



HCOOH on Hydrated Calcite from first principles

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Abstract

Organic molecules in aqueous solutions are good candidates in the inhibition of some biogenic crystals growth. The methanoic acid HCOOH is considered to study the interaction between the carboxyl functional group -COOH and the {10.4} hydrated surface of calcium carbonate, CaCO₃, in the form of calcite. In this work the inhibiting effects of protonated -COOH and deprotonated -COO⁻ headgroups on top of the {10.4} hydrated surface of calcite are investigated by means of ab initio DFT-GGA simulations. The interfacial properties and the trend of adsorption energies for different coverages are given in details and show that the adsorption is favored by the presence of water. The reaction path of the deprotonation mechanism is investigated via the climbing image nudged elastic band (CI-NEB) method.

Motivations

The interest in calcium carbonate, CaCO₃ - one of the most abundant biominerals on the Earth - is growing in many branches of science, from **biomedicine** to **environmental application**. The formation of calcite, the most stable polymorph of CaCO₃, is on one side the main cause of problems in the water treatment process and at the same time a mechanism favored to act as a pH neutralizer in water filter systems. In industrial processes, inhibition of calcite growth occurs by using chemical additives often severely impacting the environment. Natural organic materials, are good candidates as growth inhibitors as they strongly interact with calcium carbonate in aquatic system.

Method: DFT-D2

- DFT-GGA as implemented in Quantum ESPRESSO. [1]
- Ultrasoft pseudopotentials were used within the generalized gradient approximation (GGA) and more specifically with the PBE functional for the exchange and correlation term. van der Waals dispersion correction [1] is accounted for in all the calculations.
- The kinetic energy cutoffs for the electron wavefunctions and for the augmented electron density were 32 Ry and 256 Ry, respectively.
- The Brillouin zone sampling: 2 × 2 × 1
- The (10 $\bar{1}$ 4)-oriented surface is been used.
- A 3 layers slab containing 12 formula units was used to simulate this non-polar surface and image slabs were separated by 15 Å of vacuum.

Lattice parameters	
a	5.0539 Å (a _{exp} = 4.9896 Å)
c	16.936 Å (c _{exp} = 17.061 Å)

The surface energy γ and the adsorption energy U_{ad} were calculated according to

$$\gamma = \frac{U_{s+mol} - [nU_{mol} + U_B]}{A} \quad U_{ad} = \frac{U_{s+mol} - (U_s + nU_{mol})}{n}$$

where U_{s+mol} is the total energy of the relaxed system containing the surface and the adsorbed molecule(s), n is the number of molecules and U_{mol} is the total energy of an isolated molecule. When only water molecules are present U_{s+mol} is referred to as the hydration energy $U_{hyd} = U_{s+mH_2O}$ and the adsorption energy per molecule of methanoic acid on hydrated surface is thus calculated as:

$$U_{ad} = \frac{U_{s+nHCOOH+mH_2O} - (U_{hyd} + nU_{HCOOH})}{n}$$

where $U_{s+nHCOOH+mH_2O}$ is the total energy of the system containing m water molecules and n molecules of methanoic acid, with $n+m$ representing the total surface coverage. U_{HCOOH} is the total energy of an isolated HCOOH molecule. The bonding charge density has been evaluated using the expression:

$$\Delta\rho(r) = \rho_{s+mol}(r) - \rho_s(r) - \rho_{mol}(r)$$

where $\rho_{s+mol}(r)$, $\rho_s(r)$, and $\rho_{mol}(r)$ are the charge density of the whole system, the clean surface, and the isolated molecules, respectively.

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Hydration

U_{ad} (kJmol ⁻¹)	DFT-D2	other
25%	-98.7	-60.8 ↔ -87.8 ⁶ , 81.0 ⁵
100%	-96.1	87.8 ⁶ , -79.1 ⁵
γ_{wet} (Jm ⁻²)		
25%	0.87	0.36 ⁶ , 0.51 ⁵
100%	0.29	0.09 ⁶ , 0.30 ⁵

Table: Adsorption (U_{ad}) and surface (γ) energies for a surface at different H₂O coverages.

