ESRF	**WATER IN CONFINED HYDROPHOBIC SPACES: HP-INDUCED OVER-HYDRATION OF NANOPOROUS MATERIALS**	**Experiment number**: **HS- 3791**
Beamline: BM01	**Date of experiment**: from: 22/07/2009 to: 25/07/2009	**Date of report**: 28 June 2010
Shifts: 12	**Local contact(s)**: Vladimir Dmitriev	*Received at ESRF:*

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Introduction

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.

The response to compression of two different zeolites with MFI framework type (space group Pnma) was explored by in-situ synchrotron X-ray powder diffraction experiments. H-ZSM5 [$[(Na_{1.1})$ $(Al_{8.81}$ $Si_{88.87}$ $H_{7.6}$ $O_{192})\cdot 32$ $H_2O]$ and Na-ZSM-5 [$Na_{4.58}$ $K_{0.02}$) $(Ca_{0.18}$ $Mg_{0.03}$ $Ba_{0.01}Fe_{0.05}$ $Sr_{0.01})$ $(Si_{91.35}$ $Al_{4.48})$ $O_{192} \cdot 28.39$ $H_2O]$ share the same framework but present different extraframework species and different Si/Al ratios.

Experimental

H*P* X-ray powder diffraction (XRPD) experiments were performed at the SNBL1 (BM01a) of the European Synchrotron Radiation Facility (ESRF, Grenoble) with fixed wavelength of 0.70026 Å, using a Merril-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 in the 2θ range 0–37° by integrating the two-dimensional images with the program FIT2D. The unit cell refinements were carried out up to 7.6 and 7.4 GPa for H-ZSM5 and Na-ZSM-5, respectively, using GSAS software [1] and the Rietveld method. Complete structural refinements were performed from P_{amb} to 2.0 and 1.6 GPa for H-ZSM5 and Na-ZSM-5, respectively.

Results and discussion

Na-ZSM-5

From P_{amb} to 7.4 GPa, a unit cell volume reduction of about 14.6% is observed and the corresponding reductions of *a, b,* and *c* cell parameters are 6.3, 4.6, and 4.5%, respectively. No phase transitions are observed and the unit cell parameters of P_{amb} are recovered upon decompression. The complete structural refinements performed up to 1.6 GPa reveal a strong over-hydration effect - corresponding to an increase of 39% of the original water content - with the penetration of 11 additional water molecules in the partially

occupied extraframework sites of as-synthesized Na-ZSM-5 (Fig. 1). This P-induced over-hydration (PIH), which does not induce any cell volume expansion, is only partially reversible, since two of the eleven extra-water molecules remain in the Na-ZSM-5 channels upon decompression. PIH is accompanied by the increase of the ellipticity of the channel along [010] (Fig. 2), while the channels along [100] become more circular and smaller [2].

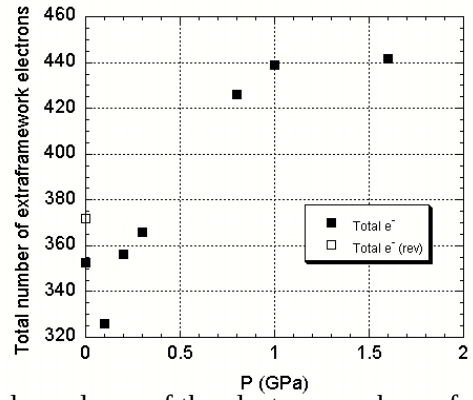

Fig. 1 P-dependence of the electron numbers of the extraframework sites of Na-ZSM-5 compressed in m.e.w.

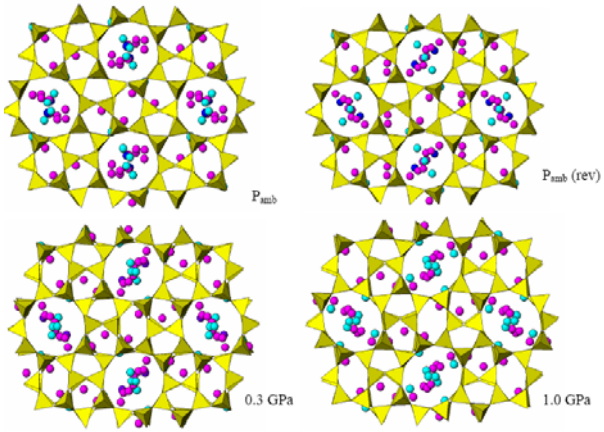

Fig. 2 Projection of the Na-ZSM-5 structure along the [010] direction at P_{amb}, 0.3 GPa, 1.0 GPa, and P_{amb}(rev).

