6494 J. Phys. Chem. A 2009, 113, 6494–6499

Theoretical Study of the Reaction between HF Molecules and Hydroxyl Layers of $Mg(OH)_2$

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Received: November 14, 2008; Revised Manuscript Received: April 14, 2009

The reaction of HF molecules with brucite, $Mg(OH)_2$, leading to the formation of $Mg(OH)_{2-x}F_x$, was theoretically studied by ab initio density functional theory (DFT) with periodic boundary conditions. We proposed as mechanism for this reaction four elementary steps: adsorption of the HF molecule, OH^- liberation from brucite as a water molecule, desorption of the newly formed H_2O, and rearrangement of the F^- anion into a hydroxyl position. For the $Mg(OH)_{2-x}F_x$ formation, with $x = 1/9$, the final product, outcome from an initially adsorbed HF molecule, we computed the Helmholtz free energy variation $\Delta F = -23$ kcal/mol. The calculated frequency for the most intense infrared band, a Mg−F stretching mode, was 342 cm^{-1}. Two transition states, corresponding to the hydroxyl reacting with a proton forming a water molecule and migration of a fluoride anion into a hydroxyl vacancy, were computed. The calculated reaction barriers indicate that the reaction between $Mg(OH)_2$ layers and HF molecules is slow and irreversible.

1. Introduction

Fluorine is usually present in nature as the F^- anion. This anion, which may originate from geological sources and industries employing fluoride-containing compounds as raw materials, can contaminate ground/surface water reservoirs. Several widely used industrial fluoride compounds, particularly aluminum smelters, may also contribute to environmental fluoride pollution. This diversity of pollution sources limits the availability of the already scarce water resources worldwide. Consequently, there is an ever-increasing need to remove fluoride excess from water.[1]

The removal of fluorides from drinking water, a process known as defluoridation, can be achieved by several chemical−physical processes, namely, adsorption, chemical precipitation, electrodialysis, ion exchange, and electrochemical processes.[1−5] Among these processes, adsorption onto a solid surface has the advantage of being a simple, versatile, and convenient approach to treat drinking water systems, usually available in small communities. Adsorption is also an economical process which can remove ions over a wide pH range, and for lower residual concentrations, this approach is more efficient than chemical precipitation.[2]

Magnesium hydroxide $Mg(OH)_2$, known as brucite, is a crystal with a structure composed by individual layers of Mg^{2+} in octahedral sites surrounded by six hydroxyl groups (Figure 1). Each OH^- anion is surrounded by three metal cations, resulting in neutral layers. The brucite structure can undergo compositional changes with slight structural modifications, when, as an example, a trivalent cation (M^{3+}) isomorphically replaces some of the Mg^{2+} cations, thereby forming a positive charge excess in the layers that must be neutralized by interlayer anions. The outcome of this type of compositional changes is a series of compounds called layered double hydroxides (LDH) or hydrotalcite-type compounds, described by the general formula $[M^{2+}_{(1-x)}M^{3+}(OH)_2]^{x+}(A^{m-})_{x/m}\cdot nH_2O$, where M^{3+} and M^{2+} are metal cations and A is a counterion with $m-$ charge.[6]

Experimental work on the formation of $Mg(OH)_{2-x}F_x$ materials supposed chemical bonding between the F and Mg atoms.[1,2,4] Maliyekkal et al. suggest an isomorphous substitution of hydroxyl anions by fluoride anions during the brucite formation from coated magnesia (MgO).[2] In other work, Lv and collaborators proposed a two-step mechanism for the adsorption.[4] The first one would be the diffusion of the fluoride anion replacing another interlayer anion. This proposal was tested on LDH compounds containing Cl^-, HCO_3^-, SO_4^{2-}, and $H_2PO_4^-$ anions by a series of batch experiments. The second step according to Lv et al. would be the fluoride anions reacting with the layers. The same work also verified that the capacity of each compound to adsorb fluoride anions increases in different ranges of acidity. The proposed total mechanism has a fast first-order step followed by a slow second-order one, and the respective activation energies were determined as 8.9 and 17.4 kcal/mol. Brucite-type compounds with isomorphous substitution of OH^- by F^- were also proposed as catalysts.[8]

