Crystal Structure of a Cyclopropane Sorption Complex of Dehydrated Fully Ca^{2+}-Exchanged Zeolite X

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The crystal structure of a cyclopropane sorption complex of dehydrated fully Ca^{2+}-exchanged zeolite X, Ca$_{46}$Si$_{100}$Al$_{92}$O$_{384}$ · 30C$_3$H$_6$ ($a = 24.988(4)$ Å), has been determined by single-crystal X-ray diffraction techniques in the cubic space group $Fd\bar{3}$ at 21(1) ℃. The crystal was prepared by ion exchange in a flowing stream of 0.05M aqueous Ca(NO$_3$)$_2$ for four days, followed by dehydration at 460 ℃ and 2×10^{-6} Torr for two days, and exposure to 100 Torr of cyclopropane gas at 21(1) ℃. The structure was determined in this atmosphere and refined to the final error indices $R_1 = 0.068$ and $R_2 = 0.082$, with 373 reflections for which $I > 3\sigma$ (I). In this structure, Ca^{2+} ions are located at two crystallographic sites. Sixteen Ca^{2+} ions fill the octahedral sites I at the centers of the hexagonal prisms (Ca-O = 2.412(9) Å). The remaining 30 Ca^{2+} ions are at sites II; each extends 0.46 Å into the supercage (an increase of 0.16 Å upon C$_3$H$_6$ sorption) where it coordinates to three trigonally arranged framework oxygens at 2.311(8) Å. Each of the 30 cyclopropane molecules was found to complex to Ca^{2+} ions at site II by the induced dipole interaction (Ca-C = 2.99(4) Å). All carbon atoms in each cyclopropane molecule are equivalent and equidistant from Ca^{2+} ions at site II with which they are associated.

Introduction

Most of the transition metal ions ion-exchanged into zeolites are unusually coordinated or coordinately unsaturated. To relieve coordinative unsaturation inside the zeolites, the cations complex readily with a variety of guest molecules that enter the zeolite channels and cavities. One aspect of the catalytic activity of zeolites is their capacity to adsorb hydrocarbon molecules within the voids and channels of the framework structure.[1] The knowledge of molecule-framework and molecule-molecule interactions is crucial to the understanding of the catalytic processes taking place in the voids of the zeolitic channel system. The selective sorption and catalytic properties of zeolites rely on not only the kinds of cations and their distribution but also on the interactions between the cations and the sorbed molecules.

Calcium-exchanged zeolites are used in industry to dry and purify natural gas, for carbon dioxide and hydrogen sulfide removal, and for the separation for *n*- and isoparaffins.[2]

In dehydrated Ca$_{46}$-X, 16 Ca^{2+} ions fill site I and 30 are at site II.[3] Upon sorption of ethylene or acetylene, each site-II Ca^{2+} ion moves 0.11 Å or 0.12 Å further into the supercage from the plane of its three nearest oxygens to coordinate laterally to a C$_2$H$_{2n}$ molecule.[4] These Ca^{2+} ions have a tetrahedral environment, 2.316 Å or 2.318 Å from three framework oxygens and 2.98 Å or 2.87 Å from each carbon atom of ethylene or acetylene molecules (C-C = 1.39(6) Å and C-C = 1.30(5) Å) (ethylene or acetylene is counted as a monodentate ligand).

The structures of Co$_4$Na$_4$Si$_{12}$Al$_{12}$O$_{48}$ · 4C$_3$H$_6$ and Mn$_4$Na$_4$-Si$_{12}$Al$_{12}$O$_{48}$ · 4C$_3$H$_6$, formed by exposure to cyclopropane gas at approximately atmosphere pressure, were completed.[5] In each structure, the transition metal cations are located on threefold axes inside the large cavity, close to three trigonally arranged framework oxygens . The metal to oxygen distances are Co(II)-O = 2.174(7) Å and Mn(II)-O = 2.122 (8) Å. Each of the four cyclopropane molecules in each structure is found to complex to a transition metal ion with Co(II)-C = 2.81(7) Å and Mn(II)-C = 3.09(6) Å. The large isotropic carbon thermal parameters and the long metal to carbon approach distances lead to the conclusion that the cyclopropane molecules are loosely bound to the metal ions by a ion to induced dipole interaction.[5]

Use of the selective and catalytic properties of zeolite is widespread. Structural information of various sorbates in inner surface of the zeolite A and X has been obtained by the very powerful crystallographic method. The environments of guest molecules such as Br$_2$[7,8], Cl$_2$[9,10], C$_2$H$_2$[11,12], C$_2$H$_4$[13,14], NH$_3$[15,16] and CH$_3$OH[17] have been studied.

