

The Pure Silica Chabazite: A High Volume Molecular Spring at Low Pressure for Energy Storage

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Water intrusion–extrusion isotherms were performed at room temperature on hydrophobic pure silica chabazite (Si-CHA). A reversible phenomenon is observed over several cycles showing that the water–Si-CHA system displays a real spring behavior. The process occurs at a quite low pressure, and the large intruded water volume makes this system interesting for applications in energetics.

Zeolites, which are crystallized microporous solids with pore diameter lower than 1.4 nm, are widely used for applications related to adsorption, catalysis, and ion exchange. Recently, a new field of application concerning the energetics was highlighted.^{1–3} The phenomenon was based on the following principle: to spread a drop of a nonwetting liquid on the surface of a solid, a certain pressure must be applied. In the same way to make penetrate this liquid in a porous matrix, the pressure which must be applied is at least equal to capillary pressure. According to the Walsburn law: the smaller the pores, the higher the pressure. During this forced penetration or intrusion into the porous matrix, the massive liquid is transformed into a multitude of molecular clusters, which develop a large solid–liquid interface. In the course of this step, mechanical energy spent by the pressure forces is converted into interfacial energy. At the microscopic scale, this process results from the breaking of intermolecular bounds in the liquid to create new bounds with the solid. By releasing the pressure, expulsion or extrusion of liquid occurs in displaying a more or less significant hysteresis.⁴ Although, the interactions are rather weak (usually, of the van der Waals type), they are acting on very high surfaces. It is thus easy to appreciate that the process may allow to stock and restore a large amount of energy in a small volume.

Such a property which was firstly shown by Eroshenko on non-zeolitic porous solids with low melting point metals as non-wetting liquids^{5,6} was extended for the water-containing systems to zeolite^{1–3} and then to functionalized organized mesoporous solids.^{7–9} Depending on the type of zeolite (pore size, dimensionality of the channel system, structure type, hydrophobic/hydrophilic character, etc.), the system made up of water and zeolite can thus store and then restore, absorb or dissipate mechanical energy.^{1–3} Such behaviors can be evidenced from the pressure–volume (*PV*) diagrams. Thus, a completely reversible process over several intrusion–extrusion cycles is observed for strongly hydrophobic silica zeolites. It was the case for the system water–silicalite-1; the latter solid constituting a real molecular spring.¹ On the other hand, for a pure silica BEA-type zeolite, whose structure consists in at least two polytypes, the phenomenon is nonreversible. The presence of defect sites at the interface of the two polytypes could explain the bumper behavior of such a solid.²

In the present work, intrusion of water was studied in a pure silica chabazite (Si-CHA). The 3-D structure of chabazite consists in rhombohedral cages delimited by eight-membered ring openings (pore diameter close to 0.40 nm). This zeolite is very interesting since it displays one of the lowest framework density (14.5 T atoms per 1000 Å³). The Si-CHA samples were synthesized according to the procedure published by Diaz-Cabanas et al.,¹⁰ in fluoride medium and using *N,N,N*-trimethyladamantammonium (TMAda⁺) as structure-directing agent. The starting gel (molar composition: 1SiO₂:0.5TMAdaOH:0.5HF:3H₂O) was introduced in a Teflon-lined stainless-steel autoclave and heated at 150 °C during 90 h. After synthesis, the products were filtered, washed with distilled water and dried at 60 °C overnight. The solid was then calcined at 600 °C to completely remove the organic template. The as-synthesized and calcined products were characterized by XRD, thermal analysis and solid-state NMR spectroscopy. The intrusion–extrusion of water in Si-CHA samples was performed at room temperature using a Micromeritics mercury porosimeter (Model Autopore IV). The cell containing the water/zeolite system consists in a polypropylene cylinder of 2 mL sealed by a mobile piston. This cell is introduced in the 15-mL glass cell of the porosimeter which is filled with mercury. The volume variation is determined from the capacity measurement which depends on the mercury height in the capillary tube of the glass cell. The maximum volume change is about 0.37 mL. The experimental intrusion–extrusion curve is obtained at room temperature after subtraction of the curve corresponding to the compressibility of pure water. The values of the intrusion (*P_i*) and extrusion (*P_e*) pressures correspond to that of the half volume total variation. Pressure is expressed in MPa, and volume variation in mL per gram of anhydrous calcined zeolite.

The calcined Si-CHA sample is very well crystallized. Its X-ray diffraction pattern was unambiguously indexed with a rhombohedral (space group *R3m*) cell with *a* = 9.251(6) Å, α = 94.245(5)°. The elemental analysis of the calcined sample leads to the idealized unit cell formula Si₃₆O₇₂. The absence of defect sites of silanol type is clearly evidenced by solid-state NMR spectroscopy. Indeed, the ²⁹Si MAS NMR spectrum displays a single component at 111.6 ppm (reference TMS) ascribed to the only one crystallographic silicon site and corresponding to Q4 groups (Si–(OSi)₄).

