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***Ab initio* simulations of hydroxylation and dehydroxylation reactions at surfaces: amorphous silica and brucite**

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Abstract

Hydroxylation and dehydroxylation reactions at the surfaces of amorphous silica and $\text{Mg}(\text{OH})_2$ have been studied by *ab initio* Car–Parrinello molecular dynamics simulations. A particular topological defect on the amorphous silica surface, the two-membered (2M) silicon ring, is shown to react fast with water thus confirming the experimental assignment of the most reactive surface sites. The mechanism of the chemisorption of both water and ammonia on the 2M ring has been identified. *Ab initio* simulations on $\text{Mg}(\text{OH})_2$ have provided information on the structural properties of the low-indices surfaces (0001), $(1\bar{1}00)$ and (1000) of brucite. Comparison of the calculated dehydroxylation energy at surfaces and in the bulk suggests that the decomposition of brucite into MgO and water would preferentially occur at surfaces.

1. Introduction

The interaction of water with solid surfaces plays a crucial role in many phenomena ranging from aqueous heterogeneous chemistry to dissolution of minerals in natural systems and metal corrosion. Hydroxylation and dehydroxylation reactions, i.e. inclusion or removal of hydroxyl (OH) groups, may occur at preferential surface sites. Identification of such surface sites is of relevance for several technological processes. To quote such an example, the surface sites of the optical fibres, made by silica glass, which are suitable to be more easily hydroxylated are nucleation centres for the condensation of water which, in turn, can weaken the fibre by way of a stress-induced corrosion mechanism [1]. *Ab initio* calculations based on density functional theory (DFT) [2, 3] can provide a valuable insight into the nature of water–solid interaction and aid in the identification of the most reactive surface sites for the hydration and dehydration processes. Here, we present two examples of the application of DFT-based molecular dynamics (MD) simulations [4, 5] to the study of hydroxylation and dehydroxylation reactions at surfaces. Namely, we have studied the interaction of water with a particular site at the surface of amorphous silica, the two-membered (2M) silicon ring. This structure is believed

to be the most reactive site for the adsorption not only of water but also of other chemicals used for instance in the technological process of coating of optical fibres with polymers [1, 6–13]. Simulations of the reaction of water and ammonia with a model of the amorphous silica surface provides insight onto the nature of the chemical activity of the ring. As a second example, we will consider the dehydroxylation reaction of the surface of $\text{Mg}(\text{OH})_2$ (brucite) which is also of relevance in the process of surface coating with polymers. In fact, brucite is often introduced as flame retardant in the polymer matrix due to the strong endothermicity of its dehydroxylation reaction leading to the formation of MgO and water. The role of surfaces in this process is here addressed by studying the condensation reactions of vicinal hydroxyls in the bulk and on different faces of $\text{Mg}(\text{OH})_2$.

2. Hydroxylation and chemical reactivity of the two-membered silicon ring at the surface of amorphous silica

Many technological application of amorphous silica rely on its specific surface properties [14, 15]. Understanding the nature of silica surface sites available for physisorption and chemisorption of gas phase molecules is crucial to understand the behaviour of silica in a wide range of applications including catalysis, optical fibres and tyre technologies [15]. On the normal silica surface exposed to air, silanols ($\text{Si}-\text{OH}$ groups) are known to represent the main adsorption sites. In contrast the precise nature of surface reactive sites on the dry (dehydroxylated) surface of silica is still very uncertain. In the current literature, it is customarily, even if rather tentatively, proposed that strongly metastable 2M silicon rings could constitute the main reactive sites on the surface of dry silica [1, 6–13]. Supporting evidence consists in a similarity between the IR spectra of dry silica, exhibiting two strong bands at 888 and 908 cm^{-1} (where bulk silica is transparent) and that of cyclodisiloxane molecules which also display in the spectral region $800\text{--}900\text{ cm}^{-1}$ two strong peaks due precisely to vibrations of the 2M ring. The silica IR peaks appear upon dehydroxylation above 500° , and disappear upon adsorption of water and other chemical species such as ammonia and methanol [6–10]. It is therefore conceivable that the surface structures responsible for the new IR bands could arise by condensation of neighbouring silanols ($\text{Si}-\text{OH}$) on the hydroxylated surface. However, this kind of evidence is so indirect, (and the alleged 2M ring so unusually strained, the required $\text{O}\ddot{\text{S}}\text{iO}$ angle being $\sim 90^\circ$), to raise legitimate concern about the validity of this overall picture of the dry silica surface reactive sites. Yet, a compelling identification of the structures responsible for the IR doublet is of paramount importance for several technological applications such as the adhesion to silica of organosilane molecules, the typical silica–polymer coupling agents in the coating of the optical fibres. In fact, although for a long time it has been generally assumed that the adhesion occurs on the few residual hydroxyls still present on the surface of optical fibres, recent experiments have shown that the silane adhesion proceeds without the attenuation of the OH stretching of surface silanols in the IR spectra [11–13]. Instead, the organosilane chemisorption is accompanied by the disappearance of the IR doublet assigned to the 2M ring. Since the organosilane presently used as silica–polymer coupling agents in the optical fibres technology are designed to react with silanols, a compelling identification of the 2M ring as the most reactive site is obviously of crucial importance to design better performing coupling agents.

