Electronic Supplementary Information

Adsorption of formic acid and water molecules on the (104) surface of calcite: A theoretical study by DFT-D3

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1. Stability of different surfaces of calcite

Table S1 Surfaces, top view, side view and lattice parameters of the cleaved cells.

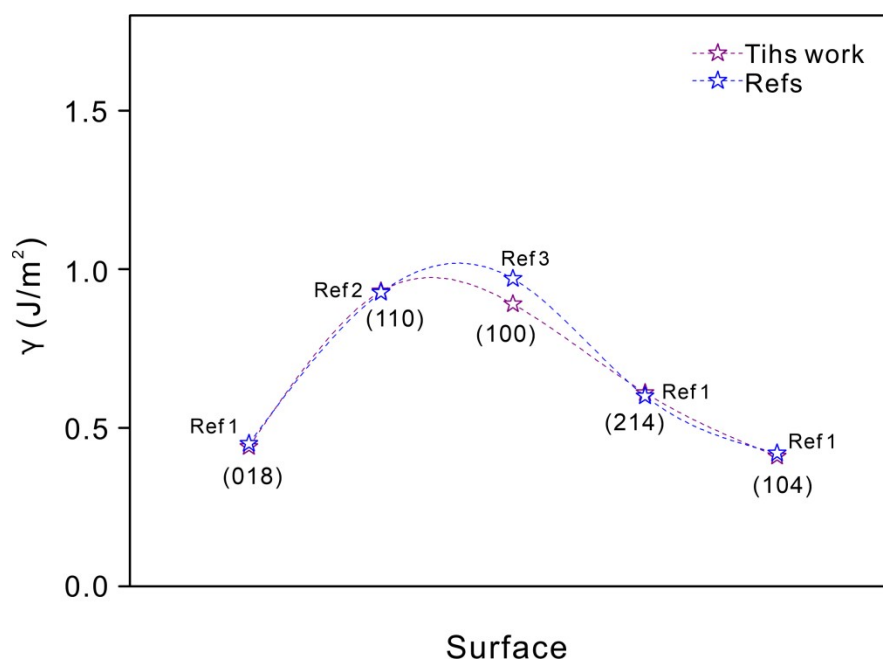| Surface	(018)	(110)	(100)	(214)	(104)
Top view					
Side view					
Lattice parameters	a = 5.05 Å, α = 90°, b = 13.01 Å, β = 90°, c = 6.81 Å, γ = 90°	a = 8.20 Å, α = 90° b = 6.46 Å, β = 90°, c = 10.17 Å, γ = 107.9°.	a = 5.05 Å, α = 90° b = 17.30 Å, β = 90°, c = 6.62 Å, γ = 90°.	a = 13.01 Å, α = 90° b = 6.46 Å, β = 90°, c = 7.01 Å, γ = 78.9°.	a = 5.05 Å, α = 90°, b = 8.20 Å, β = 90°, c = 10.81 Å, γ = 90°.

Fig. S1 Surface energy of different crystal faces of calcite. The results reported in other works[1-3] are also shown for comparison.

Five low-index surfaces were cleaved from the bulk calcite to figure out the stable surface. The details including the top and side views of the cell and the lattice parameters are summarized in Table S1. Four layers were set up and a vacuum of 15 Å was added along the c direction to build the supercell. In contrast to bulk calcite, there are many unbonded electrons on the cleaved surfaces, which induces additional instabilities. The surface energy, γ, was used to describe the stability of different surfaces.[1] The value of γ can be calculated as follows:

$$\gamma = \frac{1}{2A}(E - n\mu)$$

(1)

where E and μ are the energies of the constructed supercell and the chemical potential of calcite, n is the number of formula unit "$CaCO_3$" in each supercell, and A is the surface area of the supercell. The γ obtained in this work and those reported by others are summarized in Fig. S1. It can be seen that the surface energies in this work agree well with those reported by others,[1-3] indicating the good reliability of our calculations. The smaller the γ, the higher the stability.[1] From Fig. S1, it can be seen that the (104) surface is the most stable one. Therefore, the supercell terminated with the (104) surface was used to study the adsorption behaviors of water and formic acid molecules.

