Flexibility of the Zeolite Rho Framework. Neutron Powder Structural Characterization of Ca-Exchanged Zeolite Rho

D. R. Corbin,*[a] L. Abrams,[a] G. A. Jones,[a] M. M. Eddy,[b] G. D. Stucky,[b] and D. E. Cox[c]

[a] *Central Research and Development Department, E.I. du Pont de Nemours and Company, Inc., Experimental Station, P.O. Box 80262, Wilmington, DE 19880-0262, U.S.A., Contribution No. 4803*

[b] *Department of Chemistry, University of California at Santa Barbara, Santa Barbara, CA 93106, U.S.A.*

[c] *Physics Department, Brookhaven National Laboratory, Long Island, Upton, NY 11973, U.S.A.*

Neutron powder diffraction structural characterizations of dehydrated samples of Ca-exchanged zeolite rho show the most pronounced distortions of any zeolite framework yet observed and correspond to a 21% decrease in the lattice volume.

Zeolites are crystalline, microporous aluminosilicate materials with open framework structures. It is the shape and size of the pore openings that give a zeolite its molecular sieving ability and hence selectivity when used as a catalyst, support, or adsorbent. Generally, the framework and hence the pore openings of a zeolite are considered rigid structures. However, several zeolite frameworks have been shown to exhibit small distortions of symmetry by sorption of solvents[1] or as a function of temperature.[2] The magnitude of these observed distortions and their effects on the pore openings are insignificant when compared to the flexibility and distortions observed in the framework of zeolite rho.

The framework of zeolite rho is composed of a body-centred cubic arrangement of truncated cubo-octahedra or α-cages linked *via* double 8-rings. Structural studies[3] have shown that zeolite H–rho undergoes an appreciable distortion and loss of symmetry from $Im\bar{3}m$ to $I\bar{4}3m$ upon dehydration. This change in symmetry is directly related to an enormous 6.9% decrease in the lattice volume [a 2.3% decrease in the lattice parameter which goes from 15.031(1) to 14.678(1) Å]. Deformation of the dehydrated form also shows a temperature dependence.[4]

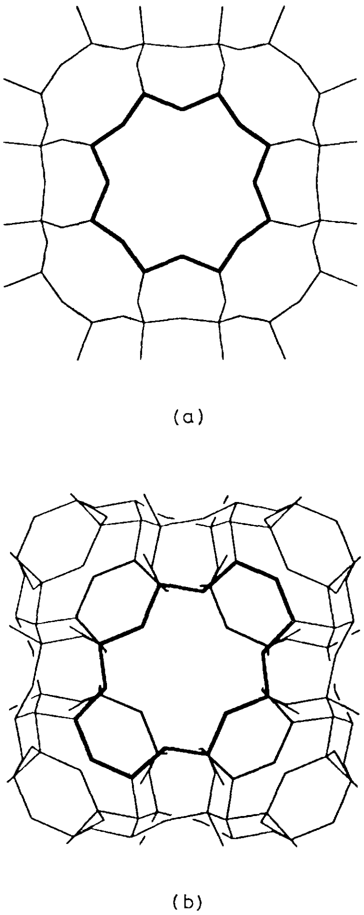

Figure 1. Projection of the zeolite rho framework from 0.0 to 1.0 in all crystallographic directions for (a) D–rho[10] [a = 15.0976(4) Å] and (b) Ca,D–rho [a = 13.9645(7) Å].

For many zeolites, control over ring aperture dimensions is achieved typically using different sized cations as in zeolites 3A, 4A, and 5A. The cations K^+, Na^+, and Ca^{2+} in the A framework eclipse the ring opening depending on their size and population. However, for zeolite rho it is the framework itself which distorts to modify the cage openings. Parise *et al.*[5] defined a parameter, Δ, to describe the distortion or ellipticity of the double 8-ring which accompanies this distortion and showed it to vary from 0 to about 1.9 Å.

For some substituted zeolites, charge-compensation by some cations produce sufficient lattice strain that can promote decomposition of that zeolite under mild conditions.[6] By virtue of its flexibility, the rho framework is able to distort and relieve the strain imposed by the charge-compensating ions. In this communication, we report our initial results of the structure refinement from neutron diffraction data of two divalent exchanged samples, Ca,ND_4–rho and Ca,D–rho, showing the largest distortion of any zeolite yet observed.

Ca,NH_4–rho, $Ca_{4.0}(NH_4)_{3.3}Na_{0.13}Cs_{0.10}Al_{11.5}Si_{36.5}O_{96}$, was prepared by conventional NH_4^+–exchange followed by Ca^{2+}–exchange of Na,Cs–rho.[7] Deuteriated forms were prepared for neutron powder diffraction study as follows. Two samples of Ca,NH_4–rho were evacuated while being heated to 250 °C and 400 °C, respectively. After prolonged evacuation at temperature, the samples were cooled to 250 °C and exchanged with D_2O vapour. After exchange, one sample was evacuated at 250 °C yielding Ca,ND_4–rho while the other was evacuated at 400 °C to produce Ca,D–rho.