Nuclear quadrupole resonance studies of C$_3$H$_6$ show[18] that all of the carbon atoms in cyclopropane molecules are sp^2 hybridized. Hence, cyclopropane has some π character by which it might interact with transition metal cations. It has been found that cyclopropane is sorbed by partially Ni(II)-exchanged zeolite A complexes with Ni(II)ions.[19]

This work was undertaken to further investigate cyclopropane sorption by zeolite X, to determine the positions of sorbed cyclopropane molecules, and to observe the shifts in cation and framework positions upon sorption.

Experimental Section

Large single crystals of sodium zeolite X, stoichiometry Na$_{92}$Si$_{100}$Al$_{92}$O$_{384}$, were prepared in St. Petersburg, Russia.[20] One of the crystals, a colorless octahedron about 0.2 mm in cross-section, was lodged in a fine Pyrex capillary.

Table 1. Positional,[a] Thermal,[a] and Occupancy Parameters

Atom	Cation Site	x	y	z	U_{iso}[b]	[b]Occupancy varied	[b]Occupancy fixed
Si		-538(2)	1227(2)	343(1)	103(7)		96.0
Al		-558(2)	357(2)	1219(2)	69(8)		96.0
O(1)		-1113(4)	3(4)	1091(4)	202(27)		96.0
O(2)		-40(4)	39(4)	1429(3)	82(21)		96.0
O(3)		-361(3)	641(4)	624(4)	157(25)		96.0
O(4)		-602(4)	779(4)	1735(4)	209(25)		96.0
Ca(1)	I	0	0	0	79(16)[c]	17.2(3)	16.0
Ca(2)	II	2277(1)	2277(1)	2277(1)	192(15)[c]	30.7(4)	30.0
C		3190(11)	2802(14)	2815(15)	2371(53)	91.6(3)	90.0

[a]Positional and thermal parameters are given ×10[4]. Numbers in parentheses are the esds in the units of the least significant digit given for the corresponding parameter. [b]Occupancy factors are given as the number of atoms or ions per unit cell. [c]A U_{eq} value; for Ca(1), $U_{ii} = 0.0077$ Å and $U_{ij} = 0.0016$ Å; for Ca(2), $U_{ii} = 0.0240$ Å and $U_{ij} = 0.0048$ Å. $i \neq j$. The anisotropic temperature factor = $\exp[(-2^2/a^2)(h^2U_{11} + k^2U_{22} + l^2U_{33} + 2hk\,U_{12} + 2hl\,U_{13} + 2kl\,U_{23})]$.

To prepare fully Ca^{2+}-exchanged zeolite X, a 0.05 M solution of Ca(NO$_3$)$_2$ was used. It was allowed to flow past the crystal at a velocity of approximately 15 mm/s for 5 d at 21(1) °C. After dehydration at 460 °C and 2×10^{-6} Torr for 2 d, the crystal was colorless. To prepare a cyclopropane sorption complex, the crystal was treated with 100 Torr of zeolitically dried cyclopropane gas (Aldrich, 99.995%) for 2 h at 21(1) °C. The resulting yellow crystal, still in its cyclopropane atmosphere, was sealed in its capillary by torch.

The cubic space group $Fd\bar{3}$ was used throughout this work. This choice is supported by (a) the low Si/Al ratio, which in turn requires, at least in the short range, alternation of Si and Al, and (b) the observation that this crystal, like all other crystals from the same batch, does not have intensity symmetry across (110) and therefore lacks that mirror plane.

