

Crystallographic Studies of Dehydrated Zeolite-X Reacting with Rubidium Vapor

루비듐 증기로 처리한 탈수한 제올라이트 X의 결정학적 연구

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ABSTRACT : A single crystal of zeolite $\text{Na}_{78}\text{Rb}_{28}\text{-X}$ (approximate composition) was prepared by exposing $\text{Na}_{92}\text{-X}$ at 350 °C to 0.1 Torr of rubidium vapor, and its structure was determined by single-crystal x-ray diffraction methods in the cubic space group, $\text{Fd}\bar{3}$, $a=25.045(4)$ Å. The structure was refined to the final error indices $R_1=0.082$ and $R_2=0.085$ with 353 for which $I > 3\sigma(I)$. Only about 28 of the 92 Na^+ ions per unit cell were reduced and only about 14 of the 28 Na^0 atoms produced were retained within the zeolite. A Na_5^{4+} cluster is present within each sodalite cavity. It is a centered tetrahedron (like CH_4) with bond length=2.80(2) Å and angle tetrahedral by symmetry, and shows the full symmetry of its site, T_d , at the center of the sodalite cavity. Each of the four terminal atoms of the Na_5^{4+} cluster bond to three framework oxygens at 2.36(2) Å. At the centers of some double 6-rings are sodium atoms which bridge linearly between Na_5^{4+} clusters to form agglomerations such as short zig-zag chains Na_5^{4+} clusters. Delocalized electrons, located primarily on the sodiums at centers of the sodalite and (likely) double-six-ring cavities, contribute to the stability of the clusters.

요약 : 제올라이트 $\text{Na}_{78}\text{Rb}_{28}\text{-X}$ 단결정을 $\text{Na}_{92}\text{-X}(\text{Na}_{92}\text{Si}_{100}\text{Al}_{92}\text{O}_{384})$ 을 350 °C에서 0.1Torr의 Rb 증기로 처리하여 만들어서 그 구조를 X-선 단결정법으로 공간군 $\text{Fd}\bar{3}$ 로서 결정하였다($a=25.045(4)$ Å). 구조는 $I > 3\sigma(I)$ 인 회절반점 353개를 사용하여 최종오차지수 $R_1=0.082$, $R_2=0.084$ 까지 정밀화하였다. 단위포당 92개의 Na^+ 이온 중 대략 28개의 Na^+ 이온이 환원되고, 환원되어 생성된 28개의 Na^0 중 약 14개만 제올라이트 골조내에 잔류하고 있다. 소다라이트 동공내에 사면체의 대칭성 (T_d)을 가지고 결합각 109.5°, 결합거리 2.80(2) Å를 갖는다. Na_5^{4+} 클라스트를 이루는 4개의 말단 원자와 골조 산소원자 사이의 결합거리는 2.80(2) Å이다. 몇몇 이중 6-링의 중심에 Na_5^{4+} 클라스트 두 개를 선형으로 연결하여 지그재그형의 덩어리로 만드는 Na^0 원자가 있다. 소다라이트 동공 중심과 이중 6-링에 있는 Na^0 원자의 비편재화된 전자가 Na_5^{4+} 클라스트를 안정화시키고 있다.

INTRODUCTION

Zeolites exposed to alkali metal vapor can sorb metal atoms into their cavities to form cationic clusters (Sun et al. 1993). By using the electron spin resonance (ESR) technique, the cationic clusters of Na_6^{5+} , Na_5^{4+} , Na_4^{3+} , K_4^{3+} , and K_3^{2+} were de-

tected in zeolites (Anderson et al. 1991a, 1991b; Kasai, 1965, 1976; Edwards et al. 1984; Harrison et al. 1984; Marten et al. 1985; Smeulders et al. 1987; Xu and Kevan, 1992). Unfortunately, the ESR method is ineffective at describing either the geometry of these clusters or their locations within the structure of the zeolite. However, indirect

arguments indicate that they are most likely in sodalite cavities. Metallic particles, not further defined, were also found.

The products of the reactions of zeolite A with Cs and Rb vapor have been studied by single-crystal x-ray diffraction methods (Han, 1991; Song, 1992; Heo and Seff, 1992). The triangular clusters, Rb_3^{n+} , ($n=1$ and 2), synthesized by exposing dehydrated zeolite $\text{Na}_{12}\text{-A}$ or $\text{Cd}_6\text{-A}$, respectively, to Rb vapor, were found in the sodalite cavities of zeolite A. Rb_3^{n+} is stabilized by further coordination to one to three Rb^+ ions. The linear Cs_3^{3+} and trigonal three-legged-stool Cs_6^{4+} were also found in zeolite A (Heo and Seff, 1992; Jeong et al. 1993).