On the theoretical side, simulations using density functional theory (DFT) with the B3LYP functional and cluster models were used to investigate hydroxide layers containing Al, Mg, and F and the comparison between calculated and experimental nuclear magnetic resonance (NMR) data pointed to Mg−F and Al−F bonding.[7] Calculations of brucite-type compounds using ab initio methodologies based on DFT are available in the literature.[9,10] These works showed that optimized geometries and calculated vibrational modes agree with the experimental data.[11] Recently, we have shown that there exists very weak interaction energies between the layers of brucite-type compounds.[12] These interaction energies were about 2 kcal/mol and indicated that an unique layer could be a good model to simulate

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10.1021/jp810047d CCC: \$40.75

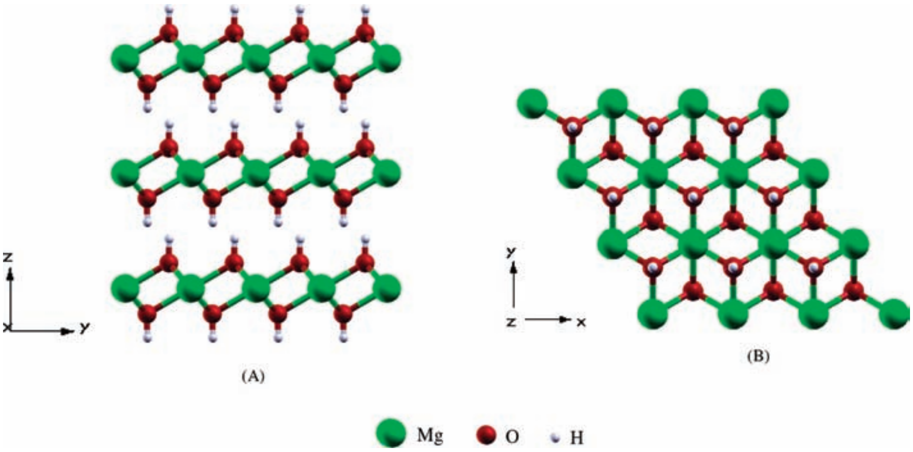

Figure 1. Two views (A and B) of the brucite structure.

surface reactions or reactions between interlayer anions and a hydroxyl layer.

The hydrofluoric acid (HF) has $pK_a = 3.45$, and because of that, part of the fluoride anions need to be protonated at acid ranges. The protonated and neutral HF forms are a possible way to start the reaction with the hydroxyl layers. For the F^- anion to be in the interlayer structure, a previous reaction with water would be necessary ($F^- + H_2O \rightarrow HF + OH^-$) followed by HF formation. Therefore, the possibility of fluoride incorporation into the brucite-like layers from HF has to be investigated. In this case, the process might include HF adsorption, OH^- liberation, and rearrangement of the F^- anion produced into a hydroxyl position. In this work we present ab initio DFT calculations for the formation of $Mg(OH)_{2-x}F_x$ compounds according to the global reaction $Mg(OH)_2 + xHF \rightarrow Mg(OH)_{2-x}F_x + xH_2O$. We propose a formation mechanism composed of four elementary reactions and computed the corresponding formation energies, reactions paths, and optimized geometries.

