Energetics: A New Field of Applications for Hydrophobic Zeolites

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The thermodynamic systems consisting of a liquid and a lyophobic porous matrix, that is a porous solid and a non wetting liquid, have the property to accumulate, transform, restore or dissipate energy.[1−3] By submitting these systems to an increasing hydrostatic pressure, the intrusion of the liquid into the pores of the solid is observed when the pressure P becomes equal to the capillary pressure P_L[1] which can be expressed by the Laplace−Washburn relation

$$P_{\mathrm{L}} = (2\sigma/\mathrm{r})|\cos\theta| \qquad (1)$$

where σ is the surface tension, r the radius of the pores, and θ the contact angle between the liquid and the solid ($\theta \gg 90°$).

During the intrusion of a nonwetting liquid into a porous material, a large interface Ω carrying the surface free energy is created. The development of this surface ($\Delta\Omega > 0$), leads to an increase in the Gibbs energy ($\Delta G > 0$) which may be written as

$$\Delta G = \sigma\,|\cos\theta|\Delta\Omega \qquad (2)$$

To minimize this energy ($\Delta G < 0$), the system spontaneously evolves and decreases its interface ($\Delta\Omega < 0$) by extrusion of the liquid out of the cavities of the solid. Depending on the external pressure, the molecules of the liquid can penetrate or are expelled from the cavities.[2,4] Therefore, there is a reciprocal transformation of mechanical energy into interfacial energy. When the stress is suppressed, the compressed heterogeneous system spontaneously expands as a result of the extrusion of the liquid and then constitutes a real molecular spring. This property could be used in engineering for devices where short-range molecular forces occur to induce important efforts and large displacements[3−5] such as the spreading of solar panels of satellites.

The originality of the present thermodynamic study results in the choice of the constituents of the heterogeneous systems. Water is well suited as the mobile phase; it is a polar liquid, not polluting, easy to obtain as a pure phase, not expensive, and characterized by a high surface tension. The very small water molecules, which are comparable to small spheres of 2.8 Å of diameter, are able to access very small micropores. The choice of water imposes the solid phase to be a hydrophobic porous material. Crystallized microporous solids such as zeolites should be good candidates. These materials show a large variety of structures with variable chemical compositions and are characterized by the presence of micropores with very well defined shape and size. During its intrusion in the zeolitic channels, liquid water disperses as clusters, constituted by few water molecules. Two types of attractive interactions can be involved: (i) the dispersion forces between the water molecules and the pore walls, (ii) the interactions between the water molecules themselves. In the case of these hydrophobic solids, the apparent repulsive interaction between the pore walls and water clusters is probably due to the fact that the latter interaction is stronger than the former.

In the present work, the behavior of several "water−zeolite" systems was studied. In particular those including purely siliceous zeolites (zeosils), which present a strong hydrophobic character, for instance zeolite β (F^-) of the BEA type,[6] silicalite-1 (OH^-) and silicalite-1 (F^-) of the MFI type.[6] For comparison, a more hydrophilic commercial sample, Na-ZSM-5, (ALSI-PENTA SN-27) of the MFI type was also studied. The first three samples were synthesized and characterized in our laboratory. The zeolite β sample was prepared according to the procedure described by Camblor et al.[7] in the presence of tetraethylammonium cations and fluoride anions. Silicalite-1 (OH^-) and silicalite-1 (F^-) were prepared in hydroxide (OH^-)[8] and fluoride (F^-)[9] media, respectively, and in the presence of tetrapropylammonium cations as templating agents. The as-made samples contain the organic molecules in their channel systems. To obtain a porous solid, these molecules are eliminated by calcination at 550 °C under air. The samples were characterized by various techniques (chemical analysis, scanning electron microscopy, XRD analysis, N_2 adsorption−desorption isotherms, high-resolution solid-state NMR spectroscopy). It should be stressed here that the ^{29}Si MAS NMR spectrum of the silicalite-1 (F^-) sample displays a very high resolution and the absence of signals corresponding to silanol groups indicates that this sample is highly hydrophobic. Although the amount of adsorbed water in silicalite-1 (OH^-) is lower than 1.5%, the low resolution of the ^{29}Si MAS NMR spectrum indicates a less hydrophobic character compared to the previous sample.

For the compressibility measurements, the "water-zeolite" systems were contained in a cell of variable volume (1.20 cm^3 under atmospheric pressure), which was immersed in an oil-containing vessel able to support very high hydrostatic pressures. The volume variations were determined at constant temperature by increasing the pressure progressively, as described in ref 10. The compression−expansion isotherms at 20 °C, are given in Figure 1. They represent the volume variation expressed in cm^3 per gram of zeolite versus the pressure in MPa. The first three systems concern the highly hydrophobic purely siliceous zeolites, that is zeolite β (F^-) (curve 1), silicalite-1 (OH^-) (curve 2), and silicalite-1 (F^-) (curve 3); the last curve (curve 4) corresponds to the ZSM-5 sample. The corresponding experimental data are reported in Table 1.