Many structural investigations have been carried out to characterize the alkali-cation distribution in faujasite zeolites (Belgelhoff et al. 1958; Breck, 1974). Baur investigated the cation and water positions in partially Ca^{2+} -exchanged faujasite and found that approximately 40 % of exchanged cations occupy positions within sodalite cavities (Baur, 1964). Recently Shepelev et al. studied crystals of partially K^+ - and Cs^+ -exchanged forms of Na-X zeolite in both the hydrated and the dehydrated (400 °C) states (Shepelev et al. 1991).

This work was initiated with the hope that Rb vapor would reduce the Na^+ ions in zeolite X to form Na and/or Rb clusters whose placement and structures could be determined crystallographically. Na and Rb should be readily distinguishable in the resulting structures because they have very different scattering factors (approximately proportional to their atomic numbers) and ionic radii ($\text{Na}^+ = 0.97 \text{ \AA}$ and $\text{Rb}^+ = 1.47 \text{ \AA}$) (Weast, 1989, 1990).

EXPERIMENTAL

Large single crystals of sodium zeolite X, stoichiometry $\text{Na}_{48}\text{Si}_{100}\text{Al}_{10}\text{O}_{384}$, were prepared in St. Petersburg, Russia (Shepelev et al. 1991). One of

these, a colorless octahedron about 0.25 mm on an edge was lodged in a fine Pyrex capillary. After complete dehydration at 400 °C and 1×10^{-6} Torr for 48 h, rubidium (99.985 % purity, Johnson Matthey Inc.) was introduced by distillation from a side-arm break-seal ampoule to the glass tube extension of the crystal-containing capillary. This glass reaction vessel was then sealed off under vacuum and placed in a long horizontal cylindrical oven. The reaction was carried out at 350 °C for 48 h with 0.1 Torr of rubidium vapor. The resulting pink crystal was sealed off from the reaction vessel by torch after cooling to room temperature.

The cubic space group $Fd\bar{3}$ was used throughout this work. Diffraction data were collected with an automated Siemens four-circle computer-controlled P3 diffractometer, equipped with a pulse-height analyzer and a graphite monochromator. Molybdenum radiation ($\text{K}\alpha_1$, $\lambda = 0.70930$; $\text{K}\alpha_2$, $\lambda = 0.71359 \text{ \AA}$) was used. The unit cell constants at 22(1) °C, as determined by least-squares refinement of 30 intense reflections of which $14^\circ < 2\theta < 24^\circ$, was 25.045(4) Å. The θ - 2θ scan technique was used for data collection. Each reflection for which $5^\circ < 2\theta < 60^\circ$ was scanned at a constant rate of 0.25° min in ω from 0.60° below the calculated $\text{K}\alpha_1$ peak to 0.6° above the $\text{K}\alpha_2$ maximum. Background intensity was counted at each end of a scan range for a time equal to one half the scan time. The intensities of three reflections in diverse regions of reciprocal space were recorded every 97 reflections to monitor crystal and X-ray source stability. Only small random fluctuations of these check reflections were noted during the course of data collection. The raw data from each region were corrected for Lorentz and polarization effects including that due to incident beam monochromatization; the resultant estimated standard deviations were assigned to each averaged reflection by the computer program, XDISK. An absorption correction ($\mu\text{R ca. 1.83}$) was made empirically using a ψ scan. Of the 1139

Table 1. positional, Thermal, and Occupancy Parameters^a.

Atom	Wyc. Pos.	x	y	z	U ₁₁ ^b	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃	Occupancy ^c varied fixed
Si	96(g)	-536(2)	353(2)	1245(3)	187(30)	174(30)	174(30)	-11(28)	-95(37)	-73(39)	96
Al	96(g)	-547(3)	1234(4)	354(2)	217(38)	134(34)	134(34)	-160(42)	42(30)	84(43)	96
O(1)	96(g)	-1048(6)	8(8)	1097(6)	308(102)	224(103)	224(103)	20(92)	-90(76)	-55(91)	96
O(2)	96(g)	-41(6)	-7(6)	1443(5)	274(97)	209(82)	209(82)	127(73)	-171(74)	-92(76)	96
O(3)	96(g)	-323(6)	697(7)	738(7)	206(104)	360(116)	360(116)	-91(95)	-123(102)	-172(84)	96
O(4)	96(g)	-709(7)	722(8)	1737(8)	377(138)	511(145)	511(145)	-93(111)	-87(119)	-227(94)	96
Rb(1)	96(g)	4226(5)	1167(22)	1363(13)	906(304)	767(279)	767(279)	-19(110)	239(109)	-206(180)	21.5(6) 22
Rb(2)	96(g)	4245(26)	597(26)	572(28)	1030(486)	1247(607)	1247(607)	916(410)	-172(407)	-18(420)	5.3(6) 6
Na(1)	32(e)	2288(5)	2288(5)	2288(5)	540(63)	540(63)	540(63)	228(78)	228(78)	228(78)	29.2(17) 32
Na(2)	32(e)	604(6)	604(6)	604(6)	757(81)	757(81)	757(81)	308(96)	308(96)	308(96)	28.0(17) 32
Na(3)	16(c)	0	0	0	1168(511)	1168(511)	1168(511)	1122(590)	1122(590)	1122(590)	5.9(14) 6
Na(4)	8(a)	1250	1250	1250	455(94)	455(94)	455(94)	0	0	0	9.8(10) 8