2. Proposed Mechanism

In order to study the formation of $Mg(OH)_{2-x}F_x$ compounds, we propose a reaction sequence, investigated by our calculations. The suggested mechanism for the global reaction $Mg(OH)_2 + xHF \rightarrow Mg(OH)_{2-x}F_x + xH_2O$ is the following

$$Mg(OH)_2 + xHF \rightarrow Mg(OH)_2 \cdots x(HF) \qquad (R1)$$

$$Mg(OH)_2 \cdots x(HF) \rightarrow [Mg(OH)_{2-x}]^+ \cdot xH_2O \cdot F^-_{\ x} \qquad (R2)$$

$$[Mg(OH)_{2-x}]^+ \cdot xH_2O \cdot F^-_{\ x} \rightarrow [Mg(OH)_{2-x}]^+ F^-_{\ x} + xH_2O \qquad (R3)$$

$$[Mg(OH)_{2-x}]^+ F^-_{\ x} \rightarrow Mg(OH)_{2-x}F_x \qquad (R4)$$

Reaction R1 is just the adsorption of HF molecules on the brucite layer. The adsorbed HF molecule is the R1 product, $Mg(OH)_2 \cdots x(HF)$, which then reacts with the $Mg(OH)_2$ layer thereby forming adsorbed water and fluoride anions in reaction R2. In reaction R3, the water molecule leaves the brucite surface. The R3 products are the free water molecule and a positive charged layer with an adsorbed fluoride anion. Finally, in R4 the adsorbed fluoride migrates into a hydroxyl vacant position, forming as final product $Mg(OH)_{2-x}F_x$.

3. Methodology

We performed ab initio DFT[13,14] calculations based on the generalized gradient approximation (GGA) using periodic boundary conditions. We adopted the exchange-correlation functional PW91.[15] The calculations employed the PWSCF code,[17] which uses pseudopotentials and plane waves basis sets. PWSCF relies on an efficient fast Fourier transform algorithm for the conversion of wave functions between real and reciprocal space and on the adaptation to a fixed potential of the band-by-band conjugated gradient method.[18] The wave functions are expanded in a plane wave basis set with maximum kinetic energy (ecut) of 30 Ry. We performed convergence tests for the employed basis set using the brucite unit cell and the total energy was converged within 0.005 Ry for the ecut between 30 and 40 Ry. The same test was made for the global reaction electronic energy difference and the convergence reached 0.0015 Ry (about 0.5 kcal/mol). We used the Vanderbilt[16] ultrasoft pseudopotentials for the H, O, F, and Mg atoms. For the Mg atoms we used a pseudocore scheme including the 2p electrons in the valence shell. The electron density was obtained at the Γ point in the first Brillouin-zone of the supercells.

Due to the fact that all computed reactions take place on the $Mg(OH)_2$ (0001) surface, the construction of supercells to represent the studied compounds starts from the brucite structure.[12] The use of small x values is equivalent to make large the distances between HF interacting molecules or incorporated F^-. This also corresponds to very large supercell models. In this work, it was used $x = 1/9$ and considered that the results would be the same or very close to the ones here described for any $x \leq 1/9$. The structural modifications for the calculated reactants and products in the four reactions was considered to be spatially localized and that a $3 \times 3 \times 1$ supercell, corresponding to $x = 1/9$, would be enough to make the reaction sites sufficiently distant from each other.

The construction of these supercells was based on the original optimized brucite structure, whose primitive cell has five atoms, the space group is $P\bar{3}m1$ having the following parameters: $a = 3.142$ Å, $c = 4.766$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$. We used periodic slab geometries consisting of one brucite layer with 3×3 reconstruction (9 Mg atoms and a total of 45 atoms in the layer) and a vacuum layer of 15 Å was added in the (0001) direction, thereby increasing the c parameter to 19.766 Å. The used supercells had the same angles of the original hexagonal brucite cell, and the new lattice parameter a was 9.426 Å. For all the calculated structures, the supercell angles and lattice parameters were kept fixed, with the atomic positions being optimized. The equilibrium nuclei positions for all structures were found by minimizing the total energy. The whole structure was allowed to relax along the computed Hellmann−Feynman forces until all the residual force components were less than 0.025 eV/Å.

