ESRF	**HP-induced host-guest interactions and phase transitions in nanoporous materials of technological interest.**	**Experiment number**: HS3360
Beamline: ID09	**Date of experiment**: from: 07/11/2007 to: 10/11/2007	**Date of report**: 10 July 2008
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Names and affiliations of applicants (* indicates experimentalists):

G.Montagna*, G.Vezzalini*, R. Arletti, Dipartimento di Scienze della Terra, via S. Eufemia 19, 41100 Modena, Italy

S. Quartieri*, Dipartimento di Scienze della Terra, Salita Sperone 31, 98 166 Messina S.Agata, Italy

M.Merlini*, ESRF, Grenoble, France.

Report:

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 three different zeolites with MFI framework (space group Pnma) were explored by in-situ synchrotron X-ray powder diffraction experiments, using silicone oil as non-penetrating pressure transmitting medium. H-ZSM5, Silicalite and Mutinaite share the same framework but present different extraframework species. Mutinaite [$(Na_{2.76}\ K_{0.11}\ Mg_{0.21}\ Ca_{3.78})\ (Al_{11.20}\ Si_{84,91}\ O_{192})\cdot 60\ H_2O$] is the natural counterpart, while H-ZSM5 [$[(Na_{1.1})\ (Al_{8.81}\ Si_{88.87}\ H_{7.6}\ O_{192})\cdot 32\ H_2O$] is the synthetic hydrogen form. Silicalite [SiO_2] pore system is empty and its Si/Al ratio is ≥300, much higher than in H-ZSM5 (10) and mutinaite (7.6). Moreover, the Si/Al ratio of mutinaite is the highest up to now found in a natural zeolites [1], but is the lowest among those of the synthetic zeolites with MFI framework, synthesized both in presence and in absence of any organic compounds.

Experimental

H*P* X-ray powder diffraction (XRPD) experiments were performed at ID09 beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble) with fixed wavelength of 0.41 Å, using a Merril-Bassett DAC and silicon oil as non-penetrating *P*-transmitting medium. 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 100 lm) was used at a fixed distance of 365 mm from the sample; the exposure time was 30s for all the pressure points of mutinaite, 25s for H-ZSM5 and 4s for silicalite. One-dimensional diffraction patterns were obtained in the 2θ range 0–36° by integrating the two-dimensional images with the program FIT2D. The unit cell refinements were carried out in the 2θ range 1.5–22° up to 8 GPa for H-ZSM5 and 6 GPa for silicalite e mutinaite using GSAS software [2] and the Rietveld method. The atomic coordinates of the adopted structural model are from [3] for H-ZSM5, [4] for silicalite and [5] for mutinaite. The

background curves were fitted by a Chebyshev polynomial with an average of 18 coefficients. The pseudo-Voight profile function proposed by Thomson et al. [6] was used with refined Gaussian (GW) and Lorentzian (LX) terms.

Results and discussion

H*P* XRPD data demonstrate that no complete X-ray amorphization is observed up to the highest investigated pressure and that the original unit-cell parameters are recovered upon decompression in the three studied phases. The following axial parameters (Fig. 1.1; 1.2; 1.3) and cell volume (Fig. 2) compressions have been observed in the whole investigated P range:

Mutinaite (Fig. 1.1): Δa= 3.9%, Δb= 5.2%, Δc= 4.7%, ΔV= 12.4% (P range = 6 GPa)
H-ZSM5 (Fig. 1.2): Δa= 7.3%, Δb= 5.4%, Δc= 5.2%, ΔV= 17.0% (P range = 8 GPa)
Silicalite (Fig. 1.3): Δa= 9.0%, Δb= 9.3%, Δc= 10.0%, ΔV= 25.7% (P range = 5 GPa)

FIGURE 1.1

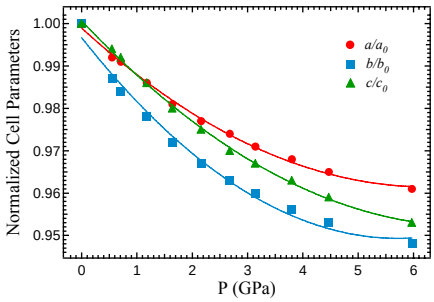


FIGURE 1.2

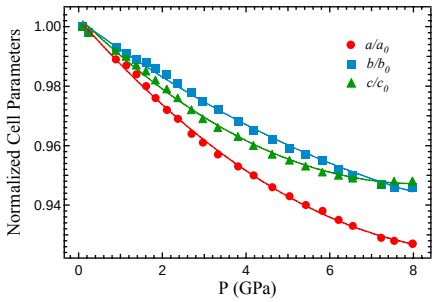
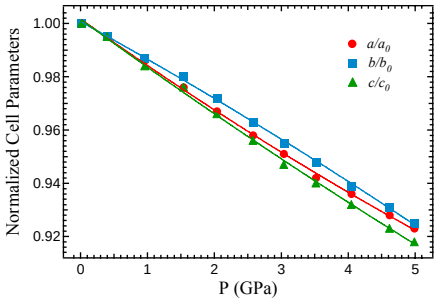


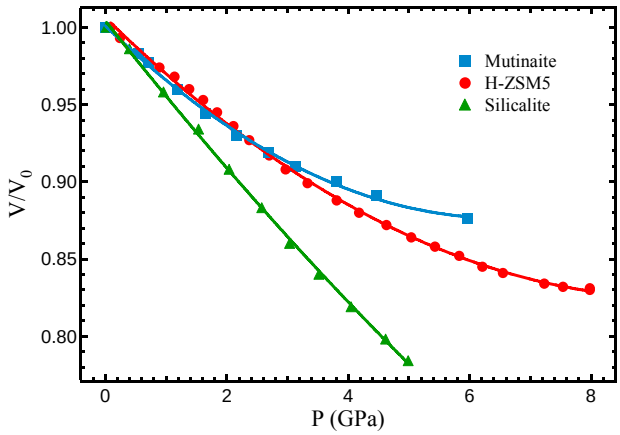
FIGURE 1.3



A comparison of the cell volume compressions observed at *4 GPa* for the tree phases shows that:

Mutinaite: ΔV= 10.4% H-ZSM5: ΔV= 12.4% Silicalite: ΔV= 18.4%

FIGURE 2



The higher cell deformation observed in silicalite, and the isotropic character of the cell parameters contractions, are consistent with the lacking of extraframework species in its pore system. On the other hand, the extraframework cations and water molecules present in mutinaite and ZSM-5 pores contribute to stiffen these structures. Finally the highest extraframework content of Mutinaite cause the lowest compressibility. These results are in perfect agreement with those recently found in other zeolites, for which a "template" effect of the extraframework content on zeolite compressibility was proposed [7].

References

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