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# Water chemisorption and reconstruction of the MgO surface

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The observed reactivity of MgO with water is in apparent conflict with theoretical calculations which show that molecular dissociation does not occur on a perfect (001) surface. We have performed *ab initio* total-energy calculations which show that a chemisorption reaction involving a reconstruction to form a (111) hydroxyl surface is strongly preferred with $\Delta E = -90.2\ \mathrm{kJ\,mol^{-1}}$. We conclude that protonation stabilizes the otherwise unstable (111) surface and that this, not the bare (001), is the most stable surface of MgO under ambient conditions.

Magnesium oxide has long provided a prototype for the study of surface structure and chemical reactions of oxides. Naturally occurring MgO, known by its mineral name of periclase, is not a common crustal mineral, but its simple structure makes it an excellent example for the investigation of mineral surface chemistry.

Reactions at mineral surfaces are responsible for much of the chemical change that occurs in the Earth's crust. Weathering reactions control the erosion of rocks and the consequent evolution of surface topography, thus providing an opposing mechanism to the more dramatic process of mountain building. Aqueous reactions in sedimentary basins are responsible for the diagenetic processes that transform unconsolidated sediments into rocks. In this work we study the nature of a simple mineral surface when exposed to an aqueous environment and the chemical interaction of water with that surface. This is both a prerequisite to studying the interaction with aqueous solutions and a tractable first step towards ligand-exchange reactions in more complex silicate minerals.

We have performed experiments on single crystals of MgO prepared with high-quality (001) faces that were reacted with acidic solutions. The experiments and results are reported in detail elsewhere,[1] the main feature being the development of an altered surface layer. Elastic recoil detection analysis[2] (ERDA) shows protonation to a depth of 900 Å with a H/Mg ratio close to 2 giving a probable chemical composition of magnesium hydroxide. Indeed brucite [the mineralogical name for $Mg(OH)_2$] is the most common alteration product of periclase in the natural environment[4] and well-crystallized intergrowths of brucite on periclase have been reported.[5]

The initial stage in the reaction is hydroxylation of the surface. MgO has the cubic rocksalt structure with (001) cleavage planes. This is the most stable surface and is the only one seen experimentally.[6] The simplest possibility for a hydroxylated surface is obtained by dissociating a water molecule and placing the OH group above each magnesium ion and the H above each oxygen of the (001) surface [see Fig. 1(a)] as postulated by Coluccia *et al.*[7]

Some striking hydroxylation experiments were reported by Jones *et al.* who studied surface roughening on (001) faces of nanocrystalline MgO in a transmission electron microscope.[8] The remarkable affinity of MgO for water is demonstrated by their *in situ* observation of hydration-induced surface roughening over 10 min under vacuum with $P_{H_2O} < 10^{-5}$ Pa. The presence of surface hydroxyl groups on MgO powders exposed to $H_2O$ has been demonstrated by infrared spectroscopy.[7,9,10] Hydroxyls are clearly distinguishable from physisorbed molecular water by the HOH bending mode, which disappears above 100 °C, while the OH stretching mode persists even above 500 °C. Furthermore, there is complete monolayer coverage of the surface by hydroxyls, as shown by microgravimetry measurements.[7]

Despite these observations, the most reliable theoretical calculations predict that water molecules do not dissociate on the (001) surface. Scamehorn, Hess, and McCarthy[11] calculated the energetics of the reaction $\{>MgO\} + H_2O \rightleftharpoons \{>Mg(OH)_2\}$ (Ref. 3) to form the hydroxylated (001) surface using periodic Hartree-Fock methods. They showed that dissociative chemisorption is energetically unfavorable and that physisorption of intact water molecules is preferred. This was confirmed by a Car-Parrinello *ab initio* molecular-dynamics study,[12] which investigated the dynamics of a water molecule at a MgO (001) surface. No dissociation occurred. Experiments performed by Jones *et al.*[8] also led to the conclusion that perfect (001) surface sites are not protonated.