The vibration modes and respective frequencies were calculated for all optimized structures to confirm their minimum or transition characters. Imaginary frequencies were not obtained for the reactants or products of the four reactions. One small imaginary frequency was obtained for each transition state. In order to analyze the thermodynamics for the four reactions, we computed the free Helmholtz energy F including vibrational contributions according to the two equations

$$F = E + \sum_i \frac{\hbar\omega_i}{2} + k_\mathrm{b}T\sum_i \ln\left(1 - \exp\frac{-\hbar\omega_i}{k_\mathrm{b}T}\right) \quad (1)$$

and

$$\Delta F_{\mathrm{R}N} = \sum_p F_p - \sum_r F_r \quad (2)$$

where E is the total electronic DFT energy, i is the index of the vibration mode, ω_i is the vibrational frequency of mode i, $\hbar$ is the Plank constant divided by 2π, k_b is the Boltzmann constant, and T is the absolute temperature. The first sum in eq 1 corresponds to the zero point energy (ZPE) contributions whereas the second sum corrects the free energy for temperature T. The subscript RN in the eq 2 identifies the reaction (R1, R2, R3, or R4) and the labels p and r refer to products and reactants, respectively. The present results for free energy were computed at 298 K. Similarly to the previous paper of Costa et al.[12] that analyzed thermodynamic potentials for brucite-like compounds, we consider that the error of the DFT ab initio methodology is not higher than 2 kcal/mol.

R1 and R3 are the direct adsorption and desorption reactions, respectively and, for this reason, reaction pathways were not calculated. For reactions R2 and R4 the minimum energy paths (MEP) were computed to obtain reaction barriers and the main structural modifications. The minimum energy paths connecting the different minimum geometries employed the nudged elastic band (NEB) method. The nudged elastic band method is an efficient method for finding the MEP between a given initial and final state of a given reaction. In this approach, the MEP is found by construction of a set of images (replicas) of the system between the initial and final states.[20,21]

4. Results and Discussion

4.1. Adsorption of the HF Molecule on the $Mg(OH)_2$ Layer (R1). The first step, reaction R1, is the adsorption of the HF molecule on the brucite surface. The optimized adsorption geometry is shown in Figure 2, and the main structural parameters are in Tables 1 and 2. There is a strong interaction between the hydrogen atom of the HF molecule (H_a) and hydroxyl oxygen atom of brucite (O_w) because the H_a−O_w distance is only 1.26 Å. This strong H−O interaction indicates that the HF molecule is chemisorbed on the brucite surface. Another result which points to HF chemisorption is the distance H_a−F = 1.13 Å, being 0.17 Å larger than that for a free HF molecule. The H_b−O_w−H_a angle is 103.14°, very close to the free water molecule angle (Table 2). Another important structural modification was the breaking of O_w−Mg_5 bond because the internuclear distance increases to 2.60 Å. These features of the R1 product are the starting point for the formation of an adsorbed H_2O molecule in the next step (R2).

The computed free energy for this adsorption reaction (ΔF_{R1}) was −25.1 kcal/mol (Table 3). This negative value of ΔF_{R1} indicates that HF adsorption is energetically more favorable than the corresponding clean $Mg(OH)_2$ layer and the free HF molecule.

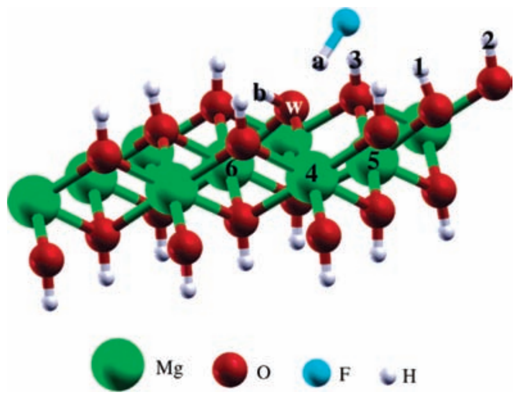

Figure 2. Adsorbed HF molecule on the brucite layer. O_w and H_b indicate, respectively, the brucite oxygen atom and the hydrogen atom involved in the HF adsorption; H_a indicates the hydrogen atom from the HF molecule. The numbers 1, 2, and 3 denote the nearest brucite hydrogen atoms from the F^- ion. The numbers 4, 5, and 6 denote the nearest brucite magnesium atoms from O_w.