^a a = 25.045(4) Å, space group Fd3, origin at center. Positional and anisotropic thermal parameters are given x 10⁴. Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter.

^b The anisotropic temperature factor = $\exp[-(-2\pi^2/a^2)(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + U_{12}hk + U_{13}hl + U_{23}kl)]$.

^c Occupancy factors are given as the number of atoms or ions per unit cell.

unique reflections only the 353 for which $I > 3\sigma(I)$ were used in subsequent structure determinations.

STRUCTURE DETERMINATION

Full-matrix least-squares refinement was initiated with the atomic parameters of the framework atoms [(Si, Al), O(1), O(2), O(3), and O(4)] of dehydrated Na-X treated with Cs(g) (Shepelev et al. 1991). This model converged with an R_1 index, $\sum(|F_o - |F_c||)/\sum F_o$, of 0.45 and a weighted R_2 index, $(\sum w(F_o - |F_c|)^2/\sum wF_o^2)^{1/2}$, of 0.53. A difference Fourier function showed the positions of Rb⁺ ions at Rb(1), (0.42, 0.125, 0.125), with peak height 7.54 eÅ⁻³; Na⁺ ions at Na(1), (0.23, 0.23, 0.23), with peak height 7.1 eÅ⁻³; and Na⁺ ions at Na(2), (0.06, 0.06, 0.06), with peak height 5.4 eÅ⁻³. Anisotropic refinement of these atoms converged to $R_1=0.178$ and $R_2=0.230$. A subsequent difference Fourier synthesis revealed two peaks at (0.125, 0.125, 0.125) and (0.0, 0.0, 0.0) with heights of 6.4 and 2.0 eÅ⁻³, respectively. These were stable in least-squares refinement, and anisotropic refine-

ment of framework atoms and Rb(1) and isotropic refinement of Na(1), Na(2), Na(3) and Na(4) (see Table 1) converged to $R_1=0.092$ and $R_2=0.114$. From successive difference Fouriers, one peak was found at (0.37, 0.06, 0.05), height=0.80e Å⁻³. Simultaneous positional and anisotropic thermal parameter refinement with fixed occupancy numbers converged to the final error indices $R_1=0.082$ and $R_2=0.085$ (see Table 1). The final difference function was featureless except for a peak at (-0.06, 0.0, 0.0) of height 0.62e Å⁻³; this peak was too close to framework atoms, O(1), O(2), and Si.

Structure calculations was done using the Structure Determination Package, SHELXTL-PLUS programs supplied by Siemens. The full-matrix least-squares program used minimized $\sum w(F_o - |F_c|)^2$; the weight w of an observation was the reciprocal square of $\sigma(F)$, its standard deviation. Atomic scattering factors (Doyle and Turner, 1968; John and Kathleen, 1974a) for Si, Al, O, Na⁺, and Rb⁺ were used. All scattering factors were modified to account for anomalous dispersion (Cromer, 1965; John and Kathleen,

Table 2. Selected Bond Distances (Å) and Angles (deg).

