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"ImPACT"- FIRB Futuro in Ricerca: Pressure-induced supermolecular organization of water and ethanol in all-silica zeolites

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One of the purposes of "ImPact" Project (financed by Italian MIUR, FIRB- Futuro in Ricerca 2013-2016) is to understand at atomistic level the supramolecular organization of different molecules in zeolites frameworks. In particular, the pressure-induced aggregation of molecules in high-silica zeolites cavities of different shapes (FER, MOR, MFI, CHA) will be studied. Water in zeolites represents a model system for a wide range of experimental as well as theoretical investigations, aimed at understanding the effect of confinement on the structure, dynamics and thermodynamics of molecular fluids [1-3]. Understanding the behaviour of nano-confined water is also relevant to such important problems as transport in ion channels, moreover, from a practical point of view, water plays a key role in many applications of zeolites such as ion-exchange and liquid phase separation [4-5].

In this paper the HP-induced confinement of water and ethanol in all-silica ferrierite [s.g Pnnm, a=14.0690(8) Å, b= 7.4177(3) Å, c= 18.708(1) Å V = 1952.3(2) Å^3] compressed with two different aqueous media [(methanol-ethanol-water (16:3:1; m.e.w.); ethanol-water (1:3; e.w.)], is presented and the structural features of the HP phase is discussed. The HP SR-XRPD experiments were performed at the BM01 beam line (European Synchrotron Radiation Facilities, Grenoble, France). While for m.e.w. experiment it was possible to collect data up to 8 GPa, the e.w. ramp was stopped at 1.3 GPa due to ice formation. In the range Pamb-8 GPa, the contraction of a, b, c, and V observed in m.e.w. are: 5.8, 5.0, 7.2 and 16.9%, respectively. From Pamb to 1.3 GPa, a unit cell volume reduction of about 3.4 % is observed for ferrierite compressed in e.w, and the corresponding contraction of a, b, c and V cell parameters are 1.3, 0.9, 1.1 and 3.4%, %, respectively. Structural refinements were performed by Rietveld profile fitting in the whole pressure range in e.w. and up to 0.2 GPa in m.e.w. (the data quality of the higher pressure patterns being too low for structural refinement). In both cases no phase transitions are observed and the unit cell parameters of Pamb are recovered upon decompression. The structural results indicated the penetration of the pressure media even at the lowest investigated pressure in both experiments.

In ferrierite compressed in e.w., a chain of water (w) and ethanol molecules (e) running along the central axis of the channels was localized even at 0.2 GPa, accounting for a total of 5 w and 3.6 e molecules. The increase of the occupancy factors of the localized sites leaded a total load of 11 w and 4 e molecules at 1 GPa. The refinement at 0.2 GPa of ferrierite compressed in m.e.w. indicated the penetration of only water (15.6 molecules) organized in chains. The interactions among these molecules and the framework oxygen atoms are very weak, due to the hydrophobicity of the framework.

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