TABLE 1: Main Geometry Parameters Associated to F^- Incorporation on Brucite[a]

	F−H_a	F−H_1	F−H_2	F−H_3
HF	0.96			
$Mg(OH)_2\cdots x(HF)$	1.13	2.01	4.03	1.99
TS_{R2}	2.73	1.56	2.25	1.56
$(Mg(OH)_{2-x})^+\cdot xH_2O\cdot F^-_x$	3.44	1.63	1.68	1.64
$(Mg(OH)_{2-x})^+F^-_x$		1.64	1.63	1.63
TS_{R4}		1.56	3.38	1.55
$Mg(OH)_{2-x}F_x$		3.31	5.36	3.32

[a] The symbols TS_{R2} and TS_{R4} correspond to transition states of reactions R2 and R4, respectively. All values are in Å.

4.2. Dissociation of the HF Molecule on the $Mg(OH)_2$ Layer (R2). In the second reaction (R2), the chemisorbed HF molecule dissociates on the brucite layer resulting an adsorbed water molecule and an adsorbed fluoride anion. The new structure, $[Mg(OH)_{2-x}]^+\cdot xH_2O\cdot F^-_x$, is shown in Figure 3. As seen in the previous section, for the chemisorption product of R1, the H_a, O_w, and H_b atoms are very close to the newly formed water molecule. In R2 the water molecule is produced from the H^+ cation, which originated from the dissociated HF molecule and a brucite hydroxyl interacting with the HF.

Table 2 presents the distances between the oxygen of the newly formed water and the closest brucite magnesium atoms. These distances were originally 2.21, 2.60, and 2.21 Å for the R2 reactant (that is the R1 product), $Mg(OH)_2\cdots x(HF)$, and become 2.27, 2.91, and 2.37 Å for the formed water molecule. These modifications in the O_w involving distances result when a hydroxyl layer oxygen bonds to the water's oxygen interacting with the charged brucite layer. The distances between the formed fluoride ion and the nearest brucite hydrogens, H_1, H_2, and H_3, are 1.63, 1.68, and 1.64 Å, respectively (Table 1). The distance between the fluoride ion and the outgoing proton (H_a) from the HF molecule is 3.44 Å.

The calculated dissociation free energy for HF on the $Mg(OH)_2$ layer (ΔF_{R2}) was 19.4 kcal/mol. From this result it is seen that the HF dissociation on the brucite layer from chemisorbed species is not an spontaneous process. On the other hand, the free energy for a dissociation process of a free HF molecule can be calculated as $\Delta F_{\mathrm{R1}} + \Delta F_{\mathrm{R2}}$; this value is −5.7 kcal/mol thereby corresponding to an spontaneous reaction.

TABLE 2: Calculated Geometry Parameters Associated to Water Molecule Formation during F^- Incorporation on Brucite[a]

structure	$\angle(H_a-O_w-H_b)$	$d(O_w-H_a)$	$d(O_w-Mg_4)$	$d(O_w-Mg_5)$	$d(O_w-Mg_6)$
$Mg(OH)_2$			2.10	2.10	2.10
$Mg(OH)_2\cdots x(HF)$	103.14	1.26	2.21	2.60	2.21
TS_{R2}	110.47	0.98	2.30	2.89	2.40
$(Mg(OH)_{2-x})^+\cdot xH_2O\cdot F^-_x$	110.45	0.98	2.27	2.91	2.37
free H_2O	104.37	0.97			

[a] The symbols TS_{R2} and TS_{R4} correspond to the transition states for reactions R2 and R4, respectively. All distances are in Å and angles are in degrees.