A crucial piece of additional evidence either in favour or against the role of the 2M rings in surface reactivity would come from a theoretical assessment of the viability of their formation mechanism upon dehydroxylation of the wet surface and of their reactivity with simple molecules. In particular, a fast reaction with water is intriguing since normal siloxane bridges (belonging to larger rings) on the surface of amorphous silica are believed to be

hydrophobic [16]. With this aim, we have recently performed *ab initio* MD simulations [4,5] of hydroxylated and dry silica surfaces [17] which have provided a simple and plausible path for the formation of the 2M ring via condensation of vicinal silanols. A periodic model of the dry amorphous silica surface displaying a 2M ring at a concentration of 0.5 nm^{-2} (close to the experimental estimate of $0.2\text{--}0.4 \text{ nm}^{-2}$) [13] has been generated by combined classical and *ab initio* MD [17]. The calculated IR spectrum shows two peaks at 849 and 856 cm^{-1} due to vibrational modes of the 2M ring, strongly supporting the experimental assignment of the IR doublet at 888 and 902 cm^{-1} .

Based on these previous gratifying results we here report on the *ab initio* simulation of reaction of the 2M ring with water (hydroxylation) and ammonia which confirm the high reactivity of the ring thus providing a further support to the assignment of the IR doublet. Before reporting the simulation results we briefly introduce our computational framework in the next section.

2.1. Computational methods

We performed *ab initio* MD simulations using the Car–Parrinello scheme [4,5]. Our approach is based on DFT within the local density approximation of the exchange–correlation functional augmented by the gradient corrections proposed by Becke [18] and Lee, Yang and Parr [19] (BLYP). Gradient corrections to the local density approximation are necessary to reproduce the correct energy hierarchy of the different crystalline polymorphs of silica [20] as shown by calculations using others exchange and correlation energy functionals [20]. We have chosen the BLYP functional because it provides a good description of the hydrogen bond [21,22]. Only valence electrons are treated explicitly and electron–ion interactions are described by norm-conserving pseudo-potentials generated according to the Troullier and Martins procedure [23]. Kohn–Sham orbitals are expanded in plane waves up to a kinetic energy cutoff of 70 Ry. The surfaces are modelled by a slab geometry with 3D periodic boundary conditions. The procedure for the generation of the amorphous silica surface is discussed in our previous work [17]. The model used here (figure 1) is obtained by cutting some layers from the bottom surface of the larger model generated in [17] and passivating the dangling bonds with silanols. The top surface of the slab is dry, fully self-passivated and contains a 2M ring per supercell. The surface density of the 2M ring, 0.5 nm^{-2} , is not too far from the experimental estimate on the dry amorphous surface ($0.2\text{--}0.4 \text{ nm}^{-2}$) [1]. The simulation of chemical reactions has been performed with the method of constraints [24] which has been used to simulate within *ab initio* MD other chemical reactions in solution [25] and at surfaces [26]. Dehydroxylation and silanization of the wet silica surfaces have been also simulated within the same framework in our previous work [27]. The method amounts to identify a reaction coordinate as the distance between two atoms involved in the reaction and perform several simulations by constraining the reaction coordinates at different values. This technique provides the energy profile as a function of the reaction coordinate and thus the activation energy. Although in principle the constrained dynamics can also provide the activation free energy [24–26], the latter has not been calculated here due to the insufficient statistical accuracy of our short simulation runs. In the Car–Parrinello simulations we used a time step of 0.12 fs and a fictitious electronic mass of 800 au.

