Cation-Dependent Compression Behavior in Low-Silica Zeolite-X

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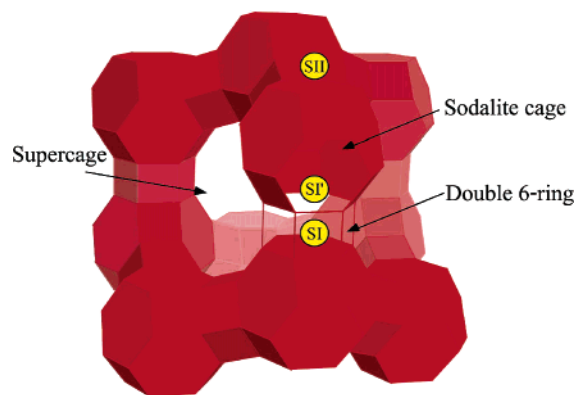
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Recent studies in the high-pressure behaviors of zeolites uncovered many unusual chemical and structural changes that occur inside the zeolitic nanopores and channels as well as in the flexible framework and created interests to explore new high-pressure chemistry of the zeolitic host−guest systems. Among these is the reversible and irreversible pressure-induced hydration (PIH) in zeolites with the NAT topology, which demonstrated how hydrostatic pressure, mediated by a fluid mixture containing water as pore-penetrating pressure medium, can be used to control the zeolitic water content and to assemble unique water structures within the confinement of the zeolitic framework.[1−3] The PIH in natrolite occurs in two distinct steps; formation of alternating single and double water bridging via 50% overhydration accompanying ∼7% volume expansion near 1.0 GPa,[1] followed by the completion of helical water wires in 4_1 symmetry along the narrow elliptical eight-ring channels upon 100% overhydration above 1.2 GPa.[2] The observed PIH and accompanying volume anomalies are induced by cooperative changes in the opening geometry of the helical eight-ring channel, which seems to be the operating mechanism of PIH for this class of small-pore zeolites. To provide further insights into the nature of PIH, in situ observation of the PIH processes in a more open-pore system, if it occurs, would be necessary.

An important clue on how the host−guest interaction would occur under pressure and affect the materials' compressibility has been shown early in a large-pore zeolite 4A,[4,5] and more recently, in silicious faujasite.[6] The latter possesses larger interconnecting supercages defined by circular 12-ring windows (Figure 1). Instead of the stepwise filling of water molecules to form distinct confined water assemblages, as observed in natrolite, PIH in silicious faujasite proceeded with gradual filling of water molecules up to 4 GPa, followed by an increase in compressibility as the major operating mode changes from PIH to framework distortion. There was also an indication that the compressibility of silicious faujasite is affected by the introduction of aluminum in the framework and thereby the presence of nonframework species.[6] The effect of nonframework composition on the PIH behavior and accompanying compressibility anomaly, on the other hand, has remained unknown. We report here that the apparent compressibility and the pore-filling pattern in a large-pore zeolite can be tuned via the combination of nonframework cation and pressure medium to show a range of volume contraction behaviors.

To maximize the effect of nonframework cation distribution, Na-, and K-forms of low-silica faujasite (LSX) with Si/Al = 1 was chosen for the present hydrostatic compression studies. This system is particularly effective as it exhibits two different volume status, that is, unit cell volume expansion, depending on the level of Na−K exchange.[7] Samples which represent Na- and K-endmembers in

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Figure 1. Polyhedral representation of the faujasite framework. Nodes represent the centers of Si/Al-tetrahedra and straight line sections represent the T−O−T linkage (T = Si/Al). Cation sites are located in the middle of the double six-ring (SI) and close to the six-rings both in the sodalite cage (SI′) and in the supercage (SII). Supercage sites are omitted for clarity.

LSX solid-solution series were prepared from the as-synthesized LSX (NaK−LSX, $Na_{74}K_{22}Al_{96}Si_{96}O_{384} \cdot nH_2O$) following the standard ion exchange procedures outlined by Sherry.[8] Direct current plasma and ICP chemical analysis for potassium and sodium content showed that pure Na and pure K forms of LSX were prepared. These samples were denoted Na−LSX and K−LSX, respectively. Each hydrated, ion-exchanged sample was equilibrated at ambient temperature prior to the hydrostatic compression experiment. High-pressure synchrotron X-ray powder diffraction measurements were performed using a Merrill-Bassett diamond-anvil cell and an imaging plate detector at the 5A-HFMS beamline at Pohang Accelerator Laboratory (PAL). Each powder sample was loaded into a 250 μm diameter/150 μm thick sample chamber in a pre-indented stainless steel gasket, along with a few small ruby chips as a pressure gauge. A mixture of 16:3:1 by volume of methanol/ethanol/water was used as a pore-penetrating hydrostatic pressure transmitting fluid (hydrostatic up to ∼10 GPa). The pressure at the sample was measured by detecting the shift in the R1 emission line of the included ruby chips. The sample pressure was gradually increased up to 7 GPa. The sample was equilibrated for about 10 min at each measured pressure. An 18 keV synchrotron X-ray beam of 200 μm in diameter was provided by a sagitally focusing monochromator and vertically focusing mirrors. Each diffraction pattern was measured for 1 min on a MAR345 imaging plate, and the data were processed using the Fit2d suite of programs.[9] The measurements were repeated using similar procedures, but silicon oil as pressure medium was used at beamline X7A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). The unit cell volume at each measured pressure was derived from full profile fitting methods using the GSAS suite of programs.[10]
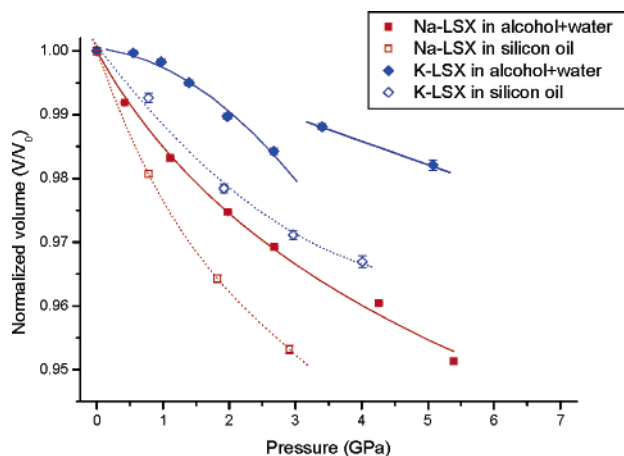
Figure 2. Normalized volume of NaK−LSX zeolites as a function of hydrostatic pressure mediated by alcohol and water mixture (filled symbols) and silicon oil (open symbols). Straight and dotted lines are guides to the eyes.

