

**HIGH- PRESSURE INDUCED OVER-HYDRATION
OF HYDROPHOBIC NANOPOROUS****Experiment
number:
HS- 4296**

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The applicability and efficiency of microporous materials as catalysts, selective absorbers, and ionic exchangers can be strongly affected by the non-ambient conditions, in particular, high temperature (HT) and high pressure (HP) under which they operate. HP can induce structural changes, which could give rise to profound modifications to the zeolite physical properties, and hence make the material useful for new specific applications. Moreover, the framework flexibility upon compression can modify the accessibility to the zeolite catalytic sites by the molecular species entering the porous material. In this experiment we have extended our

investigation on the water systems intruded under pressure into the confined porosities of high-silica and hydrophobic zeolites.

The response to compression of a synthetic Si-ferrierite (framework topology FER, s.g. Pnnm) was explored by in-situ synchrotron X-ray powder diffraction experiments at BM01. Ferrierite is a well-known aluminosilicate zeolite mineral. An understanding of the structure and properties of FER remains important because of its role as a catalyst in commercial reactions. For example, it is important in the petrochemical industry, where it has been used as a shape selective catalyst for the production of isobutene. The thermal behavior of this phase (in its high silica form) was recently studied by Bull et al [1], while its compressibility has never been investigated before.

Experimental

The microporous material was synthesized starting from pure silica and pyridine and propyl-amine as structure directing agents. HP X-ray powder diffraction (XRPD) experiments were performed at the SNBL1 (BM01a) of the European Synchrotron Radiation Facility (ESRF, Grenoble) with fixed wavelength of 0.71 Å, using a Merrill-Bassett DAC and (16:3:1) methanol:ethanol:water (m.e.w.), as "penetrating" pressure transmitting media. The pressure was measured using the ruby fluorescence method. The estimated error in the pressure values is 0.1 GPa. A MAR345 detector (pixel dimension 150 μm) was used. One-dimensional diffraction patterns were obtained by integrating the two-dimensional images with the program FIT2D. The powder patterns were collected from Pamb to 6.2 GPa. Some patterns were also measured upon pressure release up to Pamb, to check the reversibility of the compression effects. The unit cell refinements were carried out up 6.2 GPa, using GSAS software [2] and the Rietveld method.

Results and discussion

Here we report the preliminary results on the compressibility of the as-synthesized ferrierite Si- phase. The study of the compressibility of the calcined one will be carried out in the following steps of the project.

The crystal structure of ferrierite is built up of rings of fivecorner-shared SiO_4 tetrahedra (known as five-membered rings or 5MRs) building units, which form layers in the ab plane (Figure 1). The layers are connected to form a matrix of 10MR channels running parallel to the c axis, which are intersected by 8MR channels running parallel to the b axis. Six-membered rings connect the 10MRs along the c axis direction.

The main results of this study are:

- 1) No complete X-ray amorphization is observed up to about 6.6 GPa (Figure 2);
- 2) No abrupt change of the elastic behavior is observed in the whole pressure range. Between P_{amb} and 6.2 GPa the reduction of the cell parameters are 4%, 5% and 6% for a, b and c respectively, accounting for a volume reduction of about 14 % (Figure 3)
- 3) The bulk modulus obtained using a second order Birch-Murnaghan equation of state and data weighted by the uncertainties in P and V was $K_0 = 30.1(3)$ GPa. This compressibility determined in m.e.w. is one of the highest when compared with other natural and synthetic zeolites studied with “penetrating” aqueous media [3-5].
- 3) The P-induced effects on as-synthesized ferrierite structure are completely reversible (Figure 2 and 3).

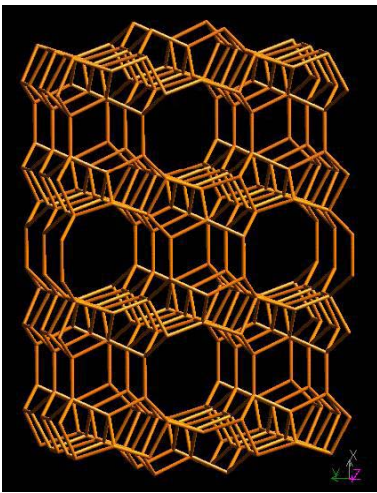


Fig. 1 Projection of the ferrierite structure along the

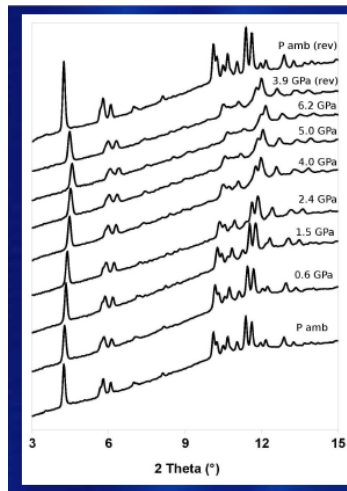


Fig. 2 Powder patterns of ferrierite as a function of P

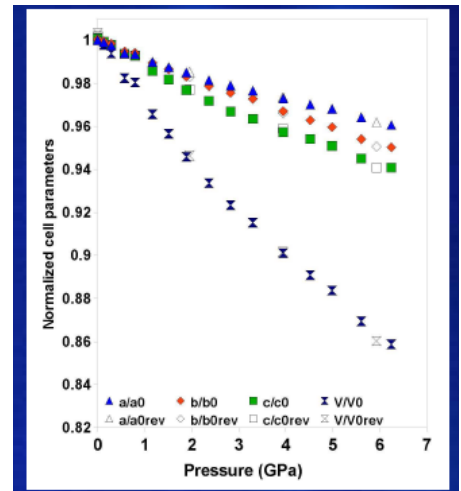


Fig. 3 Variation of ferrierite cell parameters as a function of P

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