2.2. H_2O and NH_3

The study of adsorption reactions of small molecules on the 2M ring can provide useful information of the nature of its chemical reactivity. In fact, although the chemisorption of gas

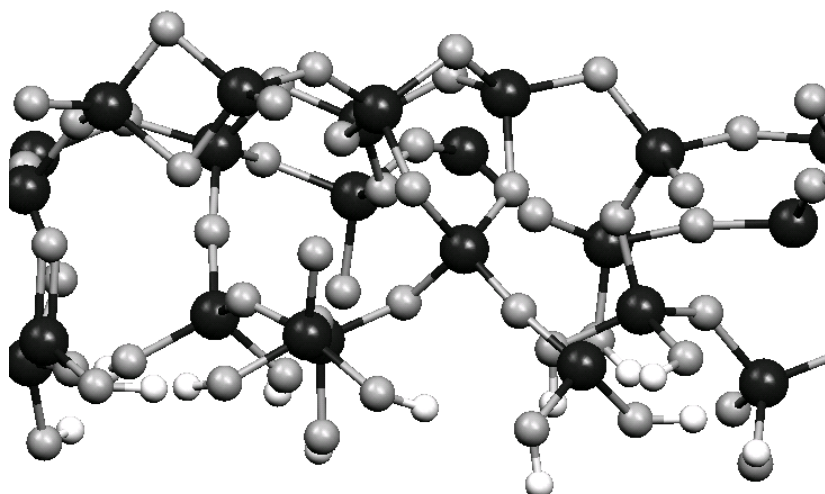


Figure 1. Side view of the slab model of the amorphous silica surface. The bottom surface is fully hydroxylated. The top surface contains one 2M silicon ring per surface unit cell. The simulation cell contains 93 atoms. Black, light grey and white spheres are silicon, oxygen and hydrogen atoms, respectively.

species at the ring is obviously triggered by its large strain energy (1.38 eV/ring with respect to β -cristobalite [17]), different reaction mechanisms are possible. In the hydroxylation reaction for instance, two reaction paths are conceivable as shown in figure 2. Along path A in figure 2, water is adsorbed on the silicon site of the ring which acts as an electron acceptor. Along the second path (B in figure 2) the reaction is driven instead by the basicity of the oxygen atom in the ring. The simulation can discriminate among the two paths and identify the prevalent basic or acidic character of the ring driving the reaction with water. With this aim, we performed two different sets of constrained MD simulations (cf section 2.1) by choosing as reaction coordinate either the distance between the silicon atom and the oxygen atom of the water molecule (path A) or the distance between the oxygen atom of the ring and the proton of water molecule (path B). The hydroxylation energy is 1.7 eV, as computed from the final configuration (ring open with two hydroxyls, cf figure 2) and the initial configuration consisting of the isolated water molecule and the clean amorphous surface. The geometries of the transition states along the two paths are shown in figure 3. By decreasing further the reaction coordinate the ring opens spontaneously. The activation energy is lower along path B (0.32 eV) than along path A (1.1 eV) which implies that the chemisorption of water is driven by the basic character of the oxygen in the ring. However, a preliminary step to the hydroxylation reaction is the physisorption of the water molecule on the ring. This occurs on the Si atom of the ring, i.e. along path A, at a distance of 2.31 Å with a physisorption energy of 0.11 eV.

Experimentally, the total rate of hydroxylation has been measured from the depletion rate of the IR doublet associated with the 2M ring [10], but no data are available on the activation energy. Therefore, to make contact with experiments we have estimated the total rate k within the transition state theory [28]:

$$k = \frac{k_B T}{h} N_A \frac{q_{\text{complex}}}{q_{\text{ring}} q_{\text{H}_2\text{O}}} e^{-E/k_B T} p_{\text{H}_2\text{O}}$$

where N_A is the Avogadro number, k_B and h are the Boltzmann and Planck constants, E is the activation energy, T and $p_{\text{H}_2\text{O}}$ are the experimental temperature and partial pressure of

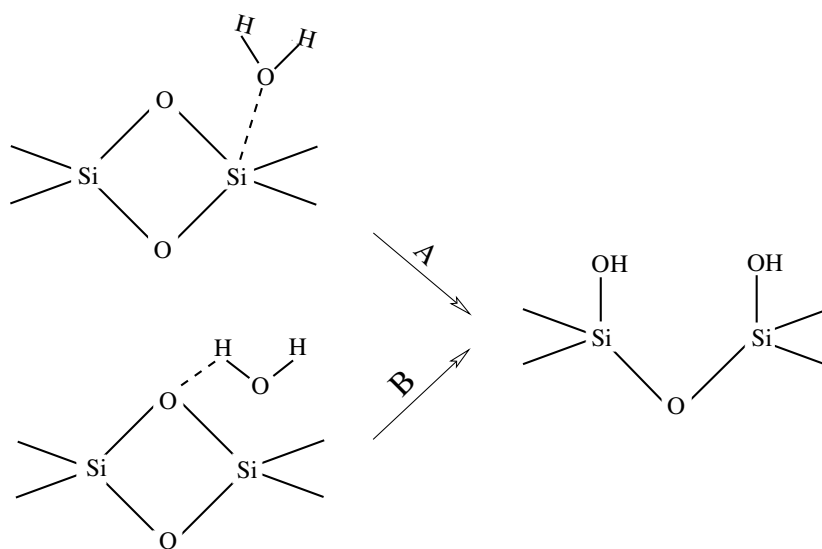


Figure 2. Sketch of the two conceivable reaction paths for the hydroxylation reaction of the 2M silicon ring. The reaction coordinate along path A is the distance between the silicon atom and the oxygen atom of the water molecule. The reaction coordinate along path B is the distance between the oxygen atom of the ring and the proton of the water molecule.

