The Crystallization of Zeolites and Other Porous Materials

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IN SITU STUDIES OF DEHYDRATION PROCESSES IN ZEOLITES USING POWDER DIFFRACTION.

By K. Stahl, Inorganic Chemistry 2, University of Lund, Sweden.

Diffraction studies of dehydration processes of zeolites have given valuable insight in the chemistry of zeolites and may provide important data to the syntheses and applications of these materials. The so far studied zeolites have shown a variety of dehydration behaviours, involving phase transitions, dehydroxylation and so on before the final breakdown of the crystal structure. The standard method for structural studies has been to heat a powdered or single crystal sample to a given temperature, cool it off and cool it to room temperature before data collection. Obviously this method will give information about the limited set of dehydration temperatures only, and the results may to some extent be obscured by the cooling down temperature. Preferably one would like to repeatedly collect complete data sets while the samples are slowly heated.

With the combination of a position sensitive detector (GIPS120 by INEL) and a synchronously rotating X-ray source (X70B, NSLS, USA), the data acquisition time for zeolite powder diffraction pattern, suitable for Rietveld analysis, can be brought down to the order of minutes. Complete powder diffraction data sets collected every five minutes during intermittent (5 K/min) heating have with this method given detailed information of the dehydration processes in a set of natural zeolites. The nature of the water evaporation, gradual or almost instantaneous, stability limits of cation coordination numbers, and the crystal structures immediately below and above phase transitions as well as some of the directly obtainable results, details of the water and sometimes cation diffusion can be extracted. The method itself and the results will be discussed in detail, where available, compared to data obtained with the standard, fixed dehydration temperature method.

EVALUATION OF ZEOLITE FRAMEWORKS WITH THE VIEW TO CLASSIFICATION, ENUMERATION AND SOLUTION OF STRUCTURES

Duncan Akpataye

SINTEF-SL, P.O. Box 124 Blindern, N-0314 Oslo, Norway.

An overview of the current range of zeolite frameworks is presented as defined by their systematic relationships derived from their classification in terms of consitent 3-connected nets. The application of the various methods for the classification and enumeration of zeolite frameworks and their usefulness in structure classification and solution is considered. Novel nets of hypothetical frameworks are evaluated, including a series for which the channel characteristics are pre-defined in two-dimensions.

RECENT ADVANCES IN THE STRUCTURAL CRYSTALLOGRAPHY AND CRYSTAL CHEMISTRY OF NATURAL ZEOLITES.

By L. Artioli, Dipartimento di Scienze della Terra, Università di Milano, Italy.

The number of known natural zeolite minerals has increased in recent years. Several new mineral species are natural analogs of known synthetic phases (silicate-kerite [KBE], phalaborite [RHO], tephroite [CAN], tephroellite [BTE]), and other natural species show novel framework topologies (bohite [BOG], maricopite, montesantinite [MON], tvedestrandite).

The crystal structures of the new minerals will be discussed, together with the recent advances in the structural analysis and modelling of other zeolite groups: the crystal structure of goslarite [GHS] has been determined, perlite [TLI] was shown to have the zeolite-L framework topology, dachsteinite [DAC] shows consistent domains having different frameworks, and the study of the fully hydrated structure of lavandinite [LAV] allows interpretation of the leonardite-hemite reversible transformation.

Several other zeolite structures were also recently studied in detail and partly covered: leovanthite [LGO], roganite [ROG], tephroite [TOD], goslarite [GSH]. The presence of tetrahedrally coordinated beryllium in natural zeolitic minerals, and the stability of interrupted framework structures are to be considered common features in zeolites. Natural (chamosite [CCH], phacopite [PAR], roganite [ROG], weakite [WEN]) and synthetic (cloverite [CLO]) interrupted framework structures will be described.

QUANTITATIVE IMAGING AND DIFFRACTION OF ZEOLITES USING A LOW-SCAN CCD CAMERA.

By M. Pan* and P.A. Cooper, Center for Solid State Science, Arizona State University, USA.

Zeolites are an important class of low-density aluminosilicate framework structures with applications to the field of catalysis, electronic materials and molecular sieves (D.W. Breck, Zeolite Molecular Sieves, John Wiley & Sons, New York, 1974). Structural determination is usually carried out by x-ray diffraction. Unfortunately, it fails partially or completely if the synthesized zeolite crystals have a small grain size (6-10 μm) or the structure contains defects. In this case, high resolution electron microscopy (HREM) and electron diffraction can be powerful techniques to help solve the structures (I.M. Newsam, et al., Proc. R. Soc. Lond. A420 (1988) 375). Zeolites undergo rigid structural damage when exposed to electron irradiation because of the low-dose and open framework structures. Hence it is necessary to employ low-dose techniques to perform high resolution structure imaging of zeolites.

Recently, the technology in solid state electronic devices has led to the development of commercially available low-scan CCD (charge-coupled device) cameras for electron microscopy (P.R. Mooney, et al., Proc. Xth Congr. for Elect. Microsoc., Seattle, WA, Vol. 1 (1990) 164). The main advantages of such a device include linear response, large dynamic range (4×10^6), high sensitivity and digital data storage. All of these are suited to acquiring image and diffraction data from radiation sensitive materials.