Si-O(1)	1.59(2)	O(1)-Si-O(2)	112.7(9)
Si-O(2)	1.61(2)	O(1)-Si-O(3)	111.8(9)
Si-O(3)	1.62(2)	O(1)-Si-O(4)	105.9(9)
Si-O(4)	1.60(2)	O(2)-Si-O(3)	106.6(8)
Al-O(1)	1.71(2)	O(2)-Si-O(4)	112.2(9)
Al-O(2)	1.75(2)	O(3)-Si-O(4)	112.7(10)
Al-O(3)	1.74(2)	O(1)-Al-O(2)	113.8(9)
Al-O(4)	1.75(2)	O(1)-Al-O(3)	109.8(9)
Na(1)-O(2)	2.28(1)	O(1)-Al-O(4)	109.5(9)
Na(2)-O(3)	2.36(2)	O(2)-Al-O(3)	107.1(8)
Na(2)-O(2)	3.06(2)	O(2)-Al-O(4)	106.1(9)
Na(3)-O(3)	2.66(2)	O(3)-Al-O(4)	110.5(9)
Rb(1)-O(1)	3.28(3)	Si-O(1)-Al	133.9(10)
Rb(1)-O(4)	3.11(4)	Si-O(2)-Al	140.6(9)
Rb(1)-O(4)	3.16(3)	Si-O(3)-Al	137.2(11)
Rb(2)-O(1)	3.09(7)	Si-O(4)-Al	146.7(12)
Rb(2)-O(1)	3.05(7)	O(2)-Na(1)-O(2)	114.6(5)
Rb(2)-O(4)	2.66(7)	O(2)-Na(1)-O(3)	102.9(9)
Na(2)-Na(4)	2.80(2)	O(2)-Na(2)-O(3)	61.0(5)
Na(2)-Na(3)	2.62(3)	O(3)-Na(3)-O(3)	87.4(5)
		O(1)-Rb(1)-O(1)	122.3(6)
		O(1)-Rb(1)-O(4)	90.1(7)
		O(1)-Rb(1)-O(4)'	82.2(8)
		O(1)-Rb(2)-O(4)	58.9(1)
		Na(4)-Na(2)-Na(3)	180.0
		Na(2)-Na(4)-Na(2)	109.5(1)
		Na(2)-Na(3)-Na(2)	180.0

1974b). The final structural parameters and selected interatomic distances and angles are presented in Tables I and II, respectively.

DISCUSSION

In this structure, 28 Rb's occupy two crystallographic sites and about 78 Na's are found at four such sites. The sum, 28+78=about 106 per unit cell, is more than the 92 monovalent cations required to balance the negative charge of the zeolite framework. The difference, 106-92=about 14, indicates that about 14 atoms (whose electrons may be delocalized) are present per unit cell.

Na⁺ ions at Na(1) lie at site II in supercage adjacent to single six ring (S6R) (see Figure 1). This position is 32-fold position and fully occu-

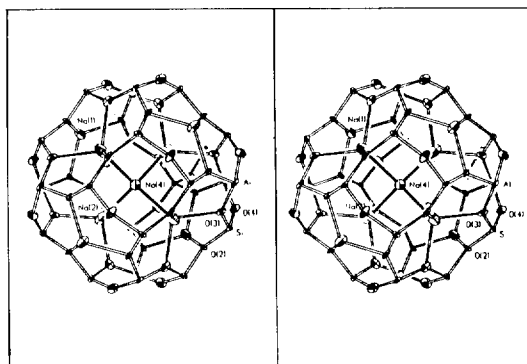


Fig. 1. The Na₅⁺ cluster in a sodalite cavity. Every sodalite cavity in this structure contains such a cluster.

Ellipsoids of 20% probability are shown.

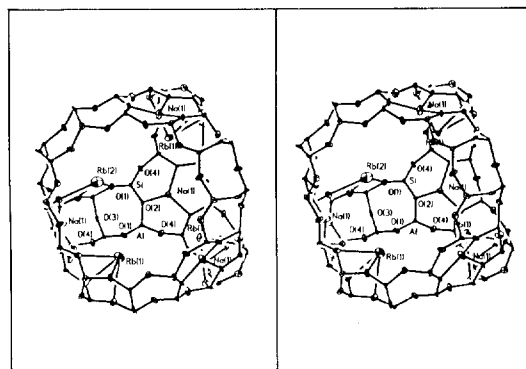


Fig. 2. A Stereoview of large cavity. Three Rb⁺ ions at Rb(1), one Rb⁺ ion at Rb(1) and four Na⁺ ions at Na(1) are shown. About 50% of large cavities have this arrangement. About 25% of large cavities may have three Rb⁺ ions at Rb(1), and four Na⁺ ions at Na(1) and another 25% of unit cell may have two Rb⁺ ions at Rb(1), one Rb⁺ ion at Rb(1) and four Na⁺ ions at Na(1). Ellipsoids of 20% probability are shown.

ried by Na⁺ ions at Na(1). Each Na⁺ ion is recessed ca. 0.68 Å from the plane of three framework oxygens, O(2)'s into supercage, and coordinates 2.28(1) Å to its three neighbors, O(2)'s. For comparison, the sum of ionic radii of Na⁺ and O²⁻, 0.97+1.32=2.29 Å (Weast, 1989, 1990).