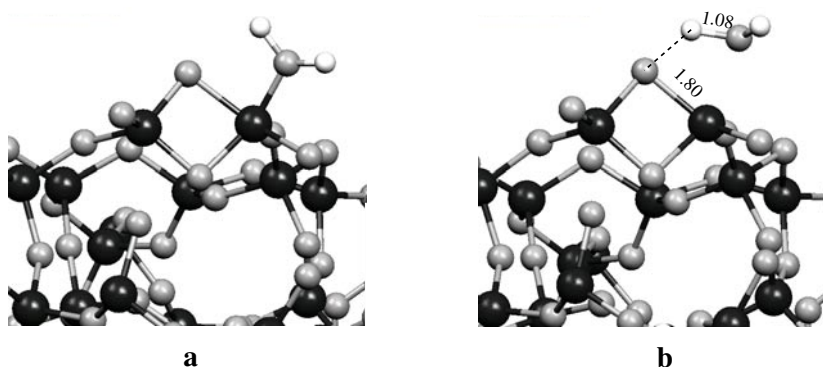


Figure 3. Atomic configuration of the transition states for the hydroxylation reaction of the 2M silicon ring along (a) path A in figure 1, and (b) path B in figure 1. The activation energies are 1.1 and 0.34 eV for path A and path B, respectively. Bond lengths are given in Å. The reaction coordinate at the transition state in (b) is 1.35 Å.

water and $q_{\text{H}_2\text{O}}$, q_{ring} , and q_{complex} are the partition functions of isolated water, isolated silica surface and water–silica complex at the transition state, respectively. The vibrational part of the partition functions has been computed in the harmonic approximation. Because of the computational cost, we have not calculated the $q_{\text{complex}}/q_{\text{ring}}$ ratio from the full vibrational spectrum of the amorphous surface, but from the smaller cluster $(\text{SiO})_2(\text{OH})_4$, i.e. a 2M ring with two bonds of silicon atoms saturated by hydroxyls. The computed activation energy for the water–ring reaction in this smaller system is 0.4 eV, not far from the value of 0.34 eV obtained on the large model of the amorphous surface. The reaction rate for the cluster model is finally $k = 9 \times 10^{-4} \text{ min}^{-1}$ as compared with the experimental value of 0.5 min^{-1} (at room temperature and $p_{\text{H}_2\text{O}} = 10 \text{ mTorr}$) [10]. Considering the large uncertainty in the estimate of

the $q_{\text{complex}}/q_{\text{ring}}$ ratio, and the fact that an error of 0.1 eV in the activation energy changes the reaction rate by two orders of magnitude, we may conclude that our results are not inconsistent with the experimental rate of hydroxylation. Our results are also consistent with previous calculations on the minimal cluster $(\text{SiO})_4\text{H}_4$ within the DFT-BLYP framework and Gaussian basis sets [29]. Although any detail is given on the geometry of the transition state, the latter work reports activation and hydroxylation energies of 0.28 and 1.4 eV close to our values of 0.34 and 1.7 eV, respectively. Apparently, the embedding of the 2M ring in a reliable model of the amorphous silica surface does not change dramatically the activation energy of the hydroxylation reaction.