TABLE 3: Calculated Free Energy for Reactions R1, R2, R3, and R4 and for the Global Reaction (in kcal/mol)

reaction	free energy
R1	−25.1
R2	19.4
R3	17.8
R4	−35.1
global reaction	−23.0

The HF molecule dissociation minimum energy path was also computed. Eleven images were used to find the MEP using the NEB method. The resulting path is shown in Figure 4. The activation energy for dissociation from the $Mg(OH)_2\cdots x(HF)$ to $Mg(OH)_{2-x}\cdot xH_2O\cdot F^-_x$ is obtained as the energy difference between the saddle point structure and the $Mg(OH)_2\cdots x(HF)$ structure. The computed value is 16.8 kcal/mol for the direct reaction. The reverse path has a small barrier of 0.5 kcal/mol.

The calculated transition state has only one imaginary frequency, $104.3i$ cm^{-1}, corresponding to a fluorine nucleus movement. Once the H_a, O_w, and H_b atoms assume a geometry close to the water geometry in R1, the structural modification in the R2 path is dominated by the rearrangement of the fluoride ion which maximizes the number of closest hydrogens. The transition state corresponds to the F^- ion becoming closer to H_1 and H_3 after leaving H_b for the water formation. In this transient structure the $F-H_1$, $F-H_2$, and $F-H_3$ distances are respectively 1.56, 3.38, and 1.55 Å. The final result is a water molecule adsorbed on a charged $Mg(OH)_2$ layer which has lost an OH^- ion, with the total charge balanced by an adsorbed F^- anion. The produced F^- anion is almost equidistant from the H_1, H_2, and H_3 atoms, their distances being 1.67, 1.72, and 1.65 Å, respectively.

4.3. Desorption of the Formed Water Molecule (R3). This reaction corresponds to the removal of a water molecule, which results in a positive charged layer with an adsorbed fluoride ion neutralizing the total charge. The distance between the F^- anion and its three nearest hydrogen atoms in $[Mg(OH)_{2-x}]^+F^-_x$ is 1.63 Å (Table 1). The computed desorption free energy for the desorbed water molecule ΔF_{R3} is 17.8 kcal/mol.

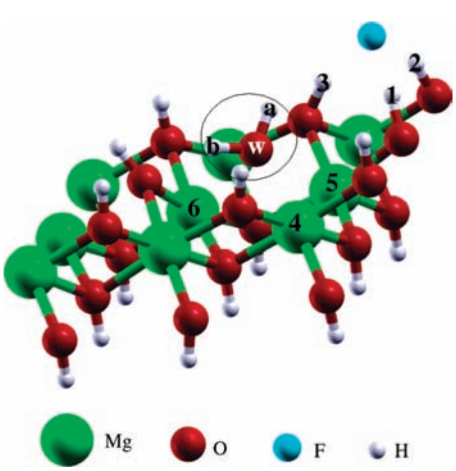

Figure 3. The reaction product R2: a dissociated HF molecule on the $Mg(OH)_2$ surface. The newly formed water molecule is surrounded by a circle. The atoms named with numbers or letters are the same ones described at the caption of Figure 2.

4.4. Formation of the $Mg(OH)_{2-x}F_x$ Compounds from $[Mg(OH)_{2-x}]^+$ F_x^- (R4). In the last reaction we studied the fluoride migration to the hydroxyl vacant position in the $[Mg(OH)_{2-x}]^+F^-_x$ structure, thereby forming as final product $Mg(OH)_{2-x}F_x$ (Figure 5). The distances between the F atom and the nearest Mg atoms in $Mg(OH)_{2-x}F_x$ are 2.09 Å whereas for isolated brucite the calculated O−Mg distances are 2.10 Å.

