Phase Transition of Zeolite RHO at High-Pressure

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Pressure is an under-explored variable in the crystal chemistry of microporous materials. Depending on the pressure-generating conditions and the size of the pore-opening of the material, pressure can be used as a probe to vary the volume in a constant chemistry[1,2] or as a function of the size of pressure-transmitting medium.[3,4] To the best of our knowledge, pressure has not yet been applied in the investigation of the influence of extra-framework cations on the flexibility of the molecular sieve frameworks.

The flexibility of zeolites has long been known from dehydration and other studies carried out at high temperature.[5,6] An understanding of how these changes occur is important since it is the regular spacing of pores and channels of molecular dimensions in these materials that is responsible for their molecular and ion selectivity. Zeolite RHO is among the most flexible of microporous materials with variable cation distributions, depending on the sample conditions. The simple cubic structure of RHO, as well as the well-known correlation between its cell length and framework distortion parameter,[7] facilitates studying the systematics of unit cell symmetry versus hydration, exchangeable cation and cell volume under various nonambient conditions. We have previously reported that the negative thermal expansion and "trap door" cation relocations observed in zeolite RHO result from changes in site-specific interaction between extra-framework cations and water molecules.[8] No experimental observations were reported on the polyhedral tilt transition of this type of material at high pressure.[9]

We recently measured the compressibility of RHO as a function of the ions occupying the channel system up to 3.0 GPa using a diamond-anvil cell and a 200 μm-focused monochromatic synchrotron X-ray beam.[10] Upon pressure increase, each centric form of RHO ($Im\bar{3}m$) shows different interaction with an alcohol-based pressure medium and results in relaxation or contraction of the unit cell volume. In all cases, an acentric form of RHO ($I\bar{4}3m$) starts to form in the pressure range between 0.2 and 0.5 GPa. The compressibility of the acentric structure is closely related to the initial cation distribution in each sample. The back transition kinetics seems to be driven by resorption or rehydration, which is in turn dependent upon the difference in the pore geometry of the high-pressure A-form.

The evolutions of the unit cell parameters of NaCs-, Cd-, and Li-forms of zeolite RHO are plotted as a function of pressure (Figure 1). The pressure-induced phase transformations from large-volume centric to small-volume acentric structures appear to be analogous to those driven by dehydration[8] and occur irrespective of the initial extra-framework cation distribution in these materials; the Cs and Cd occupy a larger double 8-ring (D8R) site and a single 8-ring site in the structure, respectively, which blocks access to the interior of the zeolite, whereas the Li occupies a single 6-ring (S6R) site away from the entry to the D8R opening to the channel system.

In the case of the NaCs-RHO, the volume of the initial centric phase expands slightly upon pressure increase, although the effect is only marginally within the cell parameter errors, probably due to the exchange of alcohol-bearing pressure media with water molecules inside the pores. This, along with the increase in the proportion of the contracted A-phase, will result in the decrease of the overall volume of the system.

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(10) Experiments were performed using a Diamond Anvil Cell (DAC) at the X7A beamline of the National Synchrotron Light Source (NSLS) of the Brookhaven National Laboratory (BNL). The primary white beam from the bending magnet is focused in the horizontal plane by a triangular, asymmetrically cut Si (220) monochromator bent to cylindrical curvature by applying a load to the crystal tip, affording monochromatic radiation of ~0.7 Å, see Lemmonier et al.[11] A tungsten wire crosshair was positioned to the center of the goniometer circle and then the position of the incident beam was adjusted to the crosshair. A pinhole collimator was used to reduce the beam size to ~200 μm. A gas-proportional position−sensitive detector was stepped in 0.25° intervals over the desired angular range of 3−18° with step counting times of 90−150 s. The wavelength of the incident beam (0.686 Å), PSD zero channel and PSD degrees/channel were determined from a CeO_2 standard (SRM 674). Powdered samples of NaCs-RHO (ICP: $Na_{8.2}Cs_{5.1}Al_{11.5}Si_{36.5}O_{96}\cdot wH_2O$), Cd-RHO (ICP: $Cd_{5.5}Cs_{0.3}Al_{11.7}Si_{36.3}O_{96}\cdot wH_2O$) and Li-RHO (ICP: $Li_{7.6}Na_{1.9}Cs_{1.3}$-$Si_{36.6}Al_{11.4}O_{96}\cdot wH_2O$) were, in turn, loaded into the DAC at ambient pressure and room temperature along with a few small ruby chips. The DAC is based on a modified Merrill−Bassett design[12] and employs two diamonds with 0.5 mm diameter culets on tungsten-carbide supports. The X−rays are admitted by a 0.5 mm diameter circular aperture, and the exit beam leaves via a 0.5 mm × 3.0 mm rectangular tapered slit, oriented perpendicular to the horizontal plane of the diffractometer. The sample chamber is provided by a 200 or 350 μm hole formed in the center of a 300 μm thick Inconel gasket, pre-indented to 100 μm thickness before drilling. A mixture of 16:3:1 by volume of methanol:ethanol:water was used as a pressure transmission medium; this is known to remain hydrostatic to ~10 GPa.[13] The pressure at the sample was measured by detecting the shift in the R1 emission line of the included ruby chips.[14] The DAC was placed at the second axis of the diffractometer, and the sample position was adjusted using the pre-centered microscope. The diffraction peaks were modeled by varying only a half-width parameter in the pseudo-Voigt profile function. Unit cell parameters were determined by least-squares fitting of the LeBail extracted reflection positions. Bulk moduli were calculated by fitting Murnaghan Equation of States to normalised volumes.