The structures of Ca,ND_4–rho and Ca,D–rho were determined from neutron powder data collected at room temperature on diffractometer H4S at the High-Flux Beam Reactor, Brookhaven National Laboratory. Structural refinements were carried out using the program G.S.A.S.[8] and in all cases soft constraints or restraints[9] were used throughout the refinements in space group $I\bar{4}3m$. From the analysis for Ca,ND_4–rho, it is apparent that two phases exist in this particular sample. This dual phase system may be caused by inhomogeneous distribution of the cations. Both phases present in Ca,ND_4–rho have a single extra-framework cation site located at the centre of the double 8-ring. The phase with the smaller unit cell dimension has a larger content of calcium ions [Phase 2, a = 14.110(1) Å, R_p = 16.1%, R_{wp} = 21.8%, Δ = 2.31 Å], which distort the 8-ring ellipse more than the bulky ND_4^+ cations [Phase 1, a = 14.410(2) Å, R_p = 9.1%, R_{wp} = 11.5%, Δ = 1.92 Å].

Data obtained for the Ca,D–rho sample show that it is a single phase [a = 13.9645(7) Å, R_p = 9.6%, R_{wp} = 12.6%, Δ = 2.49 Å]. This corresponds to a lattice volume decrease of almost 21% from the largest cell [a = 15.096(4) Å] reported for zeolite rho.[10] In this structure, the calcium cations are located at the centre of the double 8-ring, tetrahedrally co-ordinated to four framework oxygen atoms [Ca–O = 2.70(1) Å]. This distorts the 8-rings into highly anisotropic ellipses, in which Δ, the difference of the major and minor axes, is significantly greater than anything yet observed (2.49 Å). This distortion is illustrated in Figure 1. Work in progress shows that Δ is a function of the nature of the cation.

Unlike calcium-exchanged zeolite A where the calcium ions are sited in a trigonal environment within the 6-rings of the α-cage,[11] the calcium ions reside in a unique, strained tetrahedral environment in Ca,D–rho. Although such co-ordination is not uncommon in dehydrated zeolites,[12] it is unique for calcium ions. Upon removal of water, the cations must use whatever charge compensating co-ordination is available, and, in this case, the flexibility of the framework provides a tetrahedral environment rather than the trigonal site associated with the 6-ring. The significant distortion of the rho framework by the calcium ion attests to the strong interaction between the framework and the ion.

The cell dimensions refined for this sample of zeolite rho are the smallest observed to date, and emphasise the flexibility and the stability of the rho framework. Thus, we have now shown that the framework of zeolite can be manipulated from 15.098 to 13.965 Å by suitable ion exchange and calcination procedures. This ability to modify the dimensions of zeolite frameworks is essential for control of size and shape dependent sorption behaviour or for the tailoring of catalytic specificity.

The authors acknowledge R. L. Harlow for helpful discussions, as well as support by the Division of Material Sciences, U.S. Department of Energy under Contract DE-AC02-76CH0016 (D.E.C.) and the Office of Naval Research (G.D.S.).

Received, 5th July 1988; Com. 8/02674B

References

1 G. W. West, *Aust. J. Chem.*, 1984, **37**, 455; C. A. Fyfe, G. J. Kennedy, C. T. De Schutter, and G. T. Kokotailo, *J. Chem. Soc., Chem. Commun.*, 1984, 541; C. A. Fyfe, H. Stobl, G. T. Kokotailo, G. J. Kennedy, and G. F. Barlow, *J. Am. Chem. Soc.*, 1988, **110**, 3373.

2 D. G. Hay and H. Jaeger, *J. Chem. Soc., Chem. Commun.*, 1984, 1433; D. G. Hay, H. Jaeger, and G. W. West, *J. Phys. Chem.*, 1985, **89**, 1070; J. Klinowski, T. A. Carpenter, and L. F. Gladden, *Zeolites*, 1987, **7**, 73; J. M. Bennett, C. S. Blackwell, and D. E. Cox, in 'Intrazeolite Chemistry,' eds. G. D. Stucky and F. G. Dwyer, American Chemical Society, Washington, DC, 1983; *Adv. Chem. Ser.*, 218, pp. 143—158; J. M. Bennett, C. S. Blackwell, and D. E. Cox, *J. Phys. Chem.*, 1983, **87**, 3783.

3 L. B. McCusker and C. Baerlocher, in 'Proceedings of the Sixth International Zeolite Conference,' eds. D. Olson and A. Bisio, Butterworths, Guildford, 1984, pp. 812—822.

4 J. B. Parise, L. Abrams, T. E. Gier, D. R. Corbin, J. D. Jorgensen, and E. Prince, *J. Phys. Chem.*, 1984, **88**, 2303.

5 J. B. Parise, T. E. Gier, D. R. Corbin, and D. E. Cox, *J. Phys. Chem.*, 1984, **88**, 1635.

6 W. Lutz, B. Fahlke, U. Lohse, M. Buelow, and J. Richter-Mendau, *J. Crystal Res. & Technol.*, 1983, **18**(4), 513.

7 H. E. Robson, U.S. Pat. 3,720,753 (1973).

8 R. B. von Dreele and A. C. Larsen, Los Alamos Report LAUR 86—748.

9 C. Baerlocher, in ref. 3, pp. 823—833; J. Waser, *Acta Crystallogr.*, 1963, **16**, 1091.

10 W. H. Baur, R. X. Fischer, R. D. Shannon, R. H. Staley, A. J. Vega, L. Abrams, D. R. Corbin, and J. D. Jorgensen, *Z. Kristallogr.*, 1987, **179**, 281.

11 J. J. Pluth and J. V. Smith, *J. Am. Chem. Soc.*, 1983, **105**, 1192.

12 J. B. Parise and E. Prince, *Mater. Res. Bull.*, 1983, **18**, 841.