Diffraction data were collected with an automated Enraf-Nonius four-circle computer-controlled CAD-4 diffractometer equipped with a pulse-height analyzer and graphite monochromator, using Mo radiation (Kα$_1$, λ = 0.70930; Kα$_2$, λ = 0.71359 Å). The unit cell constant at 21(1) °C, determined by least-squares refinement of 25 intense reflections for which 14° < 2θ < 22°, is *a* = 24.988(4) Å. All unique reflections in the positive octant of an F-centered unit cell for which 2θ < 50°, *l* > *h*, and *k* > *h* were recorded. Of the 1410 reflections examined, only the 373 reflections for which I>3σ (*I*) were used in subsequent structure determination. An absorption correction (*R* = 0.078 mm^{-1}, ρ$_{cal}$ = 1.547 g/cm^3 and *F*(000) = 7288) was made empirically using a ψ scan.[21] The calculated transmission coefficients ranged from 0.985 to 0.995. This correction had little effect on the final *R* indices. Other details are the same as previously reported.[22]

Structure Determination

Full-matrix least-squares refinement was initiated by using the atomic parameters of the framework atoms [Si, Al, O(1), O(2), O(3), and O(4)] in dehydrated Ca$_{46}$-X.[3] Isotropic refinement converged to an unweighted R_1 index, ($\Sigma(F_o-|F_c|)/\Sigma F_o$), of 0.31 and a weighted R_2 index, $(\Sigma w(F_o-|F_c|)^2/\Sigma wF_o^2)^{1/2}$, of 0.36.

A difference Fourier function showed the positions of the Ca^{2+} ions at Ca(1), (0.0, 0.0, 0.0) with peak height 17.3 eÅ^{-3}, and at Ca(2), (0.227, 0.227, 0.227) with peak height 12.0 eÅ^{-3}. Isotropic refinement of framework atoms and these Ca^{2+} ions converged to $R_1 = 0.087$ and $R_2 = 0.14$ with occupancies of 16.7(6) and 34.01(9), respectively. These values were reset and fixed at 16 Ca^{2+} ions and 30 Ca^{2+} ions, respectively, because the maximum occupancy at Ca(1) is 16 ions, and because the cationic charge should sum to 92+ per unit cell.

A subsequent difference Fourier function showed the carbon atoms of the cyclopropane molecules at a general 96-fold position (0.289, 0.307, 0.368) with a peak height of 1.7 eÅ^{-3}. Simultaneous positional, occupancy, and isotropic thermal parameter refinement for all atoms, which was refined isotropically, converged to $R_1= 0.068$ and $R_2 = 0.082$.

Occupancy refinement of the carbon atom at C converged

Table 2. Selected Interatomic Distances (Å) and Angles (deg)[a]

Si-O(1)	1.63(1)	O(1)-Si-O(2)	112.4(5)
Si-O(2)	1.67(1)	O(1)-Si-O(3)	107.4(5)
Si-O(3)	1.69(1)	O(1)-Si-O(4)	114.0(5)
Si-O(4)	1.63(1)	O(2)-Si-O(3)	106.9(5)
Average	1.66	O(2)-Si-O(4)	101.8(5)
Al-O(1)	1.67(1)	O(3)-Si-O(4)	114.3(5)
Al-O(2)	1.71(1)	O(1)-Al-O(2)	112.3(5)
Al-O(3)	1.72(1)	O(1)-Al-O(3)	106.8(5)
Al-O(4)	1.67(1)	O(1)-Al-O(4)	115.4(5)
Average	1.69	O(2)-Al-O(3)	106.6(5)
Ca(1)-O(3)	2.412(9)	O(2)-Al-O(4)	100.3(5)
Ca(1)-O(2)	2.311(8)	O(3)-Al-O(4)	115.4(5)
C(1)-C(1)	1.24(6)	Si-O(1)-Al	125.7(5)
Cyclopropane-Ca(2)		Si-O(2)-Al	141.4(6)
Center-Ca(2)	2.85	Si-O(3)-Al	129.6(6)
C(1) -Ca(2)	2.99(4)	Si-O(4)-Al	166.8(7)
		O(3)-Ca(1)-O(3)	86.5(3)/93.5(3)
		O(2)-Ca(2)-O(2)	116.0(3)
		Ca(2)-C(1)-C(1)	78.0(4)
		C(1)-C(1)-C(1)	60.0(5)

