We have investigated non-equilibrium dehydration dynamics of cavansite \((\text{Ca}(\text{VO})(\text{Si}_{4}\text{O}_{10})\cdot 4\text{H}_{2}\text{O})\) with extremely fast time-resolved high-temperature (HT) synchrotron powder X-ray diffraction (XRD). For the first time, an in-situ dehydration experiment of a zeolite-like material was carried out with both distinct heating rates (3K/min and 10K/min) and particle sizes (crystals < 25 µm, and between 25 and 50 µm) in open 0.3 mm capillaries.

Cavansite consists of sheets of \(\text{SiO}_4\) tetrahedra, linked by intercalated vanadyl-units, with \(\text{Ca}\) and 4 \(\text{H}_2\text{O}\) molecules as extra-framework occupants. Previous in-situ HT single-crystal XRD experiments [1], from which the structures of static intermediate phases were obtained, indicate three dehydration steps at 348, 448 and 623 K, each associated with release of 1 \(\text{H}_2\text{O}\).

Our preliminary results (Fig. 1) indicate that the non-equilibrium dynamic dehydration behavior is mainly influenced by the heating rate. At steps 1 and 2, the different grain sizes behave similarly whereas different heating rates yield distinct results. The volume discrepancy with respect to quasi-equilibrated single-crystal data [1] can be explained by the fact that intermediate equilibria are not reached [2]. At step 3, \(dV/dT\) of the fine particles is steeper than of the coarse ones, which is likely due to shorter \(\text{H}_2\text{O}\) diffusion paths within the small crystals, becoming increasingly important at higher temperature. This assumption is also valid within the two 10K/min runs, in which small particles react slightly faster. The opposite behavior within the 3K/min rates seems striking. However, it is known that increasing \(\text{pH}_2\text{O}\) retards dehydration of zeolite-like materials [3,4]. Here, \(\text{pH}_2\text{O}\) is mainly controlled by the denser packing of the smaller crystals. The coarse-grained sample reacts faster because of lower \(\text{pH}_2\text{O}\). At lower temperature (3K/min rate), the influence of \(\text{pH}_2\text{O}\) is governing the dehydration, whereas it is governed by diffusion path lengths at higher temperature (10K/min).

Temperature is a thermodynamic variable often used to change and probe materials. Our data show that not only different heating rates but also particle size, packing density and atmosphere should be considered in this type of experiments.

Keywords: PXRD, zeolite-like material, in-situ high-temperature, non-equilibrium, dehydration dynamics

Figure 1. Unit cell volumes vs. temperature: 3K/min runs are shown in blue, 10K/min in red. Thin lines correspond to the < 25 µm, thick ones to the 25 < x < 50 µm sample. PXRD data at 5K/min [2] with unspecified crystal size are indicated by the dashed line, single-crystal XRD data of [1] with stars.