AFM Observation of $Ca(OH)_2$ (0001) Surfaces Reacted with SO_2: Role of Water Vapour on Product Morphology

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The morphology of single-crystal $Ca(OH)_2$ (0001) surfaces after being reacted with SO_2 at 313 K consists of "needle-like" features of $CaSO_3 \cdot (1/2)H_2O$ whose mean size increases with the relative humidity at which the reaction takes place. This trend might provide an evidence of certain mobility of product crystallites induced by adsorbed water.

The solid-state reaction between $Ca(OH)_{2(s)}$ and $SO_{2(g)}$ takes place in a number of technologies aimed at the reduction of SO_2 emission from industrial combustors.[1] It is well-known that water vapour exerts an outstanding effect on the reactivity of $Ca(OH)_2$ toward SO_2 removal, which suggests that water physically adsorbed on $Ca(OH)_2$ might play a relevant role in the reaction.[2] However, the mechanistic implications of adsorbed water on SO_2 uptake remain still controversial and constitute an intricate issue.

According to the water adsorption isotherm on $Ca(OH)_2$,[3] the formation of a water multilayer at high vapour pressure could act either enhancing $Ca(OH)_2$ surface dissolution[4] or promoting the formation of stable SO_2 hydrated complexes.[3] Moreover, the reaction product ($CaSO_3 \cdot (1/2)H_2O_{(s)}$) could also build up in a cluster-like form at high relative humidities (RH $> 70\%$),[5] which might result in a better accessibility of SO_2 to the still unreacted $Ca(OH)_2$ surface.

In the present study, we report the effect of adsorbed water on $CaSO_3 \cdot (1/2)H_2O$ morphology on $Ca(OH)_2$ (0001) surfaces attacked by SO_2 at 313 K by TM-AFM (tapping mode atomic force microscopy) imaging.

Prior to the AFM investigation, some commercial $Ca(OH)_2$ particles (Ciaries, Barcelona, Spain) (mean size, 9 µm; porosity, 14%[6]) reacted with SO_2 at several RH values were examined by SEM. The SEM micrographs revealed that the desulfurization reaction taking place at RH $< 70\%$ (not shown) left almost unchanged the shape and surface of the particles, while the surface of those reacted beyond 70% RH showed numerous "needle-like" features (see Figure 1). This observation suggests that the morphology of $CaSO_3 \cdot (1/2)H_2O$ on $Ca(OH)_2$ might depend on the RH at which reaction takes place. Thus, at RH $< 70\%$, the reaction product would be likely deposited as a continuous layer resulting in no relevant morphological changes, whereas at higher RH it would be arranged as needle-shaped features. However, the presence of small-sized needle-like product features on $Ca(OH)_2$ particles after being reacted at RH $<$ 70% (unable to be visualised by SEM) cannot be ruled out.

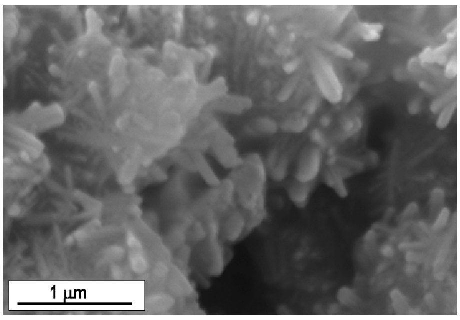

Figure 1. SEM micrograph of $Ca(OH)_2$ commercial particles reacted at 333 K, 70% RH and 2000 ppm of SO_2 for 2 h.

To elucidate this point, some $Ca(OH)_2$ (0001) surfaces reacted with SO_2 at several RHs were inspected by TM-AFM. The $Ca(OH)_2$ single-crystals were synthesised by the so-called *diffusion method*.[6] Two precursor solutions of $CaCl_2$ and NaOH were immersed in a water bath at 298 K to allow the involved ions to get into contact for further crystallisation. After 4 weeks, pure hexagonally-shaped $Ca(OH)_2$ single-crystals (space group $P\bar{3}m1$[6]) of 2–5 mm in size were obtained.

In the beginning of each AFM exploration, a freshly cleaved $Ca(OH)_2$ (0001) surface was imaged by TM-AFM to assess its smoothness and uniformity. Immediately afterwards, the cleaved crystal was exposed to an atmosphere of 5500 ppm of SO_2 (in N_2) at 313 K at controlled RH values for 30 minutes. After the reaction, the same surface region was explored again by AFM. To prevent the reacted crystals from any change due to atmospheric humidity, they were kept inside the reactor in dry N_2 until being explored. The details of the experimental set-up and reaction procedure can be found elsewhere.[6]

Figure 2 shows the AFM images of a freshly cleaved $Ca(OH)_2$ (0001) surface and of other two surfaces just after SO_2 attack at 313 K and at 15 and 70% RH, respectively. As can be seen, irrespective of the RH, the reaction product seems to crystallise showing a needle-like morphology. Furthermore, at 70% RH, the surface seems to be structured forming "needle-like" clusters. Some experiments performed at 313 K and 70% RH, but under the absence of SO_2 in the gas phase, confirmed that the change in surface morphology was exclusively attributed to $CaSO_3 \cdot (1/2)H_2O$ formation. Besides, the mean size of the product features and accordingly the surface roughness (Rms) appears to depend exponentially on the RH (see Figure 3). This trend is qualitatively the same as that found for sulphur uptake with respect to RH in some studies done on $Ca(OH)_2$ commercial particles.[7] This fact supports the assumption that the entire product is arranged on $Ca(OH)_2$ as needle-like features (i.e. no continuous layer is formed).