[a]Numbers in parentheses are estimated standard deviations in the units of the least significant digit given for the corresponding value.

at 91.6(3) and this value was fixed at 90 atoms (see Table 1), three times the number of Ca^{2+} ions at Ca(2), the maximum number that can fit at this equipoint; it is assumed that one C$_3$H$_6$ molecule is associated with each Ca(2), such coordination being the reason that each Ca(2) ion has moved 0.16 Å further into the supercage as compared with its dehydrated structure. The final error indices for the 373 reflections, for which $I > 3\sigma(I)$, were $R_1 = 0.068$ and $R_2 = 0.082$, and the corresponding difference function was featureless. The final refinement was done using the 800 reflections, for which $I > 0$, to make better use of the diffraction data: $R_1 = 0.17$ and $R_2 = 0.089$. This allowed the esds to decrease to about 40% of their former values. All shifts in the final cycles of least-squares refinement were less than 0.1% of their corresponding standard deviations.

Atomic scattering factors[23,24] for Si, Al, O$^-$, Ca^{2+}, and C were used. All scattering factors were modified to account for anomalous dispersion.[25] The final structural parameters and selected interatomic distances and angles are presented in Tables 1 and 2, respectively.

Discussion

Zeolite X is a synthetic counterpart of the naturally occurring mineral faujasite. The 14-hedron with 24 vertices known as the sodalite cavity or β cage may be viewed as the principal building block of the aluminosilicate framework of the zeolite (see Figure 1). These β-cages are connected tetrahedrally at six-rings by bridging oxygens to give double six-rings (D6R's, hexagonal prisms), and, concomitantly, to give an interconnected set of even larger cavities (supercages) accessible in three dimensions through 12-ring (24-membered) windows. The Si and Al atoms occupy the vertices of these polyhedra. The oxygen atoms lie approximately midway between each pair of Si and Al atoms, but are displaced
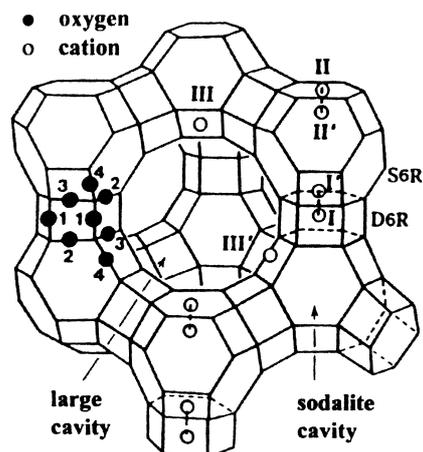

Figure 1. A stylized drawing of the framework structure of zeolite X. Near the center of the each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1 to 4. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that a silicon atom substitutes for aluminum at about 4% of the Al positions. Extraframework cation positions are labeled with Roman numerals.
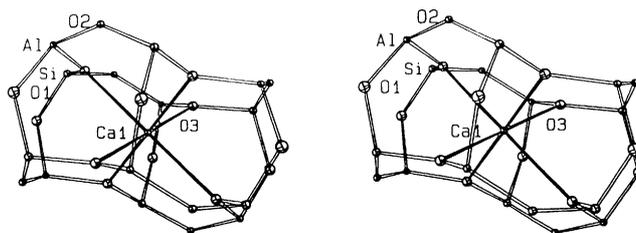

Figure 2. Stereoview of double six-ring of Ca$_{46}$-X 30C$_3$H$_6$. The Ca^{2+} ion at Ca(1) is shown at site I. Ellipsoids of 20% probability are used.

from those points to give near tetrahedral angles about Si and Al.