In summary, water demonstrably chemisorbs onto MgO but trustworthy calculations show that $H_2O$ molecules should not dissociate on the only known stable surface. Several authors have proposed that water dissociates instead at low coordinated sites such as steps, corners and other defects[8,13] and dissociation was demonstrated computationally at steps and corners.[12,14] However, one might expect this to simply saturate the defect sites. Dissociation at defects does not explain the monolayer coverage of the surface by OH groups,[7] the whole-surface roughening observed in the TEM,[8] nor the progressive transformation of the entire (001) surface and incipient bulk hydroxylation observed by infrared (IR)

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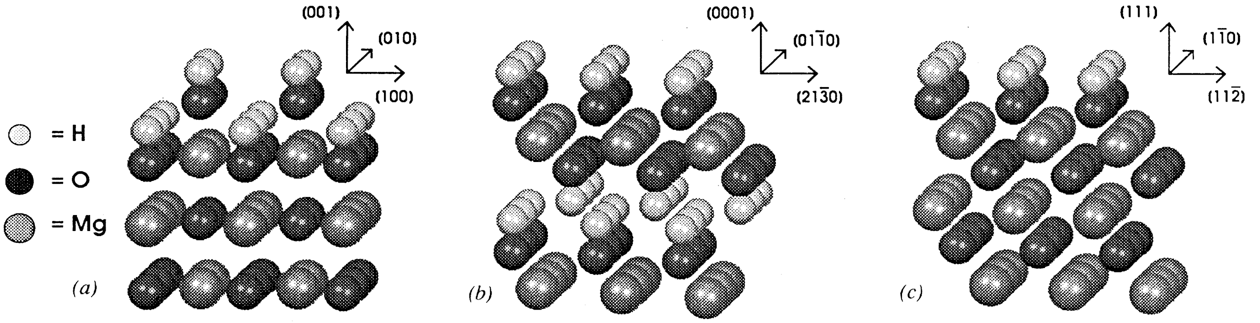

FIG. 1. (a) Hypothetical hydroxylated (001) surface of MgO, (b) (0001) surface of $Mg(OH)_2$, (c) our postulated (111) hydroxyl surface of MgO. The top three O-Mg-O layers of an oxygen-terminated MgO (111) surface have the same structure as $Mg(OH)_2$ (0001). The (111) hydroxyl surface may be equivalently constructed by protonation of an oxygen-terminated surface or by hydroxylation of a magnesium-terminated surface.

spectroscopy[8,9] and in our dissolution experiments.

In order to account for these phenomena we propose an alternative structure for the fully hydroxylated surface. The progressive formation of a bulk hydrated layer suggests consideration of the structural relationship between the oxide and the crystalline hydroxide. $Mg(OH)_2$ is trigonal and is composed of layers of $Mg^{2+}$ and $OH^-$ ions in (0001) planes [see Fig. 1(b)]. This "basal" plane is also the cleavage plane, yielding a stable type-II hydroxide surface. The trigonal symmetry means that the basal plane is incommensurate with the cubic (001) MgO surface, but closely resembles the threefold symmetric (111). Figure 1 illustrates that protonation of the (111) creates a surface with the same structure as the $Mg(OH)_2$ (0001) cleavage plane. This strongly suggests that protonation may stabilize the MgO (111) surface, and that this may be the hydroxylated surface observed by IR spectroscopy.

Supporting evidence is provided by well-crystallized natural growths of $Mg(OH)_2$ on MgO (Ref. 5) and from the inverse reaction, the dehydration of $Mg(OH)_2$ to form MgO.[15] In both cases an epitaxial relationship exists between the two phases such that the [0001] axis of the hydroxide is aligned with the oxide [111].

We have investigated the stability of the (111) hydroxyl surface using total-energy pseudopotential calculations.[16] The density-functional theory formulation of quantum mechanics is solved within the local-density approximation (LDA) (using the parametrization of Perdew and Zunger[17]) by conjugate-gradient minimization of the total energy with respect to the valence electron wave functions. Optimized nonlocal pseudopotentials are used in the Kleinman-Bylander separable representation. The system of ions and electrons is subject to periodic boundary conditions that allow the use of a plane-wave basis set. The latter gives an accurate representation of the crystalline environment. Just as importantly, it permits analytic forces to be computed, allowing for relaxation of the ions to their minimum-energy configuration. This type of calculation has been used to study defect energies in MgO,[18] OH groups as substitutional defects in quartz,[19] reconstruction of the silicon (111) surface,[20] and dissociation of $Cl_2$ at a silicon surface.[21]

One difficulty in using plane-wave pseudopotential methods for oxides has been that the tightly bound oxygen $2p$ electrons require a high-energy cutoff, making the calculations expensive to perform. Recent advances have dramatically improved the convergence properties so that oxide calculations are now routine.[22] In this work we used an optimized oxygen pseudopotential that gives complete convergence of the electronic energy (to 0.05 eV from an energy of 909 eV) at a cutoff of 500 eV. Magnesium was also represented by an optimized pseudopotential and hydrogen by a pure Coulombic potential.

