Understanding negative thermal expansion and ‘trap door’ cation relocations in zeolite rho

Barbara A. Reisner,†[a] Yongjae Lee,[b] Jonathan C. Hanson,[c] Glover A. Jones,[d] John B. Parise,*[be] David R. Corbin,[d] Brian H. Toby,[a] Andrea Freitag,[c] John Z. Larese[c] and Volker Kahlenberg[bf]

[a] *NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-8562, USA. E-mail: John.Parise@sunysb.edu*
[b] *Geosciences and [e] Chemistry Departments, State University of New York, Stony Brook, NY 11794-2100, USA*
[c] *Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973-5000, USA*
[d] *Central Research and Development, Du Pont Company, Experimental Station, P.O.Box 80262, Wilmington DE 19880-0262, USA*
[f] *Fachbereich Geowissenschaften (Kristallographie), Universität Bremen, Klagenfurter Strasse, D-28359 Bremen, Germany*

Received (in Irvine, CA, USA) 18th August 2000, Accepted 3rd October 2000
First published as an Advance Article on the web 31st October 2000

***In situ* time-resolved synchrotron X-ray and neutron powder diffraction studies indicate that the negative thermal expansion and ‘trap door’ cation relocations observed in zeolite rho result from water-mediated chemical changes that occur during dehydration.**

Zeolite rho exhibits exceptional flexibility, and its structure is particularly sensitive to cation identity, temperature, and hydration.[1] For example, Sr^{2+}-exchanged zeolite rho (Sr-rho) shows a large negative thermal expansion.[2] A more dramatic effect has been observed in Cd-rho, where Cd^{2+} cations relocate upon heating in a ‘trap door’ mechanism opening the access to the pores of RHO.[3,4] Both transformations have been previously attributed to temperature-driven phase transitions. To better understand the origin of these structural changes, time-resolved *in situ* synchrotron X-ray powder diffraction and neutron powder diffraction were performed using Pb-rho and Cd-rho. We found that both phenomena result from chemical changes that occur during dehydration rather than being a result of composition-independent, purely temperature-driven effects.

The RHO topology is composed of a body-centered cubic arrangement of truncated cuboctahedra or α-cages linked *via* double 8-rings of corner-connected tetrahedra. Three sites with unique coordination environments can accommodate charge-balancing, extra-framework cations: the single 8-ring (S8R), double 8-ring (D8R) and single 6-ring (S6R) sites. Each site has a distinct coordination environment, and cations preferentially occupy one of these sites depending upon their ionic radii. The framework can adopt a centric (C-form, $Im\bar{3}m$) or acentric (A-form, $I\bar{4}3m$) structure depending upon the unit cell composition and the temperature.[5,6]

Na,Cs-rho, the parent material used for cation-exchange, was prepared using a modification of the method described by Robson.[7] Pb-rho and Cd-rho were then prepared using standard ion-exchange techniques.‡ Time-resolved X-ray powder diffraction data were collected on the X7B beamline at the National Synchrotron Light Source (NSLS) using an *in situ* dehydration cell with an imaging plate detector.§[8] Neutron powder diffraction data were collected on the BT-1 powder diffractometer at the National Institute of Standards and Technology (NIST) Center for Neutron Research. Rietveld structure refinements[9] were performed with the GSAS package.[10]

Upon heating Pb-rho in the *in situ* synchrotron X-ray diffraction experiment, two distinct regions of cell contraction are observed (Fig. 1): a rapid decrease in cell length between 25 and 75 °C, and a second, more gradual decrease up to a temperature of approximately 500 °C. Rietveld refinements using these data indicate that the abrupt cell contraction is related to a conversion from the centric to the acentric form and that the gradual decrease in the unit cell length is coupled with a migration of Pb^{2+} from the S8R to the D8R site. Neutron powder diffraction studies were performed on partially deuterated Pb-rho.¶ Data were collected at room temperature on the sample dehydrated under vacuum at 250 °C. This sample was then heated to 550 °C under active vacuum ($< 10^{-4}$ Pa), and additional data were collected at this temperature and, after cooling *in vacuo*, at room temperature. Difference Fourier analysis of the neutron powder diffraction data collected on the sample dehydrated at 250 °C reveals the presence of D_2O at the D8R site and Pb^{2+} at the S8R site. In contrast, no D_2O is found when the sample is heated to 550 °C, nor when this sample is cooled to room temperature; in these models, Pb^{2+} ions are located at the D8R site, consistent with the changes in the Pb^{2+} occupancy observed from the *in situ* synchrotron X-ray powder diffraction data. The small difference between cell constants in these two samples is consistent with normal thermal expansion ($\approx 0.2\%$).