As already mentioned the water molecule may first physisorb with a small energy gain of 0.11 eV. In contrast we have found that ammonia has a deep physisorption well of 0.45 eV. The equilibrated geometry of physisorbed ammonia on the 2M ring is shown in figure 4. The adsorption site is the acidic silicon atom of the ring. These latter results are consistent with experimental IR data [10] which show signatures of physisorbed ammonia at room temperature while any clear evidence of physisorbed water on the 2M ring is found. Once physisorbed on the 2M ring, ammonia might dissociatively chemisorb still along two different paths as in figure 2, i.e. along the Si-N or the O-H reaction coordinates. Analogously to water, we have found that the reaction coordinate with lower activation energy is still the distance between the oxygen atom of the ring and the proton of ammonia. The activation energy for dissociation of physisorbed ammonia is 0.63 eV; the chemisorption leads to the ring opening and the final product shown in figure 5. The activation energy computed along the Si-N reaction coordinate is 1.9 eV higher. Experimentally both chemisorbed and physisorbed ammonia are detected in the IR spectra [10]. The IR peaks due to physisorbed ammonia appear at their maximum concentration immediately after the dehydroxylated silica surface is exposed to NH_3 and then decrease in intensity with time while the peaks associated with the chemisorbed molecules (vibrations of the Si-NH₂ groups) increase in intensity [10]. The chemisorption of ammonia is described experimentally by two rate constants $k_1 = 0.9\text{--}1.8 \text{ min}^{-1}$ and $k_2 = 0.05\text{--}0.06 \text{ min}^{-1}$ as obtained by monitoring the IR peaks of the 2M rings and of the Si-NH₂ groups [10]. The higher rate is assigned to a direct chemisorption on the 2M ring and the lower to the dissociative chemisorption of ammonia molecules already physisorbed on the 2M ring. The rate k_2 is in fact equal to the rate of disappearance of physisorbed molecules, as measured from the intensity of IR peaks assigned to Si-NH₃ vibrations. This latter reaction is slower than the water chemisorption ($k = 0.5 \text{ min}^{-1}$) which is in agreement with our finding of a larger activation barrier for the dissociation of physisorbed ammonia (0.63 eV) than for chemisorption of water (0.34 eV). On the other hand the transition state for ammonia chemisorption in figure 4(b) is only 0.18 eV higher in energy than the configuration with a free NH_3 molecule. If a gas phase ammonia molecule were able to access the transition state bypassing the bottom of the physisorption well, the chemisorption activation energy would be only 0.18 eV. This latter, direct, chemisorption path could be consistently assigned to the reaction with the higher experimental rate (k_1).

In summary, the outcome of the simulations of the reaction of water and ammonia with the 2M ring are in qualitative agreement with the experimental interpretation of the reaction kinetics based on IR spectroscopy [10]. The simulations reveal that, although the acidic silicon atom in the ring is the site for physisorption for both water and ammonia, chemisorption reactions proceed via an electrophilic attack to the oxygen atom in the ring. These results will be of help in the design of new families of organosilanes suitable to better react with the 2M ring. We here mention that preliminar simulations of the reaction of the 2M ring with tetraethoxysilane $(\text{Si}(\text{OCH}_2\text{CH}_3)_4)$ attacking the basic oxygen of the ring, show that the activation energy for organosilane adhesion is indeed lower on the 2M ring than on surface silanols [27].

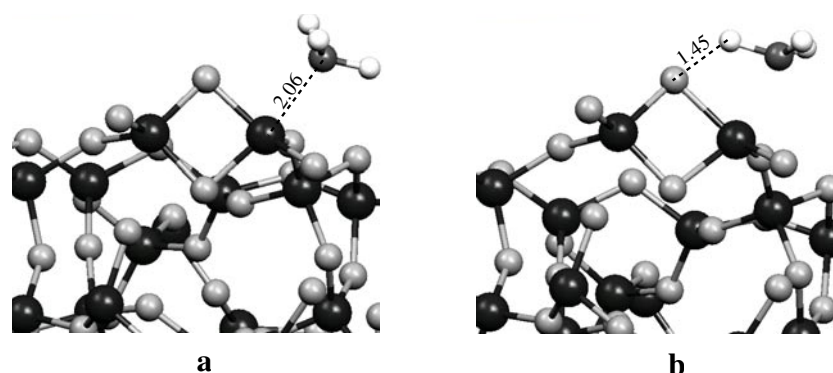


Figure 4. (a) Equilibrium configuration of ammonia physisorbed on the 2M ring. The physisorption energy is 0.45 eV. (b) Transition state for the ammonia-ring reaction. Bond lengths are given in Å.

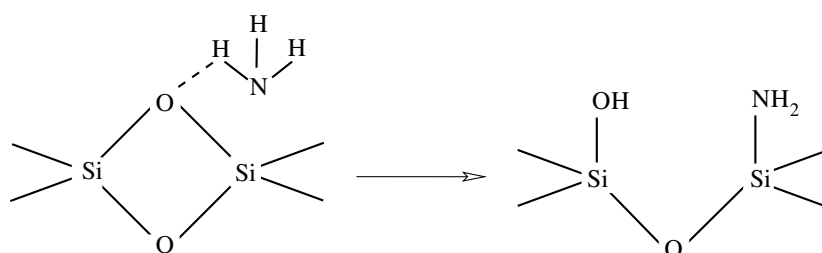


Figure 5. Sketch of the initial and final configurations for the ammonia-ring reaction.