The computed formation free energy for the $Mg(OH)_{2-x}F_x$ compounds in R4 is −35.1 kcal/mol. The minimum energy path for the $Mg(OH)_{2-x}F_x$ compounds was also studied. Eleven images were used to find the MEP using the NEB method. The resulting path is shown in Figure 4. The activation energy for the formation of the $Mg(OH)_{2-x}F_x$ compounds from $[Mg(OH)_{2-x}]^+$ F^-_x is calculated using the energy difference between the saddle point structure and structure of R4 reactant. The resulting value is 6.6 kcal/mol for the direct reaction. The reverse path has a barrier of 40.2 kcal/mol and was calculated by the energy difference between saddle point and R4 product. It can observed that the transition state corresponds to the F^- over the brucite H_1 and H_3 hydrogen atoms. In the second part of the MEP, after the transition state, the fluoride ion moves to a hydroxyl vacant position, with the final structure having the fluorine bonded to the three closest magnesium atoms (Mg_4, Mg_5, Mg_6). This migration corresponds to the only imaginary frequency of the transition state, with value of $85.7i$ cm^{-1}. The most intense band in the infrared spectrum of $Mg(OH)_{2-x}F_x$ involves a Mg−F vibration mode corresponding to 342 cm^{-1}.

4.5. Global Reaction $Mg(OH)_2 + xHF \rightarrow Mg(OH)_{2-x}F_x + xH_2O$. The free energy for the HF reaction with a brucite layer can be calculated using eq 2 for the global reaction or through the expression $\Delta F_{R1} + \Delta F_{R2} + \Delta F_{R3} + \Delta F_{R4} = -23.0$ kcal/mol. Considering the PV (pressure times volume) term very small, the result for the free energy corresponds to the Gibbs free energy; thus the global reaction is spontaneous. This result agrees with experimental work that studied fluoride adsorption on hydrotalcite-like compounds.[4] The PV term equals RT for free molecules, being about 0.6 kcal/mol for $T = 298$ K. However, for solid-state and very confined molecules, the present situation, the reaction volumes are almost constant and the PV term can be considered smaller.

The reaction barrier for the R2 direct reaction is high enough for us to consider that F^- incorporation into the brucite layers is slower than the diffusion of the anion into the layered structure. Sadhurkahan et al.[19] pointed out that pure DFT ab initio methods underestimate deprotonation barriers by about 2−3 kcal/mol. Therefore, we discuss them only qualitatively. The measured activation energy for the reaction of fluoride with a MgAl-CO_3 layered double hydroxides[4] is 17.4 kcal/mol, being

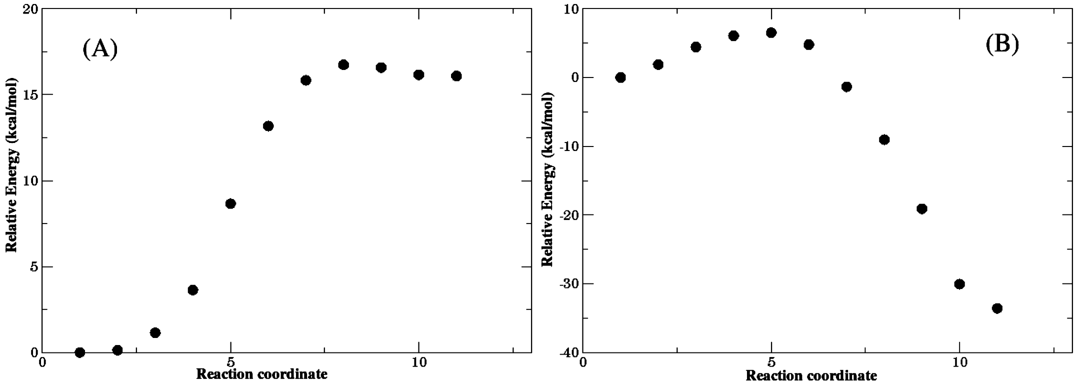

Figure 4. Calculated minimum-energy path for reaction R2 (A) and reaction R4 (B). Eleven steps were computed in each path. The relative energy corresponds to the energy difference between the image step and the reactants. In each reaction coordinate step 1 corresponds to the reactants and step 11 corresponds to the products of the respective elementary reaction.