These results indicate that Pb-rho is not completely dehydrated under the gentle heating conditions that are typically used for dehydration, $200\ °C \leqslant T \leqslant 300\ °C$. Both regions of unit cell contraction are attributable to the loss of water. The first region corresponds to the loss of unbound water, while contraction in the second region can be attributed to the loss of water coordinated to Pb^{2+}. Up to a temperature of approx-

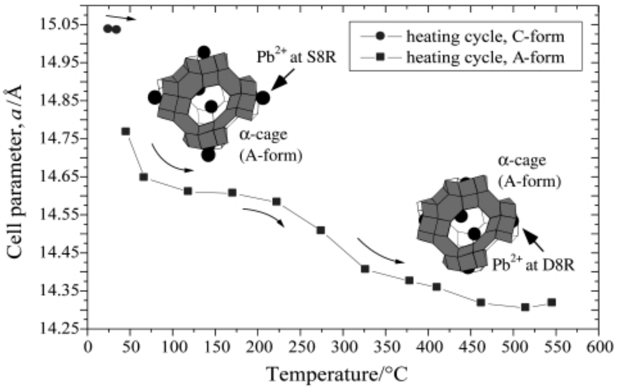

Fig. 1 The cell parameter of Pb-rho heated under air. Schematic diagrams illustrate the α-cages of the C- and A-forms and the siting of Pb^{2+}. (Vertices represent tetrahedrally coordinated Al or Si. Oxygen atoms are omitted for clarity).

---

† *Current address*: Department of Chemistry, James Madison University, Harrisonburg, VA 22807.

DOI: 10.1039/b006929i

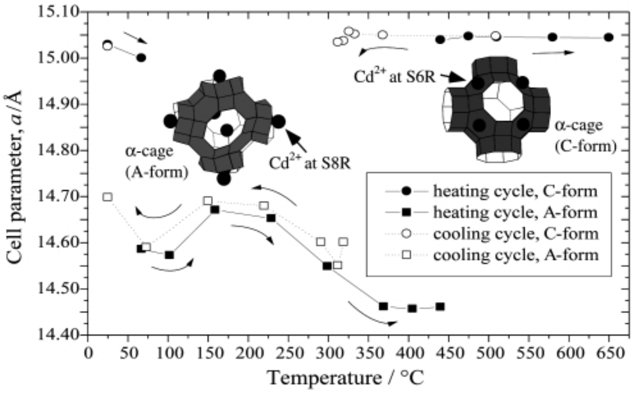

Fig. 2 The cell parameter of Cd-rho heated under air. Schematic diagrams illustrate the siting of Cd^{2+} in the α-cages.

imately 450 °C, both the cell parameter and the composition of the sample are still changing. It is likely that the presence of water strongly correlates with the siting of Pb^{2+} since they change in a concerted manner as a function of temperature. As water leaves the framework, Pb^{2+} must shift towards the D8R site, which provides a better coordination environment for Pb^{2+} in the absence of water. These observations may clarify the observation of the large negative thermal expansion observed for Sr-rho.[2] Since the large-volume, low-temperature phase was collected *in vacuo* at 100 °C and the small-volume, high-temperature phase was collected after heating at 200 °C, it is likely that dehydration was incomplete in the low-temperature phase and the observed negative thermal expansion can be attributed to dehydration.

In situ synchrotron X-ray powder diffraction data indicate that water plays an important role in the greater than 5 Å 'trap door' motion of Cd^{2+} in Cd-rho.[3] Upon heating in either air (Fig. 2) or vacuum (Fig. 3), there is an initial decrease in cell parameter from 25 to 75 °C due to the loss of unbound water, a more gradual change in cell parameter between 75 and 450 °C, then a large increase in the cell parameter which is accompanied by a change from the acentric to centric structure and a relocation of Cd^{2+} from the S8R site to the S6R site. There is a marked difference in the behavior of Cd-rho when cooling under ambient atmosphere (Fig. 2) and vacuum (Fig. 3). With the exception of a small temperature hysteresis, the reaction pathway is directly reversed upon cooling under ambient atmosphere. In contrast, these changes *do not occur* upon cooling under vacuum. These observations indicate that water plays a role in the relocation from the S6R back to the S8R. It is also likely that water acts as a transport agent in the original cation relocation from the S8R to the S6R site; the cell parameter of Cd-rho at 450 °C (14.45 Å) is larger than that of Pb-rho (14.35 Å) although the cationic radius of Cd^{2+} (1.09 Å) is smaller than that of Pb^{2+} (1.33 Å). *In situ* neutron diffraction studies are planned to determine the siting of D_2O at intermediate temperatures.

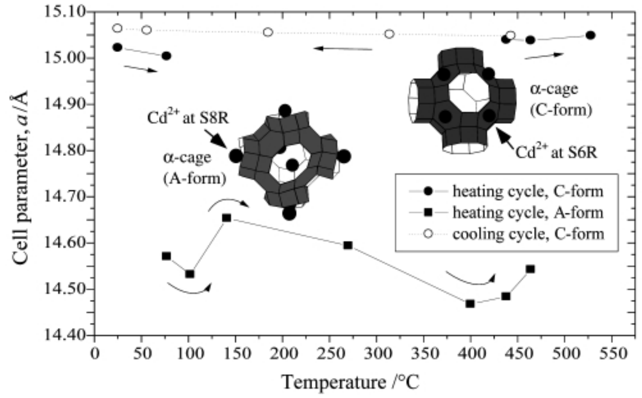

Fig. 3 The cell parameter of Cd-rho heated under vacuum. In the absence of water, there is no phase transformation upon cooling. Schematic diagrams illustrate siting of Cd^{2+} in the α-cages.