3. The surfaces of Mg(OH)₂

The surface properties of Mg(OH)₂ are also of relevance in the technological processes of surface coating with polymers. In fact, Mg(OH)₂ is introduced as a filler in the polymer blend to act as a flame retardant via the strongly endothermic dehydration reaction $\text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O}$ which occurs at ~ 580 K [30]. Recent experimental data by x-ray absorption near-edge structure (XANES) spectroscopy [31] suggest that the dehydration reaction occurs at first at the surface and then the formation of MgO phase proceeds from the surface inside the bulk. It is interesting to wonder if the dehydration reaction may occur preferentially on a particular surface of Mg(OH)₂. In this case suitably prepared samples may show a water leakage at a temperature below the temperature of massive decomposition (580 K) which can be of relevance in the technological applications of Mg(OH)₂. In order to address this problem we have studied using *ab initio* Car–Parrinello simulations [4, 5] few low-indices surfaces of Mg(OH)₂ and their dehydration mechanisms.

Mg(OH)₂ is a layered compound of hexagonal symmetry (space group $P3m1$) and lattice parameters $a = 3.147$ Å and $c = 4.769$ Å. The metal atoms and oxygen atoms occupy respectively the lattice positions $(0, 0, 0)$ and $(1/3, 2/3, z)$ with $z = 1.049$ Å (figure 6). As shown in a previous work on the high-pressure phase transitions of Mg(OH)₂ [32], the bulk structural properties of brucite are well reproduced by the DFT–BLYP framework used for silica and presented in the previous sections. Within the same framework we have studied the cleavage (0001) surface and the (1000) and $(1\bar{1}00)$ faces of Mg(OH)₂ modelled in a slab geometry. The periodically repeated slabs are separated by a vacuum 6 Å wide. We have used

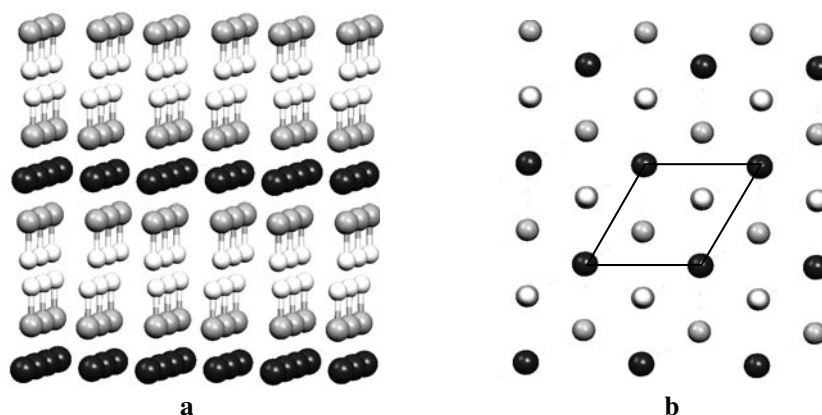


Figure 6. (a) side view of the Mg(OH)₂ crystal showing the layered structure. (b) Top view of a single layer. Metal atoms and OH groups form hexagonal sublattices in the plane perpendicular to the [001] direction. The hexagonal unit cell is shown. Black, light grey and white spheres are Mg, O and H atoms, respectively.

norm-conserving pseudo-potentials [23] and plane wave expansion of the Kohn–Sham orbitals up to a kinetic cutoff of 70 Ry. Nonlinear core corrections were taken into account for Mg. The integration of the Brillouin zone has been restricted to the Γ point of the simulation supercell. For the calculation of the surface energy we evaluated the bulk energy, to be subtracted from the total energy of the slab, by using a Brillouin zone sampling equivalent to the supercell used in the surface calculations. For the (0001) surface we have used a supercell containing one or two Mg(OH)₂ layers and up to nine surface unit cells (45–120 atoms). For the (1000) and (1 $\bar{1}$ 00) surfaces we have used slabs containing 2–6 surface unit cells and 10–12 atomic layers thick (80–140 atoms).

The cleavage (0001) surface undergoes minor relaxation (less than 0.01 Å) with respect to the ideal termination of the bulk. In contrast, on the (1 $\bar{1}$ 00) and (1000) faces the surface hydroxyls rotate outwards from the surface plane as shown in figures 7 and 8. This relaxation pattern is driven by the electrostatic repulsion among the protons of the hydroxyls which at the surface are free to rotate to minimize the electrostatic energy. The calculated surface energies are 8, 25 and 45 meV Å⁻² for the (0001), (1 $\bar{1}$ 00) and (1000) faces, respectively. The Wulff construction [33] produced by the latter surface energies predicts the equilibrium shape of the crystallites (at zero temperature) which turns out to be a hexagonal platelet with the {0001} faces as the basal, most abundant surface and with the {1 $\bar{1}$ 00} faces as the lateral surfaces, in agreement with experimental characterization by means of transmission electron microscopy and x-ray diffraction [34]. The (1000) face is not present in the shape of the crystallite at thermodynamic equilibrium at zero temperature because of its high surface energy. However, this latter face may appear as a metastable surface in the real material grown under special conditions and used for instance as filler in polymeric blend. In the study of surface dehydration, reported in the next section, we have thus considered also the (1000) face which is the most open surface among those we have investigated. In fact the coordination of the Mg atom is six-fold at the (0001) surface (as in the bulk), five-fold on the (1 $\bar{1}$ 00) face and four-fold on the (1000) face.

