Thermal Effects of Water Intrusion in Hydrophobic Nanoporous Materials

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The understanding of water intrusion in hydrophobic confined spaces has garnered increasing interest in the past decade. Early works in this field, exploring thermodynamic systems composed of hydrophobic porous materials and water as a nonwetting liquid, started in the middle 1990s on silica gels.[1,2] In later works, hydrophobic zeolitic materials were found to accumulate mechanical energy and either restore it completely and reversibly or not.[3,4] These properties of energy accumulation, restoration, or dissipation can be useful for energy storage applications such as molecular springs, dampers, shock absorbers, or actuators.[5] The knowledge of water properties in confined spaces also concerns biology when considering hydrophobic cavities of proteins and denaturation mechanisms by water under high pressure.[6,7]

Up to now, most results have been obtained for hydrophobic inorganic materials (silica gel, silicalite-1, zeolite β, ZSM-5, chabazite, MCM-41, SBA), either with an experimental approach to assess the intruded water volume along with the applied pressure[3,8−12] or by molecular simulation (Monte Carlo).[13−16] Four major points are worth noting:

1. Intruded water volume and intrusion pressure are closely related to physical stress (pore geometry, pore diameter)[9,17,18] and/ or chemical stress (presence of hydrophilic sites, such as silanol defects).[10,13]

2. The intruded water volume, appearing lower than the porous volume offered by the material, would have a lower density than the bulk liquid water.[19]

3. The phenomenon of intrusion and extrusion of water in hydrophobic porous materials can be reversible or irreversible. It leads to either molecular spring or to damper behaviors.[3,4] The origin of irreversibility would result from the creation of defects or the formation of a vapor phase by a mechanism of nucleation.[18,20]

4. Thermal effects involved in the intrusion mechanism are still poorly understood. Molecular simulations tend to show the existence of endothermic (silicalite-1) or exothermic (faujasite) effects, depending on the pore geometry of the material.[16] From an experimental point of view, calorimetric measurements using dynamical conditions (continuous pressure variation) proved the intrusion to be endothermic for silicalite and exothermic for mesoporous silica gel but did not quantify the intrusion heat.[8] Up to now, the lack of experimental data measuring heat exchange in the intrusion phenomenon does not allow validation of the background theory.

In this study, a specific high pressure calorimetric device, based on Setaram C80, has been designed to measure thermal effects involved in the intrusion phenomenon of liquid water in a hydrophobic nanoporous material. A purely siliceous zeolite, silicalite-1, prepared in fluoride media,[3,21] was selected to perform water intrusion (see left SEM picture in Figure 1).

The method used to obtain the corresponding thermal effect consists of applying a pressure increment or decrement, dp, on degassed liquid water in contact with zeolite material placed in a
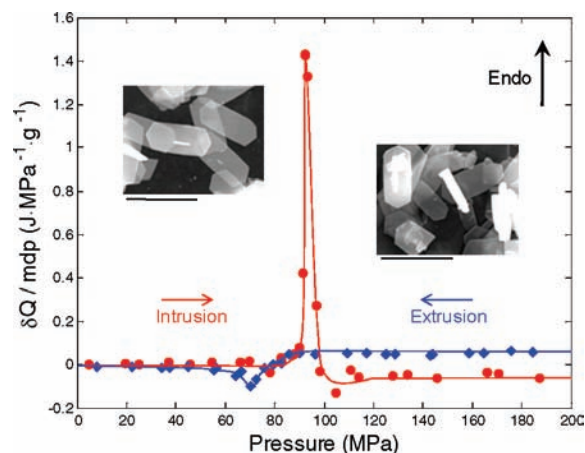

Figure 1. Thermal effects of water intrusion (red curve) and extrusion (blue curve) in silicalite-1. Also shown are two SEM pictures of silicalite crystals before (left) and after (right) the intrusion/extrusion cycle (black scale = 10 μm).

high pressure calorimetric cell, at 298 K. The reference calorimetric cell contains water maintained at atmospheric pressure. For each pressure step, the differential heat per gram of zeolite $\delta Q/m dp$ is calculated at equilibrium from the integration of the heat flow as a function of time after subtraction of the thermal effect of water compression around the zeolite.

Silicalite-1 samples were also characterized by Fourier transform infrared spectroscopy before and after water intrusion experiments. FTIR spectra were recorded at room temperature on a Bruker Equinox 55 spectrometer (200 scans averaged, 2 cm^{-1} resolution, background correction). Self-supported samples were used to perform in situ analysis under high vacuum after complete outgassing of the sample.[22]

The intrusion of liquid water into the hydrophobic nanopores of silicalite-1 produces a well-defined endothermic effect within the narrow 90−95 MPa range (Figure 1). These results confirm previous volumetric measurements which showed that water intrusion occurs in the same pressure range.[17] These measurements also agree with GCMC molecular simulations which predicted that water intrusion is endothermic.[16]

In addition, the interaction of liquid water with silicalite-1 appears to be a three-step process. First, below 90 MPa and until the intrusion pressure is reached, only compression of water around zeolite crystallites occurs. Then, intrusion of water into the nanopores gives rise to a high endothermic effect.