There are two modes of cation relocation in zeolite rho: the transition from the S8R site to the D8R site and the 'trap door' relocation from the S8R site to the S6R site. The present work indicates that these relocations are mediated by water. As coordinating water is removed from the structure, extra-framework cations must change their coordination environments by migrating to new sites in order to satisfy their coordination requirements. While dehydration is the driving force for cation relocations, cationic size appears to determine which relocation mechanism occurs. In hydrated samples, all divalent cations studied reside at the S8R site. Even though this site is large, all cations can have their coordination requirements met by binding with water in the sample. Dehydration, and the resulting loss of coordinated water, has a large effect on the cation coordination sphere. Larger cations such as Ca^{2+}, Sr^{2+}, Pb^{2+}, Ba^{2+}, can have their bonding requirements met by relocating to the D8R site. To satisfy the bonding requirements of a smaller cation such as Cd^{2+}, a larger framework distortion must occur. Because of its smaller size, the S6R site presents an attractive binding site in the absence of water. Through water mediation, Cd^{2+} can relocate to this site. Rather than being purely temperature-driven transformations, all cation relocations and the dramatic negative thermal expansion effects observed in zeolite rho appear to be a result of chemical changes that arise from dehydration.

This work was supported by a grant from the National Science Foundation (DMR 97-13375). This work made use of the X7B beamline at the NSLS, supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences (DEAC02-98CH10886).

Notes and references

‡ Chemical analysis by ICP and microprobe gave unit cell compositions of $Pb_{6.7}Cs_{0.7}Al_{11.7}Si_{36.3}O_{96}\cdot wH_2O$ and $Cd_{5.5}Cs_{0.3}Al_{11.7}Si_{36.3}O_{96}\cdot wH_2O$ for Pb-rho and Cd-rho, respectively.

§ The sample to detector distance, zero point, and imaging plate tilt were determined from LaB_6 (NIST SRM 660a) prior to the experiment[11] (Cd-rho: λ = 0.9372 Å; Pb-rho: λ = 0.9042 Å). Approximately 3 mg of powdered sample loaded in a 0.5 mm quartz capillary was exposed either to vacuum (< 1 Pa) or ambient atmosphere. A continuous heating or cooling rate between 3 °C min^{-1} and 6 °C min^{-1} was used. Temperatures were calibrated against the thermal expansion of an Ag standard. Data were integrated using FIT2D.[11] Anomalous scattering terms for Cd ($f' = -0.53$ electrons and $f'' = 1.97$ electrons) and Pb ($f' = -8.76$ electrons and $f'' = 9.30$ electrons) were taken from FPRIME.[10,12]

¶ Samples were deuterated by several cycles of vacuum dehydration at 200 °C ($< 10^{-2}$ Pa) followed by contact with D_2O vapor at room temperature.

1 D. R. Corbin, L. Abrams, G. A. Jones, M. M. Eddy, W. T. A. Harrison, G. D. Stucky and D. E. Cox, *J. Am. Chem. Soc.*, 1990, **112**, 4821.
2 A. Bieniok and W. H. Baur, *J. Solid State Chem.*, 1991, **90**, 173.
3 J. B. Parise, X. Liu, D. R. Corbin and G. A. Jones, in *Synthesis/Characterization and Novel Applications of Molecular Sieve Materials*, ed. R. L. Bedard, T. Bein, M. E. Davis, J. Garces, V. A. Maroni and G. D. Stucky, Materials Research Society, Pittsburgh, PA, 1991, pp. 267–272.
4 J. B. Parise, D. R. Corbin and L. Abrams, *Microporous Mater.*, 1995, **4**, 99.
5 J. B. Parise, T. E. Gier, D. R. Corbin and D. E. Cox, *J. Phys. Chem.*, 1984, **88**, 1635.
6 R. X. Fischer, W. H. Baur, R. D. Shannon, R. H. Staley, L. Abrams, A. J. Vega and J. D. Jorgensen, *Acta Crystallogr., Sect. B*, 1988, **44**, 321.
7 H. E. Robson, D. P. Shoemaker, R. A. Ogilvie and P. C. Manor, in *Molecular Sieves*, ed. W. M. Meier and J. B. Uytterhoven, American Chemical Society, Washington, D.C., 1973, pp. 106–114.
8 P. Norby, *J. Appl. Crystallogr.*, 1997, **30**, 21.
9 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65.
10 A. C. Larson and R. B. VonDreele, 'GSAS; General Structure Analysis System', Report LAUR 86-748, Los Alamos National Laboratory, New Mexico, 1986.
11 A. P. Hammersley, *FIT2D: V9.129 Reference Manual V3.1*, ESRF Internal Report ESRF98HA01T, Grenoble, France, 1998.
12 D. T. Cromer, *J. Appl. Crystallogr.*, 1983, **16**, 437.