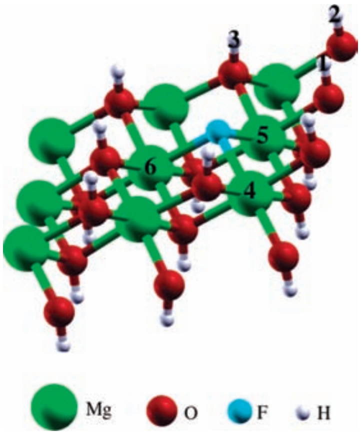

Figure 5. Optimized structure of $Mg(OH)_{2-x}F_x$ layer with $x = 1/9$. The atoms named with numbers are the same as those described in Figure 2.

very close to the 16.8 kcal/mol present computed energy barrier. Even the desorption process R3 could be interpreted as a 17.8 kcal/mol barrier, being close to the experimental data as well. The need for the water molecule formation explains the increase in the fluoride incorporation when acidity is raised. The water formation is the first step to produce an OH^- vacancy and allows the possibility of an F^- incorporation replacing hydroxyl.

The initial HF adsorption could be substituted by brucite layer protonation through other acidic species. However, the charge balance needs to be reached in real solid or liquid systems. In the sequence of the process, F^- adsorption is the most efficient outcome because no other F^- anion approximation is needed and the R4 activation barrier is only 6.6 kcal/mol. The R4 reverse reaction has a 40.0 kcal/mol barrier, and for this reason, the last step in the formation of $Mg(OH)_{2-x}F_x$, and thus the global reaction, is almost irreversible. The free energy for the formation of $Mg(OH)_{2-x}F_x$ from the structure with water and fluoride adsorbed can be computed as $\Delta F_{R3} + \Delta F_{R4} = -17.3$ kcal/mol. Therefore, the acid species that donates the proton to the water formation could be other than HF and still the final product would be formed.

5. Conclusions

We studied the reaction of HF with $Mg(OH)_2$, brucite, forming a $Mg(OH)_{2-x}F_x$ compound. This process was investigated by ab initio calculations based on DFT. A proposed formation mechanism of $Mg(OH)_{2-x}F_x$ from $Mg(OH)_2$ and HF was forwarded, consisting of four elementary steps: HF adsorption, OH^- liberation as H_2O, desorption of the formed H_2O, and rearrangement of the produced F^- into a hydroxyl position.

Using supercells with $x = 1/9$ (3 × 3 × 1), the products and reactants of all steps were calculated by DFT with periodic boundary conditions. The entire process has $\Delta F = -23$ kcal/mol and thus is spontaneous. The computed frequency for the principal Mg−F band was 342 cm^{-1}. The negative Helmholtz free energy indicates that fluoride incorporation in the layer in fact occurs when layered hydroxide compounds are used as absorbent for this ion.

Two transition states, corresponding to the hydroxyl reaction with a proton forming water and migration of the fluoride into a hydroxyl vacancy, were identified, and the highest energetic barrier for the direct reaction among the calculated ones was 16.8 kcal/mol. Therefore, it is expected that the $Mg(OH)_{2-x}F_x$ global formation reaction is slow.

The activation barrier for the reverse reaction of the last step points to an irreversible $Mg(OH)_{2-x}F_x$ formation. The proposed reaction mechanism and the corresponding computed results agree with kinetic measurements pointing to the reaction between hydroxyl layers and HF molecules.

Acknowledgment. This work has been supported through a CAPES-Brazilian Ministry of Defense grant. The authors also are grateful for support from CNPq, FAPEMIG, and FAPERJ, Brazilian agencies.

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JP810047D