As a check on the accuracy to be expected we performed calculations on bulk MgO and an isolated water molecule, the initial reactants. The results agree closely with experimental values and are summarized in Table I.

To represent a surface using periodic boundary conditions we performed calculations on a slab of MgO in a periodic cell of larger dimension leaving a vacuum separating periodic images of the slab. The surface energy is given by $\Delta E_{\text{surf}} = (E_{\text{slab}} - E_{\text{bulk}})/a^2$. To test convergence with respect to both the number of layers in the slab and the vacuum space we calculated the energy of the (001) MgO surface using 4, 6, or 8 atomic layers in the slab and different $c$ dimensions of the supercell leaving between 8 and 16 Å of vacuum. The periodic cells had dimensions $a_0/\sqrt{2} \times a_0/\sqrt{2} \times na_0$, $n = 1, 4, 6$. The lattice parameter $a_0$ was fixed at the experimental value of 4.2117 Å. The $k$-point set contained eight points for the long cells and 32 or 48 points for the compact cell used for the bulk calculation. In every case relative energies were computed using equivalent sets to cancel basis-set size errors. The total energies were well converged as a

TABLE I. Calculated properties of bulk MgO and isolated water molecule: MgO lattice parameter $a_0$, bulk modulus $K$, and $K' = dK/dP$; $H_2O$ molecular bond length and angle.

| | Property | Calculated | Experimental |
|---|---|---|---|
| MgO | $a_0$ (Å) | 4.217±0.001 | 4.2117 (Ref. 4) |
| | $K$ (Mbar) | 1.62±0.02 | 1.603±0.003 (Ref. 29) |
| | $K'$ | 4.19±0.08 | 4.15±0.10 (Ref. 29) |
| $H_2O$ | Bond length (Å) | 0.966 | 0.9572 |
| | HOH angle (deg) | 103.9–104.1[a] | 104.52 |

[a] The value depends on the size and shape of the supercell and the orientation of the molecule, indicating a very small interaction between a molecule and its periodic images.

function of $k$-point sampling, to better than 0.05 eV out of 909 eV. The coordinates of the ions in the outer layers of the slab were relaxed to their minimum-energy configuration, while the inner two layers were constrained at their bulk separation. The surface $Mg^{2+}$ ions moved inwards by 1% and the $O^{2-}$ ions by 0.1% in agreement with previous Hartree-Fock calculations.[23] The resultant surface energies are all between 1.093 and 1.103 J $m^{-2}$, which shows that a four-layer slab with 8 Å of vacuum gives energies converged to a precision of better than 0.01 J $m^{-2}$. This result is compared with previous work in Table II.

The test calculations establish that errors in the energy differences due to cell-size and basis-set effects are less than 1 kJ $mol^{-1}$. This leaves one significant source of systematic error, the LDA, which is known to underestimate molecular dissociation energies.[21] We estimated an upper bound for this error of 40 kJ $mol^{-1}$ from a calculation of the reaction $MgO + H_2O \rightleftharpoons Mg(OH)_2$(brucite) whose energy is well known. Our main result is quite robust to an error of this magnitude.

The chemisorption energy is fully determined given the structure and state of the reactants and products by $\Delta E = E_{\text{product}} - \sum E_{\text{reactants}}$. The appropriate initial states are the bare (001) surface of MgO and ice (since this is a zero-temperature calculation) and the final structures are the hydroxylated (001) and the (111) hydroxyl surfaces of Fig. 1. Scamehorn, Hess, and McCarthy showed that the fully hydroxylated (001) surface has lower energy than if partially hydrated[11] so we performed calculations for only that state. Calculations on the hydroxylated (001) surface were performed in a supercell $\sqrt{2}a_0 \times \sqrt{2}a_0 \times 4a_0$ containing four layers of Mg and O ions plus two surface layers of hydrogen or hydroxyl. Simple electrostatic considerations indicate that full hydroxylation must also be favored for the (111) surface: this is the only means of achieving a nonpolar surface.