3.1. Dehydration reactions in Mg(OH)₂

The dehydration reaction occurs via condensation of vicinal hydroxyls. In the bulk and at the (1000) surface two dehydration mechanisms are conceivable: the condensation of vicinal

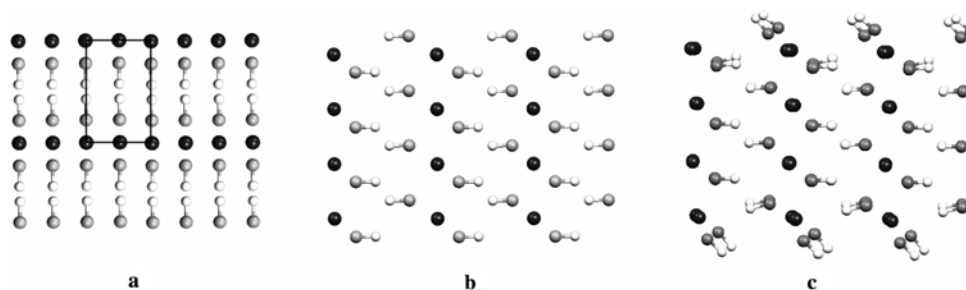


Figure 7. (a) Top view of the ideal $(1\bar{1}00)$ surface of $\text{Mg}(\text{OH})_2$. (b) Side view of the ideal $(1\bar{1}00)$ surface. (c) Side view of the relaxed $(1\bar{1}00)$ surface. The ideal surface unit cell is shown in panel (a). The simulation supercell contains six surface unit cells for a total amount of 120 atoms.

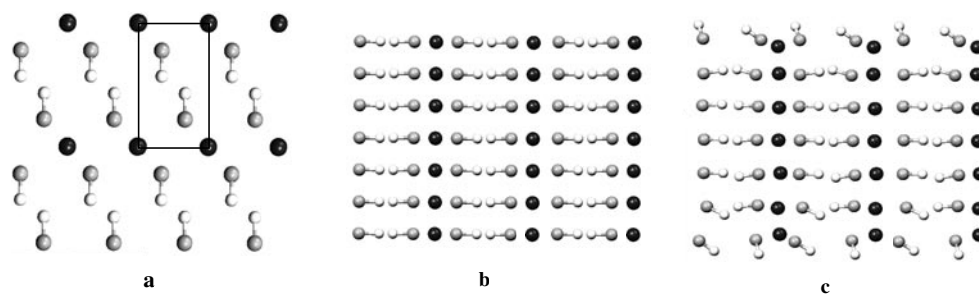


Figure 8. (a) Top view of the ideal (1000) surface of $\text{Mg}(\text{OH})_2$. (b) Side view of the ideal (1000) surface. (c) Side view of the relaxed (1000) surface. The ideal surface unit cell is shown in (a). The simulation supercell contains four surface unit cells for a total amount of 140 atoms.

hydroxyls belonging to the same $\text{Mg}(\text{OH})_2$ layer and the condensation of vicinal hydroxyls belonging to adjacent layers. The final product of the condensation reaction consists of a released water molecule, a single oxygen and a hydroxyl vacancy, as shown in figure 9 for the (1000) surface. The water molecule is supposed to leave the surface. The configuration in figure 9 is obtained by subtracting a surface hydroxyl and the proton of a neighbouring subsurface hydroxyl belonging to the same $\text{Mg}(\text{OH})_2$ layer. The geometry has been optimized by simulated annealing. The calculated dehydration energy for this process is 2.8 eV. At the (1000) surface the condensation of vicinal hydroxyls on adjacent $\text{Mg}(\text{OH})_2$ layers would produce a hydroxyl vacancy and a single oxygen both on the surface plane. This latter configuration is unstable in a MD run at room temperature which shows a spontaneous transformation into the geometry reported in figure 9. Conversely, in the bulk, both processes are possible and the final products of the two different condensation reactions are both locally stable in a room-temperature simulation (117-atom cell simulation lasting ~ 1 ps). However, the condensation energy is different for the two reactions: 2.4 eV for the condensation of hydroxyls on the same layer and 2.8 eV for the condensation of hydroxyls on adjacent layers. This difference in condensation energy can be understood simply by electrostatic consideration. In fact, the hydroxyl vacancy and the single oxygen can be seen as charged defects with opposite charges ± 1 . The lower condensation energy corresponds to the final configuration with the shortest distance among the charged defects. It should be note that at equilibrium at zero temperature, the minimum O–H distance among vicinal hydroxyls, which is the reaction coordinate for the condensation process, involves the two vicinal hydroxyls on adjacent layers.

