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Supramolecular organization in zeolitic host-guest systems at high pressure: nanoscale hyperconfinement probed by high-resolution single-crystal diffraction

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In this study, we explored the high-pressure behaviour and crystal-fluid interactions of a synthetic zeolite with ferrierite topology [Si-FER: $Si_{36}O_{72}$], by *in-situ* single-crystal X-ray diffraction with a diamond anvil cell and using a number of penetrating and non-penetrating pressure-transmitting media.

Single crystals suitable for the experiments have been selected from a synthetic pure Si-ferrierite sample. The *in-situ* high-pressure diffraction experiments have been performed at the ID09A beamline. Four different *P*-transmitting media have been used: non-penetrating silicon oil and potentially penetrating methanol:ethanol:H_2O = 16:3:1 mix (m.e.w.), ethylene glycol (egl) and 2methyl-2propen-1ol (mpo).

The H*P*-study of Si-FER compressed in silicon oil evidenced the remarkable flexibility of this framework: a first displacive phase transition was observed from the orthorhombic *Pmnn* to the monoclinic $P12_1/n1$ space group at ~ 0.7 GPa. A second displacive phase transition, involving a significant unit-cell volume contraction, was observed at ~ 1.24 GPa from the $P12_1/n1$ to the $P2_1/n11$ space group (through an intermediate *P*-1 structure, "type-II" transition). The high-*P* $P2_1/n11$ polymorph was found to be stable at least up to 3.00(7) GPa, whereas - upon pressure release - the starting *Pmnn* structure was fully recovered. The three polymorphs were found to share a virtually identical bulk elastic behavior. The structure deformation is governed by the tilting of the tetrahedra around the shared oxygen hinges. The bulk *V*-contraction is mainly accommodated, after the *Pmnn*-to-$P12_1/n1$ transition, by the compression and deformation of the 8- and 10-ring channels, running along **b** and **c**, respectively.

The compression of Si-FER using penetrating *P*-transmitting media showed different results, if compared to the silicon oil experiment. Common features among the three experiments are the following: 1) the *Pmnn*-to-$P12_1/n1$ phase transition at ~ 0.7 GPa (except for m.e.w., where it occurs at ~ 1.5 GPa) and 2) the absence of the $P2_1/n11$ polymorph (previously observed in silicon oil), coupled with a less pronounced compressibility compared to that in silicon oil. For all the *in-situ* experiments, the orthorhombic symmetry was restored upon decompression.

The different phase-transition paths and the different compressional patterns, observed using different *P*-transmitting media, suggest the occurrence of *P*-induced crystal-fluid interactions. The difference-Fourier maps of the electron density, calculated by the structure refinements at any *P*-point, showed weak and broadened peaks, which did not allow the location of the molecules within the FER-structural voids. However, the analysis of the *P*-induced framework deformation mechanisms revealed different deformational patterns of the 8- and 10-ring channels of Si-FER compressed in the different fluids. Although a direct evidence of the penetration of molecules could not be proved by the diffraction data, the different deformation mechanisms at the atomic scale are an indirect evidence of the *P*-induced intrusion of molecules from the fluid into the structural pores of the zeolite. The observed broad distribution of the electron density within channels and cages suggests the presence of numerous partially occupied extraframework sites, where *P*-transmitting media molecules can be hosted. Interestingly, a "fast compression" of Si-FER from room-*P* to ca. 2 GPa triggered the transition *Pmnn*-to-$P2_1/n11$ (with enhanced unit-cell volume contraction) both in egl and mpo, suggesting a strong kinetic control on the *P*-induced molecules penetration and crystal-fluid interactions.

The following manuscript is now "in press", partially based on the findings of the experiments CH-4271:
"Lotti P., Arletti R., Gatta G.D., Quartieri S., Vezzalini G., Merlini M., Dmitriev V., Hanfland M. (2015) Compressibility and crystal-fluid interactions in all-silica ferrierite at high pressure. *Microporous and Mesoporous Materials* (*in press*)".