The observed compressibility of each sample is expressed as a normalized volume plot as a function of pressure in Figure 2. The pure sodium form of LSX, Na−LSX, compressed in alcohol and water mixture, exhibits continuous volume contraction upon pressure increase up to 5 GPa. Unlike the compression behavior observed for Na−X,[6] the decrease in the slope near 2 GPa is only marginally noticeable in Na−LSX. This has been attributed as changes in the guest structure upon pressure-induced hydration, making less compressible material at higher pressures. On the basis of the understanding of the sodium−water distribution in Na−LSX at ambient conditions,[7] one can infer that the sodium cations in the sodalite cage (SI′) would migrate into the empty double six-ring (D6R) site (SI) as more water molecules fill the sodalite cages upon PIH (Figure 1). This would then progressively reduce the framework's compressibility as more Na cations can act as structural buttress for the D6R building unit, which has the most effect on the framework's contraction or expansion. In fact, volume expansion is observed when larger potassium cations replace smaller sodium cations at the D6R site.[7] Overall, the observed compressibility of Na−LSX appears to be "normal" with continuous contraction behavior to give rise to an apparent bulk modulus of 53(4) GPa with a large positive value of pressure derivative, $B' = 28(4)$, owing to the decreasing compressibility at higher pressures.

Fully K-exchanged sample, K−LSX, when compressed in the same alcohol and water mixture, exhibits quite different compression behavior compared to that of Na−LSX (Figure 2). The observed volume contraction of K−LSX accelerates gradually up to ca. 3 GPa, signaling a negative sign of the pressure derivative or an "inverse" mode of compressibility. Above 3 GPa, volume expansion occurs by ca. 1%, and the expanded phase appears to have larger bulk modulus than the original phase before the expansion. Compared to Na−LSX, K−LSX is, in general, less compressible in alcohol and water medium. This can be understood by the different distribution of nonframework species between these two endmembers. In K−LSX, most of the D6R sites are filled by the larger potassium cation whereas the sodalite cages are exclusively filled by water molecules at ambient conditions.[7] As mentioned above, this leads to framework expansion from the

phases containing sodium cations at the D6R sites. The D6R buttressed by larger potassium cations may well be expected to exert more resistance to the applied framework compression than that by smaller sodium cations. With the sodalite cages already filled by water molecules at ambient conditions, it is also likely that PIH in K−LSX would occur mainly in the supercages via the larger 12-ring entrance in the initial stage of hydrostatic compression. It is, however, counterintuitive to observe that PIH in the supercage would lead to progressive "softening" or an "inverse" mode of compressibility below 3 GPa. The volume expansion observed above 3 GPa indicates a possible formation of a new guest assemblage inside the supercage confinement. Rietveld analyses would be needed to understand the observed anomalous compressibility with the evolution of the host−guest structures.

When silicon oil is used as a nominally nonpenetrating pressure transmitting medium, K−LSX does not exhibit anomalous volume contraction or pressure-induced expansion (Figure 2). Instead, the unit cell volume contracts monotonously to fit a bulk modulus of 72(13) GPa and $B' = 25(11)$, approaching that of Na−LSX in alcohol and water mixture. The compressibility of Na−LSX also becomes enhanced under compression in silicon oil giving rise to a bulk modulus of 30(1) GPa and B' of 26(1) (Figure 2). These values would represent more intrinsic material's compression behaviors, and, as observed in alcohol and water medium, the framework of K−LSX exerts greater resistance in nonpenetrating medium, with the D6Rs buttressed by larger potassium cations.

The pressure response in a large pore zeolite such as LSX appears to be a complex phenomenon involving interplay between selective overhydration and cation relocation as well as framework distortion. We have shown here that the apparent compressibility of LSX can be tuned via cation exchange and (or) the choice of pressure medium. As for the temperature effect, high-pressure chemistry in zeolite is rich and needs to be explored further.

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