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

by

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Abstract:

Neutron powder diffraction structural characterizations of dehydrated samples of Ca-exchanged zeolite RHO showing the most pronounced distortions of this aluminosilicate framework from  $Im\bar{3}m$  to  $I4\bar{3}m$  symmetry yet observed and corresponding to greater than a 7% decrease in the lattice parameter are reported.



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

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G. D. Stucky<sup>2</sup>, and D. E. Cox<sup>3</sup>

## Summary

Neutron powder diffraction structural characterizations of dehydrated samples of Ca-exchanged zeolite RHO showing the most pronounced distortions of this aluminosilicate framework from Im3m to I43m symmetry yet observed and corresponding to greater than a 7% decrease in the lattice parameter are reported.

cont'd

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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<sup>1</sup> or as a function of temperature<sup>2</sup>. 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.

cont'd The framework of zeolite RHO is composed of a body-centered cubic arrangement of truncated cubooctahedra or  $\alpha$ -cages linked via double 8-rings. Structural studies<sup>3</sup> have shown that zeolite H-RHO undergoes an appreciable distortion and loss of symmetry from  $Im3m$  to  $I\bar{4}3m$  upon dehydration. This change in symmetry is directly related to an enormous 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<sup>4</sup>. (nym) E

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.<sup>5</sup> defined a parameter,  $\Delta$ ,

to describe the distortion or ellipticity of the double 8-ring which accompanies this distortion and showed it to vary from 0 to about 1.9Å. The effective cross-section of these rings or size and shape of the openings connecting  $\alpha$ -cages is related to  $\Delta$ .

For some cation substituted zeolites, the effect of the charge-compensation is to produce lattice strain that can be sufficient to promote decomposition of that zeolite under mild conditions<sup>6</sup>. 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,NH<sub>4</sub>-RHO and Ca,D-RHO, showing the largest distortion of the RHO framework yet observed.

Ca,NH<sub>4</sub>-RHO (Ca<sub>4.0</sub>(NH<sub>4</sub>)<sub>3.3</sub>Na<sub>0.13</sub>Cs<sub>0.10</sub>Al<sub>11.5</sub>Si<sub>36.5</sub>O<sub>96</sub>) was prepared by conventional NH<sub>4</sub><sup>+</sup>- followed by Ca<sup>2+</sup>-exchange of Na,Cs-RHO<sup>7</sup>. Deuterated forms were prepared for neutron powder diffraction study as follows. Two samples of Ca,NH<sub>4</sub>-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<sub>2</sub>O vapor. After exchange, one sample was evacuated at 250°C yielding Ca,NH<sub>4</sub>-RHO while the other was evacuated at 400°C to produce Ca,D-RHO.

The structures of Ca,NH<sub>4</sub>-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.<sup>8</sup> and in all cases soft constraints or restraints<sup>9</sup> were used throughout the refinements in space group  $I\bar{4}3m$ . From the analysis for Ca,ND<sub>4</sub>-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<sub>4</sub>-RHO have a single extra-framework cation site located at the center of the double eight-ring. The phase with the smaller unit cell dimension has a larger content of calcium ions (Phase 2,  $a = 14.110(1)\text{\AA}$ ,  $R_p = 16.1\%$ ,  $R_{wp} = 21.8\%$ ,  $\Delta = 2.31\text{\AA}$ ), which distort the eight-ring ellipse more than the bulky ND<sub>4</sub><sup>+</sup> cations (Phase 1,  $a = 14.410(2)\text{\AA}$ ,  $R_p = 9.1\%$ ,  $R_{wp} = 11.5\%$ ,  $\Delta = 1.92\text{\AA}$ ).

Data obtained for the Ca,D-RHO sample shows that it is a single phase ( $a = 13.9645(7)\text{\AA}$ ,  $R_p = 9.6\%$ ,  $R_{wp} = 12.6\%$ ,  $\Delta = 2.49\text{\AA}$ ). Calcium cations are located at the center of the double eight-ring, tetrahedrally coordinated to four framework oxygen atoms (Ca-O =  $2.70(1)\text{\AA}$ ). This distorts the eight-rings into highly anisotropic ellipses, in which  $\Delta$ , the difference of the major and minor axes, is significantly greater than anything yet observed ( $2.49\text{\AA}$ ). Work in progress shows that  $\Delta$  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  $\alpha$ -cage<sup>10</sup>, the calcium ions reside in a very unusual and strained tetrahedral environment in Ca,D-RHO. However, such coordination is not uncommon in dehydrated zeolites<sup>11</sup>. Upon removal of water, the

cations must use whatever charge compensating coordination is available, and, in this case the flexibility of the framework provides a tetrahedral environment rather than the trigonal site associated with the six-ring. The significant distortion of the RHO framework by the calcium ion attests to the strong interaction between the framework and the ion. The lack of degradation of the sample upon calcination is additional evidence of the stability of the RHO framework imparted by its ability to distort.

The cell dimensions refined for this sample of zeolite RHO are the smallest observed to date, and underscores the flexibility and the stability of the RHO framework. Thus, we have now shown that the framework of zeolite RHO can be manipulated from about 15.1Å to 13.965Å 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 behavior or for the tailoring of catalytic specificity.

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