

Kinetic analysis and in-situ IR/Raman spectroscopy of lizardite and chrysotile dehydroxylation

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Low pressure dehydroxylation of serpentine phases is important in processes such as the inertialisation of chrysotile asbestos or the CO₂ sequestration in ultramafic rocks. Although research on the mechanism of this process goes back to the forties of last century, the dehydroxylation mechanism is still not fully elucidated. In this study with used non-isothermal thermogravimetric (TGA) analyses, in-situ IR- and Raman spectroscopy as well as in-situ X-ray diffraction to monitor the dehydroxylation process. Reaction-progress (α) resolved apparent activation energies (E_a) were obtained by model-free treatment of TGA runs (Ozawa-Flynn-Wall isoconversional method).

The evolution of E_a vs. α is distinct for both serpentine phases: in lizardite the curve is convex, whereas in chrysotile it is concave. The initial increase in E_a observed for both phases is due to competing parallel reactions involving a) two symmetrically different OH-sites and b) several possible parallel dehydroxylation reaction steps (H and OH debonding, recombination of H and OH before debonding etc.). The simultaneous decrease of the IR absorbance for all OH-bands indicates, that dehydroxylation affects both OH-groups at the same time, but at different rates. The contribution of the reaction step/OH-group with the higher activation energy is becoming more important with increasing α . Activation energies calculated by DFT for similar dehydroxylation steps in pyrophyllite (Molina-Montes et al., 2008) compare well with the range of present values. In chrysotile, the situation is more complicated owing to the non-translational symmetry of the structure. Each TO-layer has its proper curvature and is, therefore, structurally unique. The outer layers with larger curvature are less stable than the inner layer. The latter dehydrate, therefore, at higher temperature.

Decreasing E_a for both phases (lizardite $\alpha > 0.45$, chrysotile $0.1 < \alpha < 0.5$) are attributed to transport processes becoming rate determining for certain parts of the sample (activation energy typically below 100kJ). No water bands have been observed, which is compatible with the idea (Zhang et al, 2010), that the main species during transport are not water molecules but hydrogen, hydroxyl and oxygen ions. A support of this transport model is the appearance during dehydroxylation of a transient OH-band in the present in-situ IR- and Raman spectra, which is not attributable to one of the structural OH-groups. In chrysotile, transport along the interlayer is fast but over a very long distance, whereas across the interlayer, transport is over a short distance but slow. The reaction progresses from the outer to the inner layers of the chrysotile wall i.e. the contribution of transport to the overall rate increases (=decrease of E_a) until the reaction front reaches the center of the nanotube wall, and decreases (=increase of E_a) again beyond. Initial and final reaction rates correspond to E_a of the outer- and innermost layers.

A frequency jump of the A_{1G} Mg(O,OH)₆ mode, residual Si-O-Si bands and the appearance of a new band at 183 cm⁻¹ around the temperature, where the lizardite respectively chrysotile related bands disappear, are evidence for the existence of a hydroxyl bearing transient phase coexisting with forsterite. The observed new bands are close to frequencies characteristic for talc, the second solid phase appearing in the stable decomposition of serpentine phases. The formation of a possible dehydroxylation intermediate with a T-O-T arrangement was already proposed by MacKenzie and Meinhold (1994) based on NMR studies.

References

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