	DFT-D2	other	exp.
25%	d(Ca-O _w) 2.39	2.39 ³ , 2.41 ³	
	d(H-O _s) 1.74	1.97 ³ , 2.20 ³	
100%	d(Ca-O _w) 2.39	2.35 - 2.61 ^{2,4,5} 2.31 ⁷	2.50 ± 0.12 ⁶
	d(H-O _s) 1.74	1.74 - 1.86 ²	

Table: Bond distances (Å) in 25% and 100% hydrated surface.

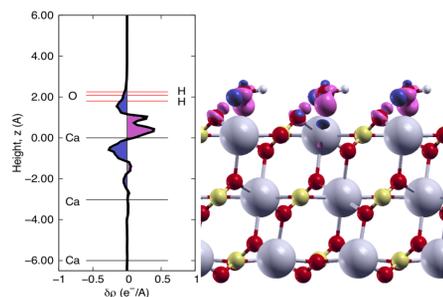


Figure: Left: bonding charge integrated in planes perpendicular to the surface as a function of the distance from the surface; right: bonding charge plotted at the value of 0.0065 electrons/Å³. Electron accumulation and depletion are represented by purple and blue areas, respectively.

All the **water molecules** are physically sorbed onto the surface via the Ca-O_w interaction with a H atom pointing at the closer O_s above the surface to form the hydrogen-bond. All the **carbonate groups** are, in the (10 $\bar{1}$ 4) calcite surface, alternatively oriented in such a way that the topmost O_s atoms form a narrow **zigzag**, within the Ca sublattice, that drives the orientation of water molecules, accordingly.

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Methanoic acid on Hydrated Calcite

Every pre-adsorbed H₂O molecule was replaced, one by one, by a molecule of HCOOH both undissociated and de-protonated (HCOO⁻). HCOOH and HCOO⁻ can arrange alternated in two ways on the mineral surface (henceforth referred to as *chess* configuration) or can lie in the same row (henceforth *row* configuration). When considering HCOO⁻ ions, the dissociated proton resulted bound to a surface oxygen. The final geometries corresponding to 50% acid coverage are shown.

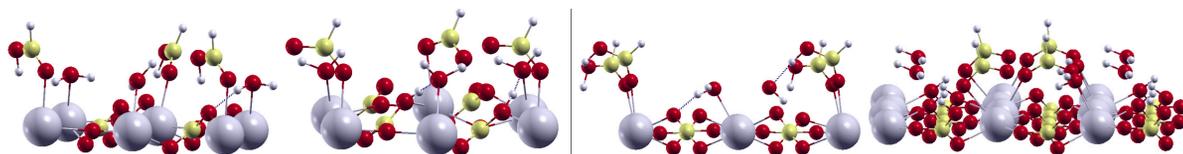


Figure: Adsorption of 50% of HCOOH on calcite in the chess (left: undissociated and de-protonated) and in the rows arrangement (right: undissociated and de-protonated). Note the bridge between two Ca²⁺ ions formed by HCOO⁻ in the rows configuration. The blue dotted lines represent the H-bonds.

U_{ad} (kJmol ⁻¹)	HCOOH	HCOO ⁻	HCOOH + HCOO ⁻
25% HCOOH + 75% H ₂ O	-371.3	-791.3	
50% HCOOH + 50% H ₂ O	-195.0	-605.8 (chess)	-403.3
			-373.2
		-597.3 (rows)	-384.5
distances	other		
d(Ca-O _m)	2.34	2.28	2.21 - 2.26 ⁸ , 2.25 ⁹ , 2.35 ¹⁰
d(H _m -O _s)	1.48		2.41 - 2.52 ⁸ , 2.48 ⁹ , 1.4 ¹⁰
d(Ca-O _w)	2.40	2.40	
d(H _w -O _s)	1.71	1.71	
d(H _s -O _s)	1.03	1.03	

Table: Adsorption energy (U_{ad}) of methanoic acid on a hydrated surface at different coverages and typical distances.

The presence of H₂O and HCOOH in the same solution leads to the most stable configuration. The adsorption energies are much higher than those relative to the systems where the methanoic acid is undissociated: HCOO⁻ adsorption is more favorable.