Figure 3 also shows that the Rms values determined at the tested RH values corresponding to different regions of the (0001) surface of several $Ca(OH)_2$ single crystals are quite dispersed, especially at high RHs. Figure 4 shows the regions of $Ca(OH)_2$ with different Rms values. The fact that different regions of a crystal show different Rms suggests the presence of

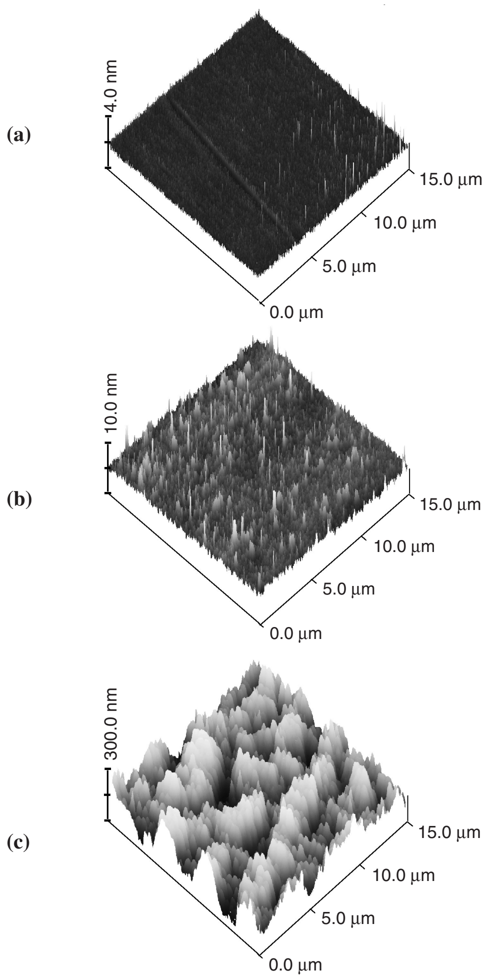

Figure 2. TM-AFM images of freshly cleaved $Ca(OH)_2$ (0001) surfaces reacted at 313 K and 5500 ppm of SO_2 for 30 min. (a) Freshly cleaved surface, Rms: 0.1 nm; (b) 15% RH, Rms: 1.1 nm; (c) 70% RH, Rms: 59.6 nm.

crystalline domains of different reactivity. The anisotropy in the reactivity of $Ca(OH)_2$ (0001) with SO_2 might be stressed at higher reaction rates (i.e. higher RHs).

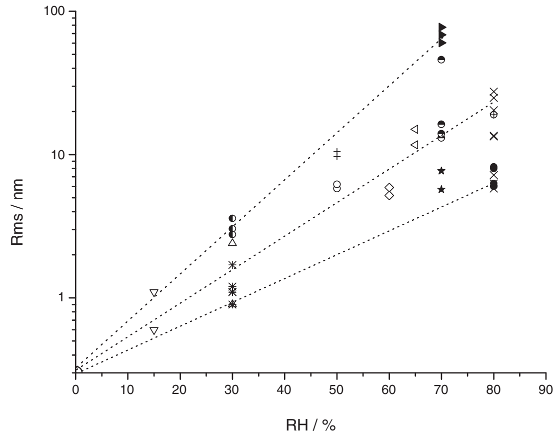

Figure 3. Dependence of the surface roughness of cleaved $Ca(OH)_2$ (0001) surfaces on the RH for 30 min of reaction. Each symbol indicates different regions of the same crystal.

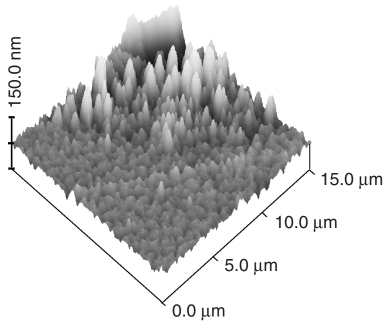

Figure 4. TM-AFM image of a freshly cleaved $Ca(OH)_2$ (0001) surface reacted at 313 K, 5500 ppm of SO_2 and 80% RH for 30 min, where two adjacent regions with surface Rms (5.2 and 26.7 nm) can be distinguished.

In conclusion the product of the reaction between $Ca(OH)_2$ and SO_2 is structured on $Ca(OH)_2$ (0001) surfaces forming needle-like features, whose mean size is strongly dependent on the amount of adsorbed water. This observation suggests that larger features might be formed from the rearrangement of smaller ones along the reaction, which would involve certain mobility of product crystallites induced by adsorbed water. This process might open up new fresh $Ca(OH)_2$ surface for further reaction, thus accounting for the widely reported observation that the reactivity of the system $Ca(OH)_2$–SO_2 is strongly enhanced by water vapour. Further research is required for in situ imaging of $CaSO_3{\cdot}(1/2)H_2O$ morphology after exposure to a humid atmosphere and to provide more direct evidence of $CaSO_3{\cdot}(1/2)H_2O$ mobility on $Ca(OH)_2$ (0001) and its implications on the chemistry of the system.

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