2. Tests of adsorption height and functionals

Table S2 The initial distance (d_I), distance between Ca···O (d_{Ca-O}) and adsorption energy (E_{ads}) of H$_2$O/HCOOH molecules on the (104) surface of calcite. The oxygen of Ca···O formed between calcite and HCOOH is carbonyl oxygen.

Parameters	H$_2$O			HCOOH		
	PBE|DFT-D3			PBE|DFT-D3		
d_I (Å)	2	2.5	3	2	2.5	3
d_{Ca-O} (Å)	2.42|2.42	2.43|2.43	2.47|2.47	2.43|2.43	2.41|2.41	2.42|2.42
E_{ads} (eV)	-0.82|1.26	-0.84|1.26	-0.83|1.26	-0.90|1.24	-0.92|1.24	-0.92|1.24

In order to find out the appropriate height between the adsorbed molecule and the underlying substrate, three values including 2 Å, 2.5 Å and 3 Å were set as the initial height. The PBE and DFT-D3 functionals were considered. The initial distances, distance of Ca···O and adsorption energies are summarized in Table S2. For water molecules, the length of Ca···O becomes the same after complete relaxation (2.43 Å), and the adsorption energies of PBE and DFT-D3 are 0.83 eV and 1.23 eV, respectively. For formic acid, the same results are obtained. Therefore, in subsequent calculations, 2.5 Å was set as the initial distance between the adsorbed molecule and underling substrate.
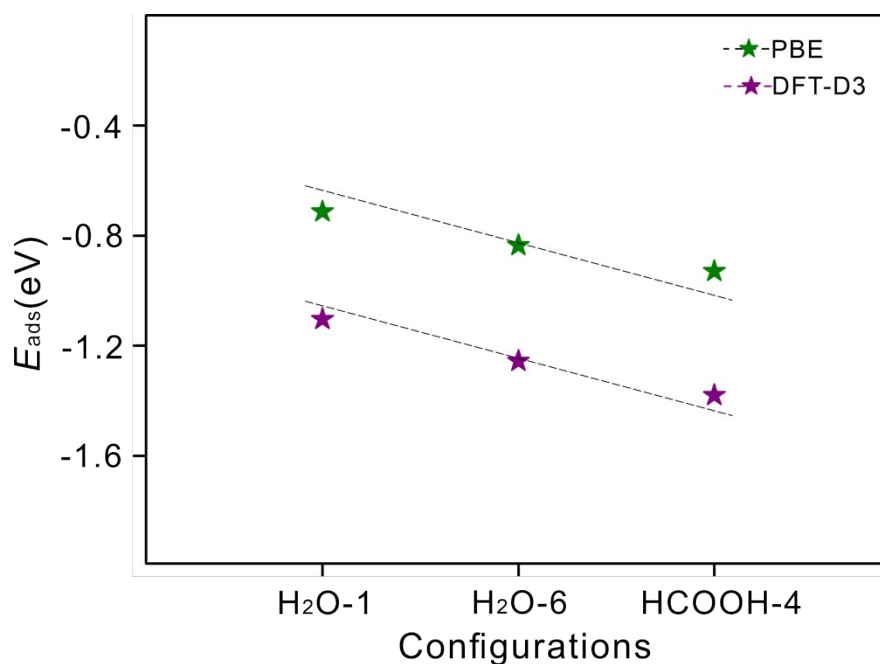

Fig. S2 Adsorption energies of water and formic acid calculated with PBE and DFT-

D3 corrections.

The formation energies of water and formic acid calculated with PBE and DFT-D3 corrections are summarized in Fig. S2. It can be seen that the values obtained from PBE and DFT-D3 corrections are almost parallel, indicating that both functionals can be used to calculate the adsorption behavior of water and formic acid. In order to obtain more details of the configuration, DFT-D3 correction was considered in all simulations.