Exchangeable cations that balance the negative charge of the aluminosilicate framework are found within the zeolite's cavities. They are usually found at the following sites shown in Figure 1: site I at the center of a D6R, I' in the sodalite cavity on the opposite side of one of the D6R's six-rings from site I II', inside the sodalite cavity near a single six-ring (S6R) entrance to the supercage, II in the supercage adjacent to a S6R, III in the supercage opposite a four-ring between two 12-rings, and III' off the twofold axis, somewhat or substantially distant from III but otherwise near the inner walls of the supercage.[26,27]

The mean values of the Si-O and Al-O bond lengths are 1.66 Å and 1.69 Å, respectively. The individual bond lengths, however, show marked variations: Si-O from 1.63(1) Å to 1.69(1) Å and Al-O from 1.67(1) Å to 1.72(1) Å. The Si-O and Al-O distances depend on Ca^{2+} ion coordination to framework oxygen; Ca^{2+} ions coordinate only to O(2) and O(3). As a consequence of these (substantially ionic) interactions, the Si-O(2), Si-O(3), Al-O(2), and Al-O(3) bonds

Table 3. Deviations of Atoms (Å) from Six-Ring Planes

at O(3):	Ca(1)	-1.30^a
at O(2):	Ca(2)	0.47^b

^{a}A negative deviation indicates that the atom lies in a D6R. ^{b}A positive deviation indicates that the atom lies in a supercage.
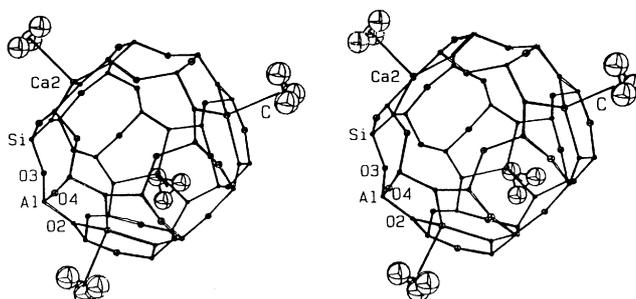

Figure 3. A stereoview of a sodalite cavity. Four Ca^{2+} ions, Ca(2), are shown at site II. Each Ca^{2+} ion at Ca(2) coordinates to one cyclopropane molecules. The hydrogen atoms, whose positions were not determined, are not shown. All D6Rs have this arrangement. At least 75% of sodalite cavities have this arrangement. The remaining 25% have only three Ca^{2+} ions at Ca(2), each of which coordinates to one cyclopropane molecule. Ellipsoids of 20% probability are shown.

are somewhat lengthened (see Table 2). This effect is frequently observed, for example in dehydrated Ca_{46}-X.[3]

Only small changes from the framework geometry of the dehydrated structure are observed upon sorption. The cell constant decreased somewhat from 25.024(4) Å in dehydrated Ca_{46}-X[12] to 24.988(4) Å in its cyclopropane sorption structure. Smaller decreases upon sorption were seen in its ethylene (a = 25.003(5) Å) and acetylene (a = 25.013(5) Å) sorption structures.[4]

The Ca^{2+} ions are found at only two high occupancy sites. Sixteen Ca^{2+} ions at Ca(1) fill the octahedral site I at the centers of the D6R's (see Figure 2). The Ca(1)-O(3) distance, 2.412(9) Å, is a little longer than the sum of the ionic radii of Ca^{2+} and O^{2-}, 0.99 + 1.32 = 2.31 Å,[28] indicating a reasonably good fit. In empty Ca_{46}-X, the Ca(1)-O(3) distance is similar, 2.429(8) Å.[3] The remaining 30 Ca^{2+} ions at Ca(2) are at site II in the supercage (see Figures 3 and 5); these Ca^{2+} ions are 2.311(8) Å from their nearest neighbors, three O(2) framework oxygens. Recently, the crystal structures of fully dehydrated Ca_{46}-X[3], Mn_{46}-X[29], and Sr_{46}-X[30] were determined by single-crystal x-ray diffraction methods. In these structures, all Ca^{2+}, Mn^{2+}, and Sr^{2+} cations are located at sites I and II, also with the same occupancies, 16 and 30, respectively.