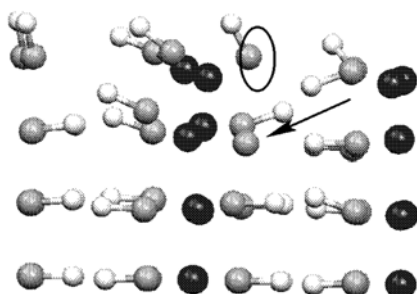


Figure 9. The (1000) surface after the condensation of two vicinal hydroxyls. The circle indicates the position of the hydroxyl vacancy, the arrow indicates the single oxygen of the other hydroxyl involved in the condensation reaction. Only half of the slab is shown.

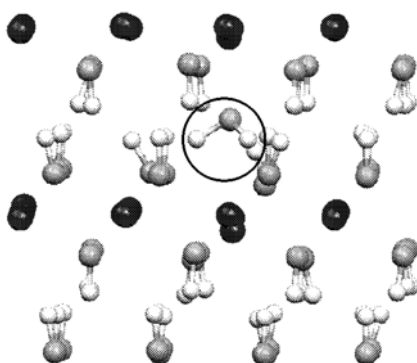


Figure 10. Equilibrium configuration of a water molecule inserted in bulk $\text{Mg}(\text{OH})_2$. The simulation cell contains 120 atoms.

However, in a MD simulation at the decomposition temperature of 580 K, we have observed that the hydroxyls undergo large librational motions and the O–H distance among vicinal hydroxyls on the same layer becomes the shortest. Therefore, although we have not estimated the activation barrier for these processes, we expect the condensation of vicinal hydroxyls on the same layer to be favoured also from the kinetic point of view with respect to condensation of hydroxyls on adjacent layer. On the cleavage surface (0001) all surface hydroxyls obviously belong to the same $\text{Mg}(\text{OH})_2$ layer. We have estimate the condensation energy of two hydroxyls on this face from the total energy of the fully dehydrated surface whose surface bilayer is equivalent to the 2×1 -reconstructed (111) surface of MgO [35]. The resulting condensation energy is 2.9 eV, close to the value of 2.8 eV calculated for the (1000) surface. The surface condensation energies turn out to be larger than the condensation energy in the bulk (2.4 eV) which might suggest that the dehydration would occur preferentially in the bulk. However, in the energy balance of the condensation reaction in the bulk we have to add the insertion energy of a water molecule. The released water molecule is free to leave the sample at the surface but experiences a large steric hindrance in the bulk. We have found the equilibrium position of a water molecule in a bulk supercell containing 120 atoms via simulated annealing up to 600 K. The final configuration is shown in figure 10. The insertion energy is as high as 3.2 eV. At high temperature the insertion energy would probably decreases due to thermal expansion which widens the gap between two adjacent layers and reduces the steric hindrance of the inserted water molecule. However, the insertion energy is so high to let us confidently

conclude that the dehydration reaction is energetically favoured at the surface. Inclusion of the vibrational contribution to the condensation free energy would not change dramatically the energy balance even at 580 K. Moreover, the surface condensation energies are close to the experimental estimate of 2.6 eV obtained from the Arrhenius plot in the early stage of dehydration [36].

4. Conclusions

Based on Car–Parrinello simulations we have provided insight onto the nature of hydroxylation and dehydroxylation reactions at the surface of silica and brucite. In silica, the hydration occurs preferentially at a particular surface site, a 2M silicon ring. The simulations have revealed that water can physisorb on the acidic silicon of the ring, but the subsequent chemisorption leading to the ring opening and formation of surface hydroxyls is driven by an electrophilic attack to the oxygen of the ring. Similar behaviour is found for ammonia. The calculated physisorption energies and activation barriers for chemisorption are in qualitative agreement with the reaction kinetics inferred experimentally from IR spectroscopy [10]. Concerning brucite, we have presented the first *ab initio* study of the structural properties of the low-indices surfaces of $\text{Mg}(\text{OH})_2$. The calculations of condensation energies of hydroxyls at the surface and in the bulk suggest that dehydroxylation of $\text{Mg}(\text{OH})_2$ would initially take place at the surface as proposed in a recent experimental work [31]. The more open (1000) surface of brucite is only marginally favoured for dehydration than the cleavage (0001) plane.

Acknowledgments

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