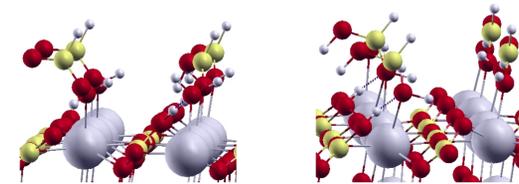


Figure: Detail of the adsorption of 50% of HCOOH + HCOO⁻ and 50% of water on calcite in the chess₁ (left) and in the chess₂ (right) configurations.

50% acid concentration: Energy barriers relative to the migration of a proton from adsorbed HCOOH to the (10 $\bar{1}$ 4) calcite surface are calculated according to the CI-NEB method. The chess configuration leads to the lowest activation barrier (\approx 0.8 eV) for the dissociation.

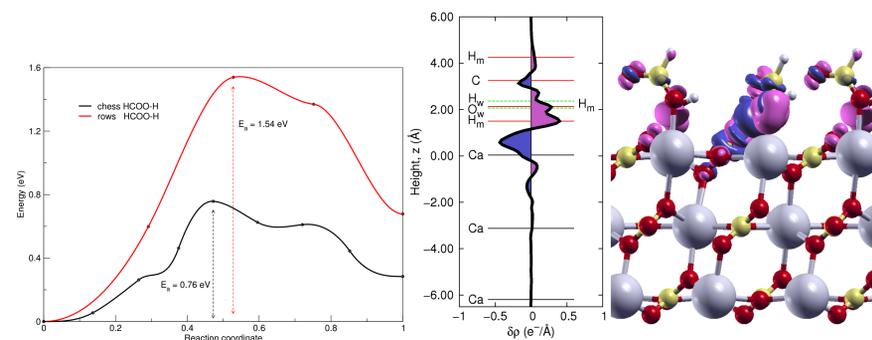


Figure: Activation barriers in 50% acid concentration on calcite in the chess (left) configuration and Bonding charge analysis (right). Electron accumulation and depletion are represented by purple and blue areas, respectively.

Comparing the bonding charge integrated along z with the increasing concentration of methanoic acid, two effects must be highlighted: the shift of the blue and purple peaks to higher z values and their increased intensity. When the coverage is 100% water, the adsorbed molecules are very close to the surface of calcite and we observe a charge transfer from the mineral to the O of water as large as 0.09e. Increasing the concentration of methanoic acid the charge transferred from the surface to the molecules increases (\approx 0.22e) as well.

Main Question and Answer: Does the calcite growth inhibiting mechanism take place via a surface coating or through a more complex kinetic process in which the driving force of the adsorption is the entropy change due to the replacement of water molecules by the acid?

Assumption: Experiments and theoretical results show that organic additives may influence nucleation and growth of CaCO₃ [11 and refs. therein]. To this end, adsorption of methanoic acid in both undissociated and de-protonated form on the cleavage surface of calcite, in different combinations is performed.

At this stage of the study, calculations suggest:

- The HCOO-H adsorption is favored in presence of H₂O. A dilute coverage of methanoic acid and water leads to higher adsorption energies and lower surface energies;
- The bonding charge analysis resulted in a charge transfer from the surface to the molecules consistent with a positively charged surface, experimentally observed. This fact, together with a sort of negative charge alignment formed by adsorbed methanoate ions, makes it difficult for Ca²⁺ and CO₃²⁻ to reach the surface and contribute to the crystal growth.
- The displacement of water molecules from the calcite surface by HCOO⁻ and the trend of the adsorption energies of methanoic acid with the decreasing number of water molecules supports the idea of a dehydration mechanism of the surface occurring during the adsorption of HCOOH. The inhibition process might be driven both by the entropy change and the blockage of the active sites. (Molecular dynamics calculations may help in this regard.) The combination of the protonation of the carbonate group and the weakening of the surface bonding of calcium ions is suggestive of the formation of acid-calcium compounds that prevent the formation of the layer and the nucleation of the crystal.

We acknowledge computational support by CRS4, Pula (Ca), Italy and CINECA (Bologna, Italy)
Also, the authors acknowledge **Fondazione Banco di Sardegna** (<http://www.fondazionebancodisardagna.it>) and **Consorzio AUSI** (<http://www.consorzioausi.it>) for partial financial support.