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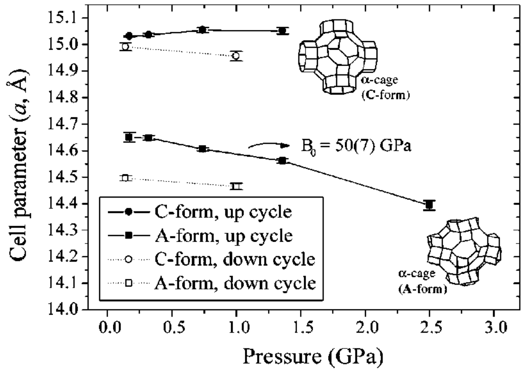
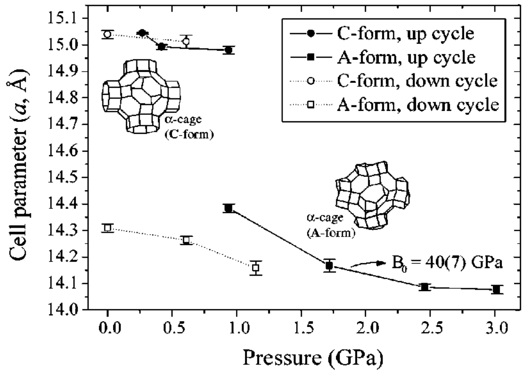
(a) NaCs-rho



(b) Cd-rho



(c) Li-rho

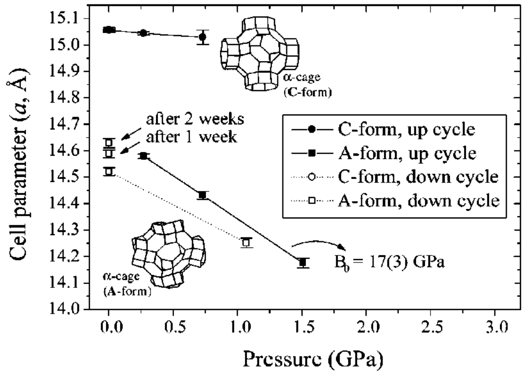


Figure 1. Changes in cubic cell constant (*a*, Å) of (a) NaCs-RHO (b) Cd-RHO, and (c) Li-RHO as a function of pressure. Esd's are multiplied by 3 at each point. Schematic diagrams illustrate the α-cages in the C- and A-structures. Extra-framework cations are not shown.

While the interpretation of the pressure response of low-pressure C-form is complicated due to the interaction between cations and different sorbates inside the pores, the observed compressibility of high-pressure A-form is commensurate with initial extra-framework cation distribution in each sample. Having most cations at the S6R site at ambient conditions, Li-RHO appears to be more compressible at high-pressure than NaCs- and Cd-RHO, which may well retain their initial cation distribution around the D8R building unit at elevated pressure, resisting the collapse of the framework (Figure 1).

It is also interesting to note that the A-form is consistently more compressible than the C-form. This suggests less internal pressure of the α-cage in the A-structure, caused by desorption or dehydration during the phase transition.

The cubic lattice constant of the acentric phase is characterized by the presence of hysteresis upon pressure release. In the case of Li-RHO, the transition back to the centric structure on pressure release is sluggish and occurs over a period of weeks (Figure 2), whereas NaCs-RHO and Cd-RHO show only a centric and a mixture of centric and acentric phases immediately upon removal of the applied pressure, respectively.

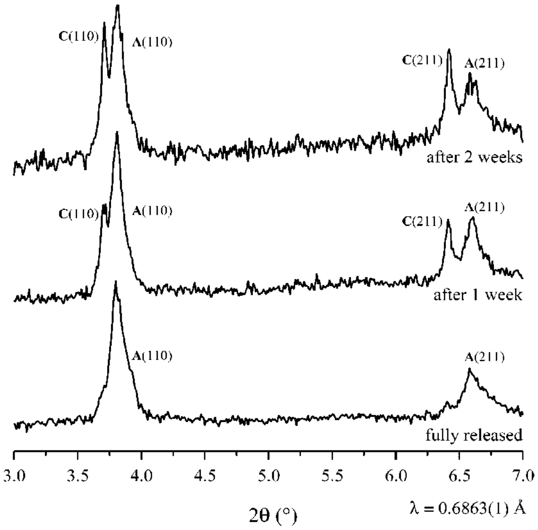


Figure 2. Changes in powder diffraction patterns of Li-RHO as a function of time after pressure release. Intensities are in relative scale.

It could be envisaged that the back-transformation into the large-volume C-form upon pressure release is a diffusion-controlled mechanism. Here the geometry of the pore-opening (elliptical 8-ring window) plays an important role in resorption or rehydration and back-transition kinetics. The observed data indicate the fastest resorption or rehydration in NaCs-RHO and the slowest in Li-RHO. This is in line with the degree of the distortion parameter of the cage opening in each acentric structure. The ellipticity of the 8-ring opening (Δ), which can be extrapolated from its relationship with unit cell length,[7,8] increases in the order of NaCs-RHO ($\Delta = 1.67$), Cd-RHO ($\Delta = 2.14$) and Li-RHO ($\Delta = 2.20$) at 1.5 GPa.

The peak half-width of the A-phase is consistently larger than its C-counterpart (Figure 2). This is another indication of the phase transition being driven by sorption/desorption processes. The difference in the internal and external pressure of the cages in the A-form, presumably caused by desorption or dehydration, will generate deviatoric stress and peak-broadening, which is then released on resorption or rehydration and transition back to the large-volume C-form.

Despite the evidence of structural changes in RHO as a function of pressure, details of cation-specific pressure responses and sorption mechanisms, which are crucial to understanding the structure−property relationship in this type of framework materials, are not yet clear. To clear these ambiguities, high-intensity neutron diffraction data will be collected for Rietveld structure analyses.

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