interactions with oxide surfaces: heterogeneous catalysis, adhesion, corrosion. Major progress on metal surfaces has been achieved in the past decades, but further work is needed for polar surfaces due to fundamental problems for their stabilisation. Stabilisation could be gained by adsorption of adsorbates.

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[*] Corresponding author. Tel.: +33 0 1 44 27 25 25.
E-mail address: dominique-costa@enscp.fr (D. Costa).

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In this paper we studied the (0001) polar surface, of Zincite (ZnO) [1] which is an interesting case of a non centro-symmetric bulk structure. When the crystal is cleaved to get a (0001) surface, two polar surfaces, oxygen and zinc terminated, are formed. The aim of the present work is to model using *ab initio* methods dry and hydroxylated Zn–ZnO and O–ZnO surfaces and their reactivity with 1,2-diaminoethane (DAE), which was recently studied experimentally [2,3].

ZnO is interesting as a model for metal/oxide/polymer systems. In ambient conditions, the Zn metal surface is covered with a native ZnO oxide film [2]. ZnO is an interesting case of non centro-symmetric bulk structure and the (0001) orientation is a polar surface. When the crystal is cleaved to get a (0001) surface, two different polar surfaces can be formed with oxygen (O(0001)-ZnO, or (000-1) ZnO surface) or zinc (Zn(0001)-ZnO, or (0001) ZnO surface) terminations. Polar surfaces can be stabilised by reconstruction, by charge transfer and/or by charged molecule adsorption [4]. Experimental data on the Zn–ZnO surface do not report atomic reconstruction, as the LEED pattern of Zn–ZnO has essentially a (1×1) structure [5,6]. Theoretical calculations performed on the ideal Zn–ZnO and O–ZnO surfaces [7–10] showed that these surfaces are stabilised by charge transfer from the O–ZnO surface to the Zn–ZnO one [7,10], resulting in a metallic character of both surfaces. It was found by grazing incidence X-ray diffraction that the Zn–ZnO surface is stabilised by the formation of a (1/4) ML of Zn^{2+} vacancies [11,12]. STM showed triangular reconstructions of size $\sim$30 Å and further DFT calculations confirmed that these reconstructions are energetically favourable [12]. Alternative to relaxation or reconstruction, charged species adsorption may stabilise polar surfaces, as OH groups on Zn–ZnO in conditions of rich O and H concentrations in the gas phase [12]. Indeed, it has recently been confirmed experimentally that large flat terraces of hydroxylated Zn–ZnO surface are stabilised by the adsorption of a hydroxide layer [13].

It is generally stated that the oxidised or Hydroxylated metal surface/polymer bonding occurs through acid/base interactions [2,3,14]. Diaminoethane (DAE) (NH_2–CH_2CH_2–NH_2) is a typical basic ligand used as a probe molecule to characterise surface acid and basic sites. The interaction of DAE with Zn surfaces was studied in previous experimental works. Both –NH_2 terminations contain a pair of non-bonding electrons that may form a covalent bond with a zinc metal ion [3]. Thus, DAE may interact with Lewis or Brönsted acid sites acting as a Lewis base (electron donor). In addition, DAE may form H bonds with hydroxyl groups at the surface, following a Brönsted acid/base reaction [3].

2. Computational details

Geometry optimisation has been performed using the VASP code [15], in the periodic Density Functional-theory framework. The Kohn–Sham equations have been solved by the generalised gradient approximation (GGA-PW91) [16]. The electron–ion interaction was described by the Projector Augmented-wave method (PAW) [17] with core radius of 1.52 Å for oxygen. The *k*-points grid was optimised up to $8 \times 8 \times 8$ with an energy cutoff value set at 400 eV. The *k*-points grid was set to $8 \times 8 \times 8$ for the bulk cell, as the energy convergence was achieved at 10^{-2} eV/cell.

We reproduced the bulk and the surfaces on the base of DFT calculations already performed on the Zn–ZnO surface. In the bulk, all Zn and O arrangements are hexagonal with atoms occupying tetrahedral sites. ZnO crystallises in the space group P63mc. The unit cell for the bulk optimisation contained 2 ZnO units. The optimised cell parameters are $a = 3.25$ Å and $c = 5.24$ Å, in good agreement with the experimental values ($a = 3.2497$ Å, $c = 5.2042$ Å, $\alpha = \beta = 90°$ and $\gamma = 120°$) [18] and with previous calculated values ($a = 3.293$ Å and $c = 5.266$ Å) using the same functional and ultrasoft pseudopotentials [10] and the values of ($a = 3.282$ Å, $c = 5.309$ Å) using a lower cutoff of 280 eV [12].

We then investigated the zinc terminated (0001) surface in the (1×1) structure. The slab was 5 ZnO bilayers (S5) thick. A 15 Å vacuum space in the supercell was added in order to avoid interaction between the surface cells along the *z*-axes. A dipolar correction was introduced in the axis perpendicular to the surface to take into account the polarity of the surface. This dipolar correction did not exceed 0.015 eV/cell (for a 1×1 cell), as expected from a symmetric slab [7]. It was shown that the geometric and electronic structures converged rapidly with slab thickness, and were converged for a S4 and thicker slabs [8]. The central layers in the slab were kept frozen in the geometry of the bulk, whereas the Zn–O–Zn (for the Zn–ZnO surface) and the O–Zn–O (for the O–ZnO surface) surface layers