H-ZSM-5

From P_{amb} to 7.6 GPa a unit cell volume reduction of about 14.6 % is observed, while the unit cell axes undergo the following reductions: Δa = 5.8%, Δb = 4.8%, Δc = 4.4%. No phase transitions are observed.
A strong P-induced re-organization of the extraframework system is observed and is accompanied by an increase of the total extraframework content, which can be ascribed to the penetration of extra-water molecules in the channels. This PIH produces an increase of even 44% with respect to the initial water content (36 molecules) (Fig. 3). This percentage is the highest up to now observed in zeolites which undergo P-induced over-hydration without any cell volume expansion. As for Na-ZSM-5, PIH is accompanied by the increase of the ellipticity of the channel along [010] (Fig.4). An interesting difference between the PIH of H-ZSM-5 and Na-ZSM-5 concerns the reversibility of the phenomenon: while the extra water molecules are completely released upon decompression in H-ZSM-5, Na-ZSM-5 over-hydration is only partially reversible, and hence, in this last case, a new material with a different extraframework composition is obtained at the end of the process [2].

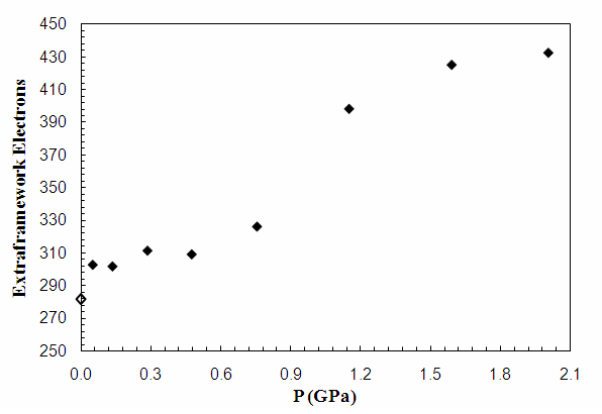

Fig.3 P-dependence of the electron numbers of the extraframework sites of H-ZSM-5 compressed in m.e.w.

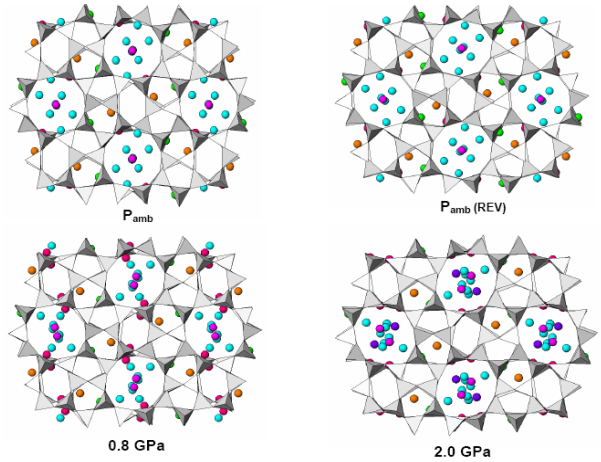

Fig. 4 Projection of the H- ZSM-5 structure along the [010] direction at P_{amb}, 0.8 GPa, 2.0 GPa, and P_{amb}(rev).

References
[1] Larson, A.C., Von Dreele, R.B. (1994) Report LAUR 86-748, Los Alamos National Laboratory, Los Alamos, New Mexico.
[2] Arletti, R., Quartieri S., Vezzalini G., Dmitriev V. (2010) Elastic behavior of MFI-type zeolites: 1- Pressure-induced over-hydration of Na-ZSM-5. Microporous and Mesoporous Materials, submitted.