



Microporous materials under extreme conditions - EMU Medal for Excellence in Research 2013 presentation

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Zeolites are a class of “microporous materials” characterised by open-structures with cavities (i.e. channels or cages) with free diameters smaller than 20 Å. In Nature, zeolites with SiO_4 - AlO_4 - PO_4 -tetrahedra form open frameworks; polar molecules (in particular H_2O) and monovalent or divalent cations, which are commonly exchangeable, are the extra-framework species. The selective cation-exchange capacity, along with T-induced reversible hydration/dehydration and the catalytic activity (mainly promoted by Brønsted acid sites) of zeolites have made this class of natural or synthetic materials an object of attention for their advanced technological applications, spanning from water treatment, soil remediation, cements production, biomedical and veterinary applications, gas separation to catalysis in the petroleum industry and nuclear-waste processing. As a consequence, zeolites are an important bulk commodity: the world production of natural zeolites in 2012 was about 2,800,000 tons and the consumption of synthetic zeolites was approximately 1,900,000 tons. Over the last 60 years, many experiments have addressed the behaviour of zeolites in response to applied temperature, describing the mechanisms of T-induced dehydration, cation migration and the rearrangement of extra-framework species. On the other hand, experiments on zeolite at high pressure have been done only in the last 10-15 years, shedding new insight into the elastic behaviour and phase stability in response to changing pressure, coupled with the P-induced deformation mechanisms at the atomistic level, P-induced over-hydration and its corresponding volume expansion, P-induced amorphization processes along with the effect of pressure on the ionic conductivity of zeolites.

The comparative elastic analysis and the high-P structural data of zeolites so far reported allow us to make some generalizations: 1) The range of compressibility among this class of open-framework silicates is large, with bulk moduli ranging between 15 - 70 GPa; 2) Microporosity does not necessarily imply high compressibility, as several zeolites are less compressible than other non-zeolitic rock-forming minerals; 3) Compressibilities of zeolites do not seem to be directly related to microporosity, at least if we model microporosity with the “framework density”; 4) The flexibility observed in zeolites under hydrostatic compression is mainly governed by tilting of rigid tetrahedra around O atoms that behave as hinges within the framework. P-induced tilting commonly leads to continuous rearrangement of the framework without any phase transition. More rarely, tilting induces displacive phase transitions, and isothermal P-induced reconstructive phase transitions (i.e. with change in framework topology), have not been reported in this class of materials; 5) Deformation mechanisms in response to applied pressure are generally dictated by the topological configuration of the framework rather than the Si/Al-distribution or the extra-framework content. The channel content governs the compressibility of the cavities, leading to different unit-cell-volume compressibilities in isotropic structures.