The intrusion heat $Q_{int} = \int (\delta Q/m dp)\, dp$ is calculated from the integration of the calorimetric curve in the pressure range where $\delta Q/m dp$ is positive. It is ~7.8 J per gram of zeolite. For 1 mol of water intruding into the microporosity, the enthalpy is equal to 1.3 kJ·mol^{-1}. This is quite low compared to the adsorption enthalpy of water vapor on silicalite-1 (~30 kJ·mol^{-1}), which is slightly
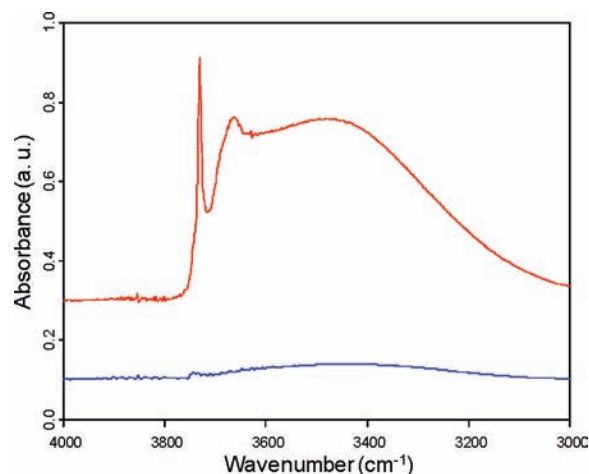
Figure 2. FTIR absorbance spectra in the wavenumber range 4000−3000 cm^{-1} of silicalite-1 before (blue) and after (red) water intrusion.

below the liquefaction enthalpy of water (44 kJ·mol^{-1}).[14,21] The last step, over 95 MPa, corresponds to the compression of water around the zeolite and inside the porosity. It may be noted, in Figure 1, that a low exothermicity persists even when the thermal effect due to the compression of bulk water and intruded water (assumed as a liquid) inside nanopores is subtracted. This means that the physical state of the intruded water phase in hydrophobic nanopores differs from that of the liquid bulk water surrounding zeolite crystallites. As suggested in other materials, it could exist as a vapor film separating water from the hydrophobic solid,[12] with strong orientation effects in the interfacial region of water molecule/nanopore internal surface.[23]

The extrusion process of liquid water from silicalite-1 nanopores does not follow the same pathway as that for intrusion (Figure 1). Extrusion occurs at a lower and broader pressure range and gives a small exothermic effect reduced 5-fold when compared to intrusion. Water intrusion clearly leads to an irreversible phenomenon. This is the first time this irreversibility between intrusion and extrusion is pointed out in silicalite-1, probably thanks to the very high sensitivity of equilibrium high pressure calorimetry compared to other techniques, such as "water porosimetry" experiments. Therefore, this hydrophobic zeolite could not be seen as an inert chemical system for which the intrusion/extrusion process only depends on pore size and pore geometry.[17]

What is the origin of this irreversibility? In the pressure range needed to force water intrusion in hydrophobic nanopores, the material is susceptible physically and/or chemically to modifications with increased pressure. On the one hand, the SEM pictures in Figure 1 show that silicalite-1 crystallites are not very damaged before and after an intrusion/extrusion cycle. On the other hand, the infrared spectroscopic investigation of silicalite-1 before and after an intrusion/extrusion cycle indicates material modification (Figure 2). The two spectra displayed in Figure 2 were obtained by in situ FTIR after outgassing and, therefore, after complete desorption of the physisorbed water. The initial material contains very few silanol defects as shown by the very small contributions of the Si−OH stretching vibrations in the wavenumber range 4000−3000 cm^{-1}. Water intrusion produces significant changes in the FTIR spectrum of the material: a sharp and intense band at

3731 cm^{-1}, a wider band at 3700−3650 cm^{-1}, and a very large band in the 3200−3650 cm^{-1} interval. The two first bands correspond to stretching modes of isolated or terminal OH groups, while the third band, at lower frequency, is attributed to stretching modes of hydrogen-bonded OH groups.[24] This leads to the conclusion that silicalite-1 becomes chemically modified during water intrusion in the nanoporosity. The creation of silanol defects consecutive to the breaking of siloxane bonds renders the material slightly hydrophilic and, thus, explains why the extrusion occurs at lower pressures than intrusion. Microscopic investigations are currently underway to further investigate these preliminary findings.

In summary, the investigation of liquid water intrusion in a hydrophobic silica by high pressure calorimetry allows a better understanding of this phenomenon. We have first quantified the thermal energy involved in the phase transition for silicalite-1. This thermal energy involved during the intrusion process does not correspond exclusively to the phase transition enthalpy from the bulk phase to the intruded phase but also includes the energy involved in the formation of silanol defects and the interaction of water with them. Moreover, we have demonstrated that the intruded water phase behaves differently than the liquid bulk. In any case, the experimental evidence for chemical modifications of the material during the intrusion process is of great importance from a fundamental viewpoint, as well as for the practical purposes of energy storage or dissipation.

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