Curves 1, 2, and 3 present a linear part, corresponding to the compressibility of the bulk phase (water + zeolite). When the capillary pressure is reached, water molecules penetrate into the pores of the solids (eq 1). The intrusion isotherm, which is

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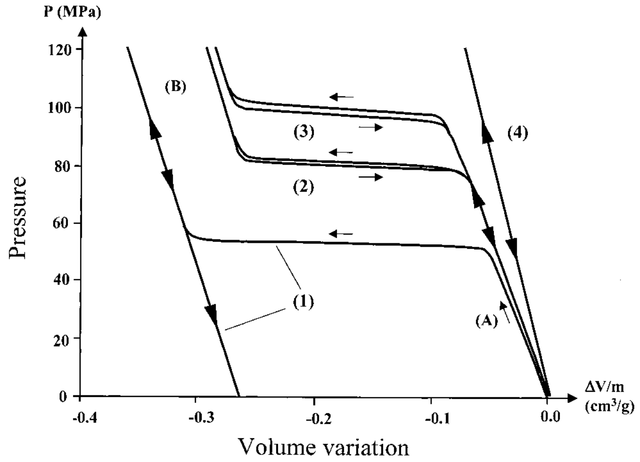

Figure 1. Pressure−volume isotherm of the various "water−hydrophobic zeolite" systems. (1) "water−zeolite β (F^-)" system. (2) "water−silicalite-1 (OH^-)" system. (3) "water−silicalite-1 (F^-)" system. (4) "water−Na−ZSM-5" system. (A) Step before intrusion. (B) Step after intrusion.

Table 1: Characteristics of the Various Systems

parameters	zeolite β (F^-)	silicalite-1 (OH^-)	silicalite-1 (F^-)	Na−ZSM-5
sample mass (g)	0.185	0.070	0.146	0.132
sample volume (cm^3)	0.119	0.039	0.082	0.067
density (g/cm^3)	1.557	1.790	1.790	1.77
total porosity (cm^3/cm3)	0.48	0.37	0.37	0.22
intrusion pressure (MPa)	56.7	81.2	99.3	−
extrusion pressure (MPa)	−	80.2	96.5	−
measured porous volume (cm^3/g)	0.255	0.186	0.183	−
theoretical porous volume (cm^3/g)[a]	0.308	0.207	0.207	0.111

[a] From the crystal structure.

characterized by a plateau at the pressure P_i, leads to the formation of a large interface Ω, with an increase of ΔG according to eq 2. After a complete filling of the pores, a classical compression step takes place.

During the pressure release, the phenomenon is completely reversible for the "water−silicalite-1" systems (curves 2 and 3). The extrusion of water (spontaneous reduction of the interface) occurs at a pressure P_e, almost identical to P_i. The reversible phenomenon, essentially without any hysteresis, was confirmed on several cycles, showing the reproducibility of the isotherm. These two systems "water−silicalite-1 (OH^-)" and "water−silicalite-1 (F^-)", which are able to reversibly accumulate and restore surface energy, constitute real molecular springs.

The behavior is different for the zeolite β sample (curve 1): the volume varies linearly with pressure, and no plateau is observed during the pressure release. In this case, the phenomenon is not reversible; the system absorbs mechanical energy and acts as a bumper.

The last system, based on the more hydrophilic ZSM-5 sample, displays a linear isotherm, without any plateau, which can be assigned to an elastic behavior. As this hydrophilic sample already contains about 10 wt % of water, the matrix can accept only a small amount of additional water in its porosity, which is quickly adsorbed at the beginning of the compression.

According to the Laplace−Washburn law, for curves 1, 2, and 3, the value of the pressure where a plateau is observed depends on the size r of the zeolitic channels, the wetting character (contact angle θ) and the surface tension of the liquid σ. In the case of silicalite-1 (F^-), the most hydrophobic sample, with the hypothesis that $|\cos \theta|$ is close to 1, the application of eq 1 leads to a value of the surface tension σ equal to 1.39×10^{-2} N/m. This value, which is 5 times less than the one of bulk water ($\sigma = 7.27 \times 10^{-2}$ N/m[11]), might be attributed to water clusters. Indeed, at the nanometric scale, the usual surface tension concept is questionable and we may assume that it is proportional to the number of bonds to be broken around one molecule and would depend on its coordination number. The introduction of this new value of σ in eq 1, leads to contact angles θ equal to 145° and 137° for the silicalite-1 (OH^-) and zeolite β samples, respectively. This result confirms a lower hydrophobicity degree for these two samples.

The structure of zeolite β, consists of several distinct polytypes,[12] and in this case the non reversibility of the phenomenon could be due to the presence of silanol defects at the interface of the polytypes. It may be assumed that these defects are really accessible to water molecules only after the first intrusion at the end of the compression step. During the pressure release, the occluded water molecules which are in strong interaction with the silanol groups would not be expelled. After the compressibility tests, the analysis of this sample indicated that there was no loss of crystallinity and no formation of mesopores. However, the low resolution of the ^{29}Si MAS NMR signal corresponding to the Q4 groups ($Si(OSi)_4$) might be due to the presence of residual adsorbed water.

The length of the plateau ($\Delta V/m$) observed for curves 1, 2, and 3 represents the porous volume really filled by the water clusters. The experimental values (Table 1) are in good agreement with the theoretical ones; they are systematically lower by 10−15%. The small slopes observed for the plateau might be due to the slight differences between the pore sizes of the two types of channels present in these zeolitic structures. Moreover, before the intrusion of water, the high hydrostatic pressures lead to a distortion of the zeolitic framework and to a slight reduction of the available porous volume. After the filling of the pores, the pressures inside and outside the solid matrix being identical, there is no effect on the pore walls, and the structure relaxes. The small pressure difference $P_i - P_e$ for the intrusion and the extrusion of water partially reveals the deformation of the inorganic framework when the latter is submitted to high pressures. It is worth noting that for the first three systems, the slopes of the isotherms ($\Delta[\Delta V/m]/\Delta P$) before (A) and after (B) the intrusion are different. The slope of the first step (A), which is higher than for the second one (B) corresponds to the compressibility of the whole system (water + empty zeolitic matrix) and after the intrusion, the smaller slope of the final step (B), similar to that of curve 4, is only due to the water compressibility.

As a conclusion, the present novel results confirm the possibility to accumulate, restore, and dissipate mechanical energy by means of the development of an interface and open new application perspectives in the field of energetics for very hydrophobic zeolites in contact with water.

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