Rb⁺ ions at Rb(1) and Rb(2) lie in supercage (both at site III). These positions are 96-fold positions, but only 22 and 6 such positions, respec-

tively, are filled (see Figure 2). Rb^+ ions at $\text{Rb}(1)$ are loosely held to framework oxygens ($\text{Rb}(1)-\text{O}(1)=3.28\text{ \AA}$, $\text{Rb}(1)-\text{O}(4)=3.11\text{ \AA}$, and $\text{Rb}(1)-\text{O}(4)=3.16\text{ \AA}$), while Rb^+ ions at $\text{Rb}(2)$ are strongly bound to the framework oxygens ($\text{Rb}(2)-\text{O}(4)=2.66(7)\text{ \AA}$, $\text{Rb}(2)-\text{O}(1)=3.09(7)\text{ \AA}$, and $\text{Rb}(2)-\text{O}(1)'=3.05(7)\text{ \AA}$). For comparison the sum of the corresponding ionic radii is $1.47+1.32=2.79\text{ \AA}$ (Weast, 1989, 1990).

The Na^+ ions at $\text{Na}(2)$ lie at site $1'$, in the sodalite cavity opposite double six-rings (D6R's). This 32-fold position is also fully occupied. Each Na^+ ion coordinates at $2.36(2)\text{ \AA}$ to three $\text{O}(3)$ framework oxygens, and is recessed ca. 1.01 \AA into sodalite cavity from their plane.

$\text{Na}(4)$ is at the very center of the sodalite cavity. This eight-fold position is fully occupied by Na species which, because they are very far from the framework oxygens, must essentially be sodium atoms. Also the $\text{Na}(2)-\text{Na}(4)$ distances, $2.80(2)\text{ \AA}$, indicate that the $\text{Na}(2)-\text{Na}(4)$ interactions must be moderated by excess electron density. Each $\text{Na}(4)$ atom coordinates tetrahedrally (exactly by symmetry) to four Na^+ ions at $\text{Na}(2)$ to form a Na_5^{4+} cluster. Na_5^{4+} is tetrahedral and shows the full symmetry of its site, T_h , at the center of the sodalite cavity (see Figure 1).

$\text{Na}(3)$ is at the center of a D6R. Only about six Na species ($\text{esd}=1.4$) are found at this 16-fold position. The $\text{Na}(3)-\text{O}(3)$ distance, $2.66(2)\text{ \AA}$, may be too long to be a $\text{Na}^+-\text{O}^{2-}$ interaction (although such long distances have been found before for Na^+ at this site) but the $\text{Na}(3)-\text{Na}(2)$ distance, $2.62(3)\text{ \AA}$, is certainly too short to be an unmoderated Na^+-Na^+ interaction. $\text{Na}(3)$ therefore appears to be essentially reduced and the $\text{Na}(3)-\text{Na}(2)$ interaction must be something of a Na^0-Na^+ interaction. The valence electron from the Na^0 atoms retained by this crystal are in the sodalite unit/double six-ring system, delocalized among the $\text{Na}(2)$, $\text{Na}(3)$ and $\text{Na}(4)$ positions.

On average, each Na_5^{4+} cluster is surrounded by $1.5(\text{esd}=0.35)$ Na^0 atoms at $\text{Na}(3)$. These

bridge linearly between Na_5^{4+} clusters to form agglomerations such as short zig-zag chains.

The Na_5^{4+} cluster is stabilized by charge delocalization (1 electron per Na_5^{4+}), with some additional electron density (likely) from the bridging $\text{Na}(3)$ sodium atoms. $\text{Na}(2)-\text{O}(3)$ interactions maintain this cluster at its position within the sodalite cavity.

This cluster does not appear to be the Na_5^{4+} cluster identified by ESR, because its atoms are not all equivalent. Of course, if these sodium exchange rapidly, they may appear equivalent to ESR. Perhaps the four ions per sodalite cavity at $\text{Na}(2)$ are responsible for the ESR signals which have been attribute to Na_5^{3+} .

In summary, a fraction of Na^+ ions in Na-X were reduced by $\text{Rb}(g)$ $350\text{ }^\circ\text{C}$. Some of the Na^0 atoms produced retained at the centers of the sodalite cavities and at the centers of D6R. Each sodalite cavity contains a tetrahedral Na_5^{4+} cluster. These are linked together to some degree by bridging Na^0 atoms in double 6-rings.

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