

Reactivity of Formic Acid on Calcium Carbonate Single Particle and Single Crystal Surfaces: Effect of Adsorbed Water

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Formic and organic acids are ubiquitous in the atmosphere and are the most abundant organic acids present in urban areas. Calcium carbonate, an important mineral, plays a vital role in the neutralization of acidic gases in atmospheric aerosols [1]. As indoor air pollutants resulting from the decomposition of wood and cellulose acetate, formic and acetic acids are responsible for deterioration of carbonate building materials, as in museum objects (Byne's disease) [2].

The reactivity of formic acid (HCOOH) under relatively dry (RH<15%) and humidified (RH>15%) conditions on calcium carbonate (CaCO₃) single particles and (1 0 -1 4) single crystal surfaces was investigated using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Figure 1 shows formation of small islands and microcrystallites of calcium formate at the edges of CaCO₃ single particle in the presence of 80% RH water vapor. No microcrystallites were observed with SEM after exposure to the same concentration of formic acid in the presence of 10% RH water vapor.

AFM images of freshly cleaved CaCO₃ (1 0 -1 4) single crystal surface before and after exposure to HCOOH at saturation pressure are shown in Figure 2, a and b. Formation of crystallites ~ 45 nm in height can be observed along step edges (Fig 2, b). Increase in crystal size, height, step edge roughening and enhancement in the crystallinity can be observed following exposure to water vapor at the saturation pressure for 10min (Fig 2, c) and for 24 hours (Fig 2, d). Thus, calcium formate changes from adsorbed to crystalline phase as the extent of the reaction increases with increased relative humidity.

It can be concluded, that at higher RH formic acid can react to greater extent with calcium carbonate. Adsorbed water on the surface of the carbonate particles participates in the greater reactivity of these by means of new reaction pathways due to dissociation of carbonic acid and formation of calcium formate islands and crystallites [1].

References

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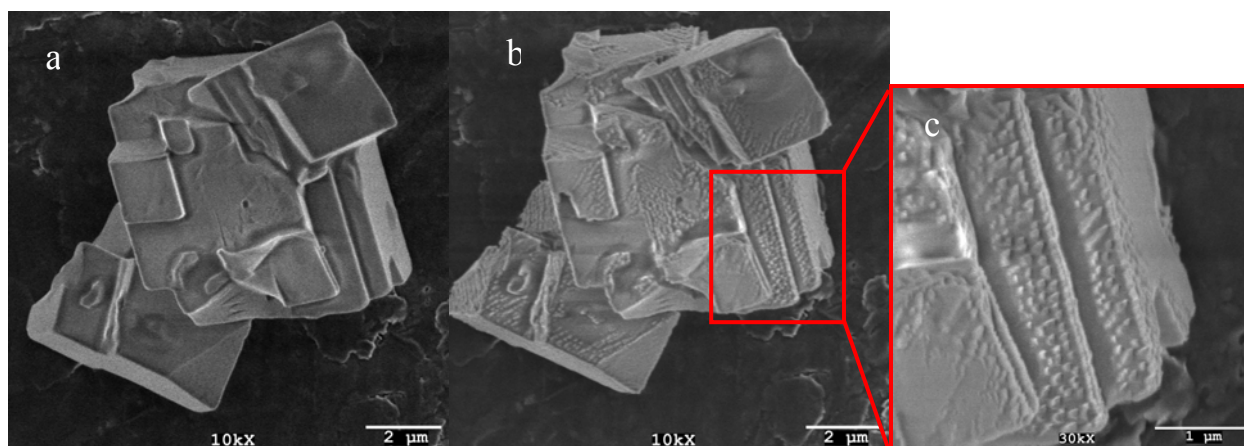


Fig. 1. A single CaCO_3 particle before (a) and after (b) reaction with HCOOH in the presence of water vapor corresponding to 80% relative humidity (RH). Formed crystallites are shown in (c).

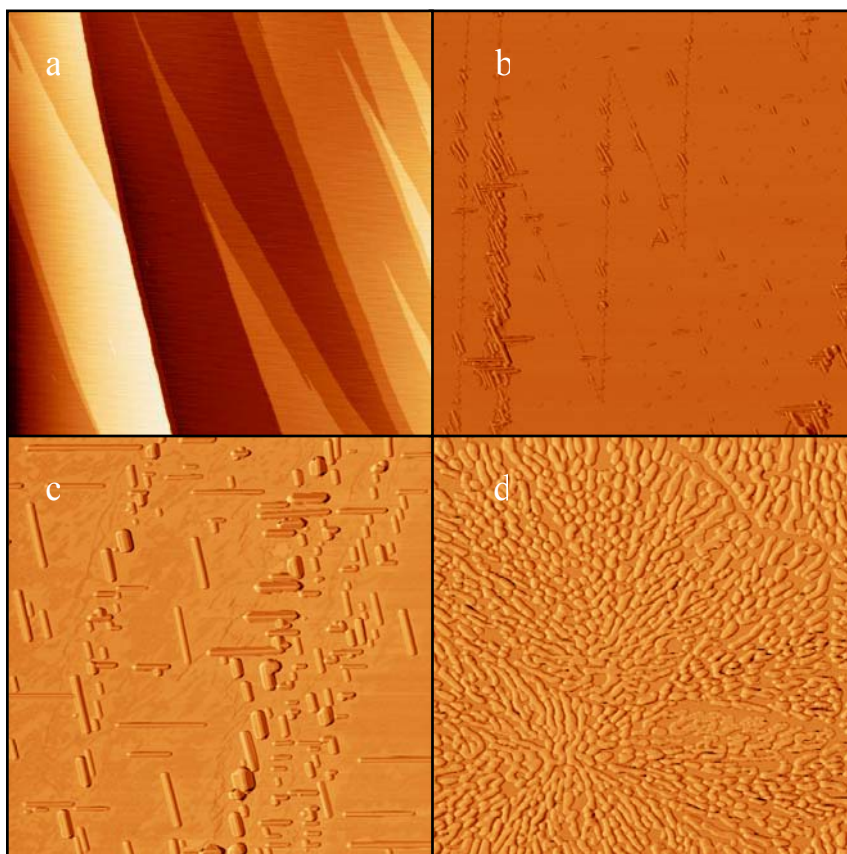


Fig. 2. AFM images of CaCO_3 (1 0 -1 4) crystal surface (a) freshly cleaved, (b) following exposure to HCOOH vapor at the saturation pressure for 10 min., (c) following exposure to HCOOH vapor at the saturation pressure for 10 min. then to H_2O vapor at the saturation pressure for 10 min., and (d) following exposure to HCOOH vapor at the saturation pressure for 10 min. and to H_2O vapor at the saturation pressure for 24 hours. All images are $5 \times 5 \mu\text{m}$ size.