An in situ study of the edingtonite dehydration process from X-ray synchrotron powder diffraction

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Abstract: The dehydration process of the zeolite edingtonite, Ba_{1.6}Ca_{0.2}Al_{14}Si_{6}O_{20}·8H_{2}O, has been studied in situ by X-ray synchrotron radiation powder diffraction. 51 consecutive powder patterns were collected between 310 and 684 K, in steps of 6 K, at 5 minute intervals, and the structures were refined using the Rietveld method. At 310 K the two water sites in edingtonite, OW(1) and OW(2), are both 3/4 occupied. Between 310 and 400 K the occupancy of OW(1) drops smoothly to 1/2. At the same time as the OW(1) expulsion continues, the OW(2) occupancy starts to increase to reach a maximum of 88% at 450 K. A simple electrostatic model is suggested to explain this behaviour. Between 450 and 600 K, OW(2) shows a regular dehydration behaviour. The remaining water is then rapidly expelled as the water contents drop below one per Ba ion. Finally, as a consequence of an unstable Ba-O coordination, the edingtonite structure breaks down between 660 and 680 K. The framework responds to the dehydration first by a chain rotation and later by an intra-chain folding. Both mechanisms can be related to the electrostatic and spatial needs of the Ba ion.

Key-words: in situ powder diffraction, X-ray synchrotron radiation, zeolite dehydration, edingtonite.

Introduction

Edingtonite belongs to the group of fibrous zeolites. It has an ideal composition of Ba_{2}Al_{14}Si_{16}O_{20}·8H_{2}O with fully ordered Si/Al distribution. The crystal structure was solved by Taylor & Jackson (1933) from X-ray data. A structure refinement based on neutron single crystal data by Kvick & Smith (1983) gave accurate parameters of all atoms including hydrogens. Two projections of the structure are shown in Fig. 1.

Gottardi & Galli (1985) suggested a transition to lower symmetry to explain the dehydration rate variations observed by Mazzi et al. (1984) from TG analyses, and the irregular unit cell variations seen by van Reeuwijk (1974) from a Guinier-Lenné study. To resolve this question, and to arrive at a more exhaustive picture of the dehydration process in edingtonite, it was decided to follow the structural changes step by step by means of powder diffraction, while slowly heating the sample. Combining a position sensitive detector (CPS120 by INEL) and an X-ray synchrotron source (NSLS, Brookhaven National Laboratory, USA), consecutive, complete powder diffraction patterns, suitable for Rietveld refinements, can be collected within five minutes. Similar in situ studies have previously been performed on scolecite and mesolite...