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

Marta Bausach, Marc Pera-Titus, Javier Tejero, and Fidel Cunill$^*$

Chemical Engineering Department, University of Barcelona, 08028, Barcelona, Spain

(Received September 16, 2005; CL-051184; E-mail: mbausach@ub.edu)

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$_2$•(1/2)H$_2$O 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)$_2$, the formation of a water multilayer at high vapour pressure could act either enhancing Ca(OH)$_2$ surface dissolution$^3$ or promoting the formation of stable SO$_2$ hydrated complexes.$^3$ Moreover, the reaction product (CaSO$_2$•(1/2)H$_2$O)$_n$ 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$_2$•(1/2)H$_2$O 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$_2$•(1/2)H$_2$O 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.

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 $P3m1$)$^7$ 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$_2$•(1/2)H$_2$O 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

Copyright © 2006 The Chemical Society of Japan
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).

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\(_3\)·(1/2)H\(_2\)O morphology after exposure to a humid atmosphere and to provide more direct evidence of CaSO\(_3\)·(1/2)H\(_2\)O mobility on Ca(OH)\(_2\) (0001) and its implications on the chemistry of the system.

References