The pressure–volume diagrams at room temperature after one, two, three, and four intrusion–extrusion cycles are reported in Figure 1, and the experimental characteristics summarized in Table 1. For the four intrusion–extrusion cycles, a general description can be made. Initially, the curves exhibit a linear part due to the compressibility of the condensed phases. When the pressure increases and the capillary pressure is reached (*P_i* = 37–42 MPa), water molecules penetrate into the pores of

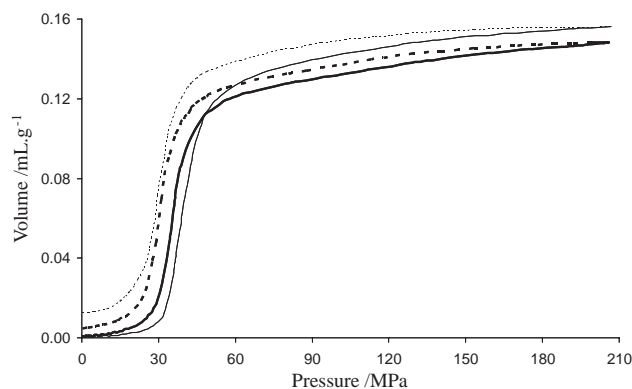


Figure 1. Pressure–volume isotherms of “water–Si-CHA” system at room temperature: intrusion curve (full line: thin line for cycle 1 and thick line for cycles 2–4); extrusion curve (dotted line: thin line for cycle 1 and thick line for cycles 2–4). For cycles 2, 3, and 4, the intrusion curves are completely superimposable; idem for the extrusion curves.

Table 1. Characteristics of the system “water–Si-CHA”

	Cycle 1	Cycle 2	Cycle 3	Cycle 4
Pore volume (mL/g) ^a		0.30		
BET surface area (m ² /g) ^a		850		
Intrusion pressure (MPa)	42	37	37	37
Extrusion pressure (Mpa)	30	31	31	31
Intruded volume (mL/g)	0.157	0.148	0.148	0.148

^aDetermined from nitrogen adsorption isotherm (77 K).

the solid. An important variation of volume is observed (ranging from 0.15–0.16 mL/g of zeolite). Finally, after a complete filling of the pores, a classical compression step takes place. When the pressure is released, the phenomenon is reversible. However, the extrusion of water occurs at a lower pressure ($P_e = 30\text{--}31$ MPa) indicating a very slight hysteresis.

After the four intrusion–extrusion cycles no significant changes are observed by XRD analysis. The water–Si-CHA system, as it was previously observed for the water–silicalite-1 system, constitutes a real molecular spring. However, by comparison with silicalite-1 (MFI structure type), the pore diameter is lower (8 MR instead of 10 MR) and the intrusion of water was expected to occur at a higher pressure. Surprisingly an opposite variation is observed. While the pressure of intrusion is close to 100 MPa for silicalite-1 in that case, the pressure is about one third of this value making this molecular spring particularly interesting for applications. A similar behavior was found for the clathrasil DDR.² In both cases (CHA and DDR), the structure displays cages connected by small windows while the structure of silicalite-1 displays channels with larger apertures. This would mean that the intrusion pressure would be better related to the diffusion of water in the structure than to the pore openings. In the cage structure, the water molecules can also adopt a geometry similar to that of the bulk water (with hydrogen bonds between the molecules) which is more difficult for water

molecules trapped in small channels with a constant diameter. Another characteristic of the Si-CHA sample is the larger intruded volume which is close to 0.16 mL/g while for the silicalite-1 the latter was close to 0.11 mL/g. However, from these compressibility curves, the intruded volume is lower than the pore volume determined from nitrogen adsorption–desorption experiments (see Table 1). As it was shown by Desbiens et al.,^{11,12} for silicalite-1, the value of the intruded volume determined for a water density of 1 has to be corrected since the average computed water density in the MFI structure is around ≈ 0.6 g/mL. Taken also into account this correction for the Si-CHA sample, the intruded volume is thus totally consistent with the pore volume determined from nitrogen adsorption data, i.e., ≈ 0.3 mL/g.

It is worthy to note that a small but reproducible difference is observed in pressure and in volume between the first and the second cycle and curiously for the other cycles the intrusion curves on one side and the extrusion curves on the other side are completely superimposable. Depending on the Si-CHA samples the observed variation in volume between the first and the second cycle can reach 6%. This indicates that some water molecules after the first intrusion interact with the inorganic framework and do not expel when the pressure decreases. Such a peculiarity can be due to a structure effect (cage-like structure) or to the presence of nonhydrophobic zones in the porous network, for example the presence of Q3 defects (Si–(OSi)₃OH), even if, the first NMR experiments do not evidence the presence of such sites.

To conclude, this work shows that the water–Si-CHA system is a new system capable to accumulate and restore energy at a quite low pressure.

Investigations are still in progress to clearly understand the differences observed (volume variation, intrusion pressure) between the first and the second cycle.

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