Ideally calculations on the reactants and products should use equivalent supercells to achieve cancellation of basis set errors in the computed $\Delta E$. This rules out a direct calculation for the bare (001) $\rightleftharpoons$ (111) hydroxyl reaction as the symmetries differ and no cell can accommodate both structures. However, the reaction may be split into two stages $\{>MgO\}^{(001)} \rightleftharpoons MgO^{\text{bulk}}$ and $MgO^{\text{bulk}} + H_2O \rightleftharpoons \{>Mg(OH)_2\}^{(111)}$ whose partial energies sum to the desired result. Each stage can be computed using cells of the appropriate symmetry since bulk MgO is commensurate with both. The first stage is simply the surface energy. The second used trigonal cells with $a = a_0/\sqrt{2}, c = \sqrt{3}a_0$, and 24 $k$ points for bulk MgO and $a = a_0/\sqrt{2}, c = 2\sqrt{3}a_0$ with 12 $k$ points and contained five layers of Mg and O ions in a hydroxylated slab. The outer layers were relaxed in all these calculations.

TABLE II. Calculated MgO(001) surface energies and comparison with previous measurements and calculations.

| Technique | $\Delta E_{\text{surf}}$ (J $m^{-2}$) |
|---|---|
| DFT/LDA (this work) | 1.10 |
| DFT/LDA using Gaussian basis set (Ref. 30) | 1.16 |
| Periodic HF[a] | 1.43 |
| Pair potentials (Ref. 31) | 1.07 |
| Experiment[b] | 1.04–1.20 |

[a] These calculations (Ref. 23) used a basis set containing only $s$ and $p$ orbitals. Birkenheuer *et al.* (Ref. 30) showed that including $d$ orbitals decreased their $\Delta E_{\text{surf}}$ from 1.32 to 1.16 J $m^{-2}$.

[b] Summarized by Tosi (Ref. 32 and references therein).

The initial state of water was based on calculations of an isolated molecule in supercells equivalent to those used for the bulk MgO calculations but of twice the linear dimensions to minimize interaction between periodic images. To this we added the experimental value for the sublimation energy of ice, $-47.35 \pm 0.02$ kJ $mol^{-1}$.[24]

The results are listed in Table III. As expected the hydroxylation of the (001) surface is energetically unfavorable. Our hypothesis that hydroxylation stabilizes the (111) surface is confirmed, with a $\Delta E$ of $-90.2$ kJ $mol^{-1}$ with respect to ice, or (by using the results of Scamehorn, Hess, and McCarthy[11] for the physisorption energy) $-117.3$ kJ $mol^{-1}$ relative to physisorbed water. This provides a ready explanation of the spectroscopic observations of surface hydroxyls and the observed reactivity of MgO with water manifested as rapid roughening of the (001) surfaces of microcrystals. The chemisorption reaction must involve a reconstruction of the (001) surface.

We conclude that the (111) hydroxyl, rather than the bare (001) is the normal surface of MgO under ambient environmental conditions. A (001) MgO surface will chemisorb water and reconstruct except under ultrahigh vacuum or high temperature. Dehydroxylation is experimentally observed only under UHV (Ref. 13): indeed hydration reactions occur under lesser vacuum in the TEM at a partial pressure of water of $< 10^{-5}$ Pa. Upon heating dehydroxylation begins at 200 °C but is gradual with residual hydroxyls persisting until over 700 °C.[7,10]

This solves a number of experimental puzzles. (1) The $H_2 \rightleftharpoons D_2$ exchange reaction is catalyzed by MgO at temperatures as low as 78 K.[25] Structural surface protons provide the necessary exchange site.[26] (2) It may also re-

TABLE III. Computed energies for the chemisorption reaction of water with MgO, formally $\{>MgO\}^{\text{initial}} + H_2O \rightleftharpoons \{>Mg(OH)_2\}^{\text{final}}$. The initial states are bulk MgO or the (001) surface plus ice at 0 K. The final states are the hydroxylated (001) or (111) hydroxyl surfaces. The (111) surface energies are expressed per unit of the *original* (001) surface area assuming a ratio of $\sqrt{3}$:1. A periodic HF study found a significantly more positive $\Delta E$ for the hydroxylation of (001) of 77–90 kJ $mol^{-1}$ (Ref. 11). The measured enthalpy of water chemisorption on MgO at 613 Pa and 543 K is in the range $-113$ to $-189$ kJ $mol^{-1}$ (Ref. 33). Approximate thermodynamic corrections to $\Delta E$ at 0 K for the (111) hydroxyl give $\Delta H_{543} \approx -138$ kJ $mol^{-1}$, consistent with those experiments.