3. Adsorption of water and formic acid on (104) surface with different coverage

In actual experiments, the adsorption coverage may vary. To simulate the actual adsorption, we also simulated the adsorption of H_2O and HCOOH with different coverages, including 25%, 50%, 75% and 100%. The supercell constructed with the (104) surface is shown in Fig. S3a. The adsorption sites are also marked with Arabic numbers. Side and top views of the configuration are shown in Fig. S3b. All configurations are summarized in Table S3. The average adsorption energy[4] was used to evaluate the stability of various configurations and it can be calculated as:

$$\overline{E}_{ads} = \frac{1}{n}\left(E_t - nE_M - E_{sub)}\right)$$

(2)

where E_t, E_M and E_{sub} are the total energy of the system, the adsorbed molecule and the supercell, respectively; n is the number of H_2O/HCOOH molecules. The average adsorption energies are summarized in Fig. S3c. It can be seen that formic acid is always more stable than water on the (104) surface for the same coverage.

Table S3 Configurations of water and formic acid molecules adsorbed at different sites.

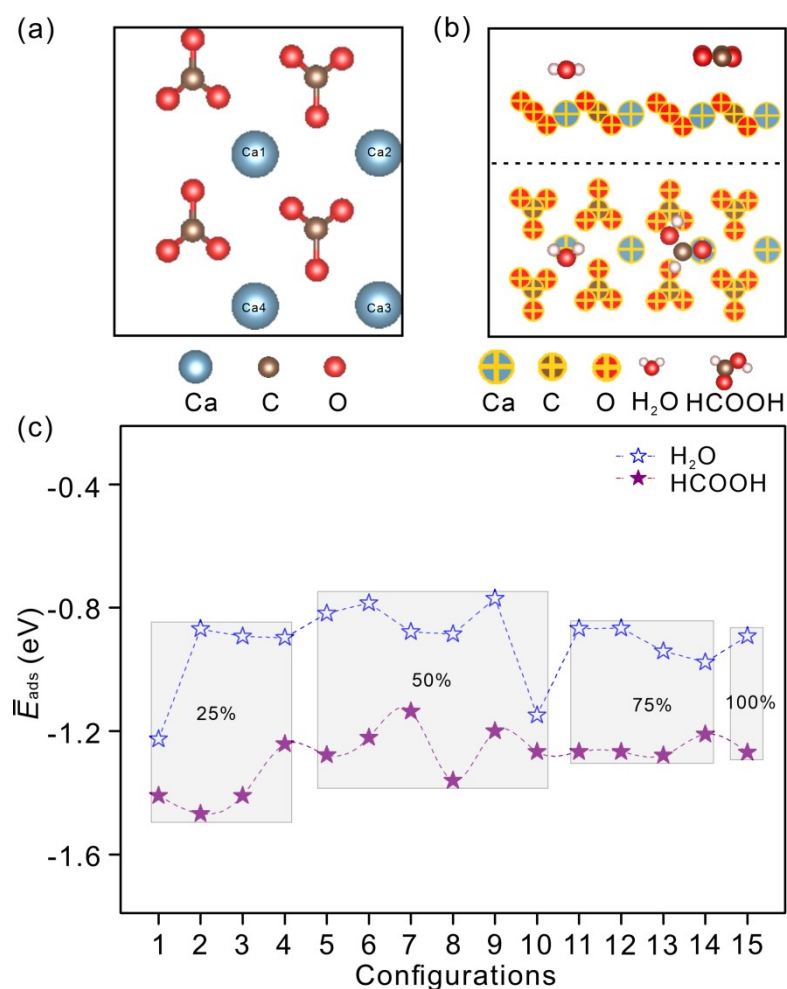| Confs.	Adsorption sites	Confs.	Adsorption sites	Confs.	Adsorption sites
1	Ca1	6	Ca1&Ca3	11	Ca1&Ca2&Ca3
2	Ca2	7	Ca1&Ca4	12	Ca1&Ca2&Ca4
3	Ca3	8	Ca2&Ca3	13	Ca2&Ca3&Ca4
4	Ca4	9	Ca2&Ca4	14	Ca1&Ca3&Ca4
5	Ca1&Ca2	10	Ca3&Ca4	15	Ca1&Ca2&Ca3&Ca4

Fig. S3 (a) Supercell constructed with the (104) surface of calcite. Only the topmost layer is shown to demonstrate the adsorption sites more clearly. (b) Side (upper panel) and top view (lower panel) of the configuration with water and formic acid paralleling to the substrate. (c) The average adsorption energy of configurations with different coverage.

References

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