To coordinate to cyclopropane molecules, the Ca^{2+} ions at site II have moved 0.16 Å further into the supercage, further from their triads of three O(2) oxygens as compared with
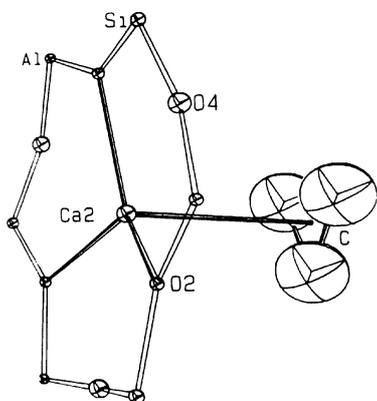

Figure 4. $Ca(C_3H_6)^{2+}$ complex on the inner surface of a supercage is shown in stereview. The positions of the hydrogen atoms were not determined. Ellipsoids of 20% Probability are shown.
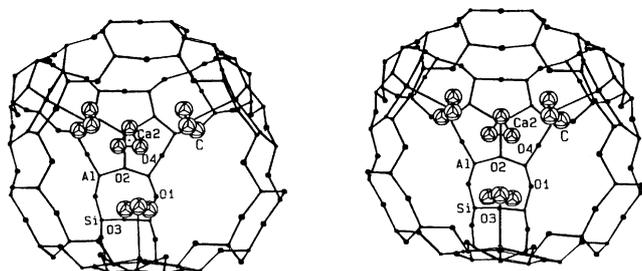

Figure 5. Stereoview of the supercage of the C_3H_6 complex of Ca_{46}-X. Four Ca^{2+} ions at ions at Ca(2) (site) are shown. Each coordinates to one cyclopropane molecule. Ellipsoids of 20% probability are used.

dehydrated Ca_{46}-X[3] (see Figures 3-5). Similarly, in the crystal structures of the ethylene and acetylene sorption complexes of dehydrated fully Ca^{2+}-exchanged zeolite X,[4] the Ca^{2+} ions at site II moved only 0.11 Å and 0.12 Å further into the supercage, respectively, as compared with dehydrated Ca_{46}-X.[3]

As a consequence of the movement of the Ca^{2+} ions at Ca(2) into the supercage upon complexation, the Ca(2)-O(2) bonds have increased from 2.276(5) Å in dehydrated Ca_{46}-X[3] to 2.382(7) Å. The O(2)-Ca(2)-O(2) angle has correspondingly decreased from near trigonal planar (118.3(2)°) in dehydrated Ca_{46}-X,[12] to 116.0(3)° in the cyclopropane complex (see Table 2 and Figures 4 and 5).

The Ca(2)-C bond distance is relatively long (Ca^{2+}-C = 2.99(4) Å), and the changes to the framework upon sorption are relatively small. The present Ca^{2+}-C distance in zeolite X is very similar to those in zeolite A (Co(II)-C = 2.81(7) Å and Mn(II)-C = 3.09(6) Å) The bonding in these complexes appears to be the result of electrostatic interaction between the Ca^{2+} ions and the polarizable π-electron density of the cyclopropane molecules. These interactions are relatively weak.

A more detailed presentation of the previously discussed π character of cyclopropane is possible. Miller,[31] using Hellmann-Feynman arguments and ring bending strain energies, calculated a "negative pole" in cyclopropane to be 0.288 e⁻. This negative pole or π cloud would be polarized by the field of the Ca(II) ion to form the bond between cyclopropane and Ca(II). In this work, cyclopropane molecule is loosely bound to Ca^{2+} ion by the induced dipole interaction.

The intermolecular carbon-carbon distances are observed to be short, 1.24 Å, as compared with the 1.52 Å in free C_3H_6 molecules[32] (C-C = 1.10(12) Å in Co_4Na_4-AC_3H_6 and Mn_4Na_4-AC_3H_6). These observed C-C bond lengths are somewhat foreshortened, an effect of thermal motion, by an amount which can be estimated to be a few tenths of an angstrom. Accordingly, the C-C bonds have not been shown to be shortened by complexation.

Summary, all Ca^{2+} ions are found at sites I and II. Each of the 30 cyclopropane molecules sorbed per unit cell coordinates to site II Ca^{2+} ion in the supercage. The Ca^{2+} ions at site I do not interact with cyclopropane molecules. The Ca^{2+}-C bonds are long, and the interactions are weak, so the changes in Ca_{46}-X due to sorption are small.

Supporting Information Available. Tables of calculated and observed structure factors (10 pages). Ordering information can be found on any current masthead page.

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