| Initial | Final | $\Delta E$ (J $m^{-2}$) | $\Delta E$ (kJ $mol^{-1}$) |
|---|---|---|---|
| (001) | (001) | +0.78 | +41.6 |
| Bulk | (111) | −0.59 | −31.3 |
| (001) | (111) | −1.69 | −90.2 |

solve discrepancies between experimental and theoretical energies of adsorption of CO onto MgO.[27] The appropriate surface for molecular adsorption is the (111) hydroxyl surface, not the bare (001). (3) Vermilyea showed that the dissolution rates of MgO and $Mg(OH)_2$ are identical over the *p*H range 2–5,[28] an observation easily explained by the almost identical surface structures.

Identification of the actual reconstruction pathway is beyond the scope of this paper, but a plausible mechanism must account for both the dissociation of the water molecule and the transport of surface $Mg^{2+}$ and $O^{2-}$ ions. Previous *ab initio* calculations have shown that water molecules dissociate at surface defects, particularly steps and corners,[12,14] corroborating the observation that the reconstruction is more rapid if the surface is damaged.[8] The activation barrier for ion transport may be estimated given that the inverse reconstruction, the annealing of $\{100\}$ facets on a (111) surface, is observed to occur at 1000 K.[13] The equivalent thermal energy is 12 $\text{kJ mol}^{-1}$, rather less than the chemical energies of the hydroxylation reaction. It is also possible that the barrier for $Mg^{2+}$ transport away from the defect site is reduced by hydration with either the product $OH^-$ ion or an intact $H_2O$ molecule. This would expose low coordinated oxygen sites able to dissociate incoming water molecules and thereby continue the process.

Stabilization of a type-III polar surface by protonation or hydroxylation to form a nonpolar type-II surface is unlikely to be unique to MgO. We would also expect reconstructive chemisorption to occur in other fcc binary metal oxides such as NiO.

The consequences of the stability of the hydroxyl surface over the bulk are substantial but rather harder to predict. It does provide a driving force for the layer hydration observed by us and others, which apparently leads to a topotactic oxide-hydroxide transformation. However, a much better characterization of the hydroxylated layer is needed and further studies to establish its composition and structure are under way. Whatever its nature it is demonstrably a vital precursor stage in the dissolution of magnesium oxide and may also prove relevant to understanding recrystallization and precipitation reactions.

*Note added in proof.* The hydroxylated (111) surface has now been observed experimentally in NiO using LEED by Rohr *et al.*[34] This work demonstrates its stability with respect to the (reconstructed) bare (111) surface but makes no comparison with the (001).

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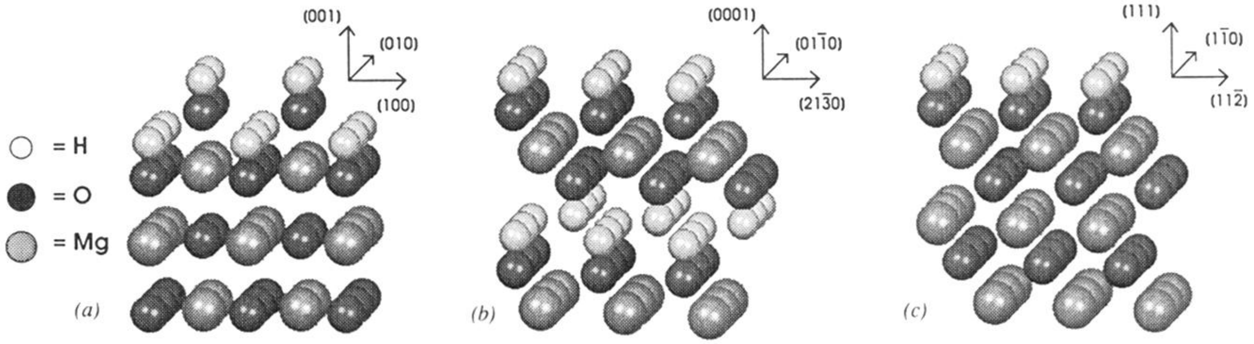

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