

# Crystal Structure of Fully Dehydrated Partially Cs<sup>+</sup>-Exchanged Zeolite X, Cs<sub>52</sub>Na<sub>40</sub>-X (The Highest Cs<sup>+</sup>-Exchanged Level Achieved by Conventional Method and Confirmation of Special Site Selectivity)

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The crystal structure of fully dehydrated partially Cs<sup>+</sup>-exchanged zeolite X, [Cs<sub>52</sub>Na<sub>40</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>],  $a = 24.9765(10)$  Å, has been determined by single-crystal X-ray diffraction techniques in the cubic space group  $Fd\bar{3}$  at 21 °C. The crystal was prepared by flow method for 5 days using exchange solution in which mole ratio of CsOH and CsNO<sub>3</sub> was 1 : 1 with total concentration of 0.05 M. The crystal was then dehydrated at 400 °C and  $2 \times 10^{-6}$  Torr for 2 days. The structure was refined to the final error indices,  $R_1 = 0.051$  and  $wR_2$  (based on  $F^2$ ) = 0.094 with 247 reflections for which  $F_o > 4\sigma(F_o)$ . In this structure, about fifty-two Cs<sup>+</sup> ions per unit cell are located at six different crystallographic sites with special selectivity; about one Cs<sup>+</sup> ion is located at site I, at the centers of double oxygen-rings (D6Rs), two Cs<sup>+</sup> ions are located at site I', and six Cs<sup>+</sup> ions are found at site II'. This is contrary to common view that Cs<sup>+</sup> ions cannot pass sodalite cavities nor D6Rs because six-ring entrances are too small. Ring-opening by the formation of -OH groups and ring-flexing make Cs<sup>+</sup> ions at sites I, I', and II' enter six-oxygen rings. The defects of zeolite frameworks also give enough mobility to Cs<sup>+</sup> ions to enter sodalite cavities and D6Rs. Another six Cs<sup>+</sup> ions are found at site II, thirty-six are located at site III, and one is located at site III' in the supercage, respectively. Forty Na<sup>+</sup> ions per unit cell are located at two different crystallographic sites; about fourteen are located at site I, the centers of D6Rs and twenty-six are also located at site II in the supercage. Cs<sup>+</sup> ions and Na<sup>+</sup> ions at site II are recessed *ca.* 0.34(1) Å and 1.91(1) Å into the supercage, respectively. In this work, the highest exchange level of Cs<sup>+</sup> ions per unit cell was achieved in zeolite X by conventional aqueous solution methods and it was also shown that Cs<sup>+</sup> ion could pass through the six-oxygen rings.

**Key Words :** Zeolite X, Cesium, Sodium, Double six-rings, Six-rings

## Introduction

Many investigations have been committed to the characterization of cation distribution in faujasite-type zeolites. Zeolite X has a framework with a structure similar to that of the natural mineral faujasite. The chemical composition can vary according to the silicon and aluminum content from a Si/Al ratio = 1.0-1.5. The increase in the aluminum content leads to the increase of the number of exchangeable cations and affects their distribution in the different possible sites in the framework cavities. Zeolite X has a wide range of industrial application primarily due to the excellent stability of the crystal structure and a large available pore volume and surface area.<sup>1</sup> In addition to the accessible pore volume, the adsorptive and catalytic properties of zeolites depend on the size, charge density, and distribution of cations in the lattice.

Among alkali-metal cations, Cs<sup>+</sup>-exchanged zeolite X is an active base catalyst for the reaction of ethylene oxide and carbon dioxide to form ethylene carbonate.<sup>2</sup> Basic zeolites are well-adapted catalysts for selective condensation reactions.<sup>3</sup>

Beginning in 1956, Breck *et al.* reported that Cs<sup>+</sup> ion exchange into zeolite A with a 100% excess of Cs<sup>+</sup> (0.14 M aqueous solution at 90 °C) resulted in the replacement of only 31% of the Na<sup>+</sup> ions in the structure.<sup>4</sup> Later Barrier *et*

*al.* increased the level of Cs<sup>+</sup> exchange to 45% by the exposing the zeolite to successive concentrated aqueous solution at 25 °C.<sup>5</sup> When "adjusted to a standard equilibrium solution strength" of 0.01 M, the level of Cs<sup>+</sup> exchange of zeolite A was calculated to be about 60%, about 7/12.<sup>5,6</sup>

In 1987, Seff and Heo<sup>7</sup> succeeded in preparing fully dehydrated, fully Cs<sup>+</sup>-exchanged zeolite A with cesium vapor. In 1991, single crystal of Cs<sub>92</sub>-X-36Cs<sup>8</sup> was synthesized by exposing Na-X to the all sodalite and supercages are full of cesiums in its structure.

In zeolite NaY, a maximum of about 70% of the Na<sup>+</sup> cations can be replaced by Cs<sup>+</sup> by applying ion exchange in aqueous cesium salt solution at room temperature. This limit in the degree of exchange has been interpreted in terms of the inability of the bulky cesium cations (ionic diameter *ca.* 3.38 Å)<sup>9</sup> to enter the sodalite cavities and hexagonal prisms in the faujasite structure through the small six-ring windows (van der Waals diameter (aperture) *ca.* 2.2 Å).<sup>10,11,12</sup> For the same reason, and perhaps also because the double six-rings (D6Rs) are too small in volume, Cs<sup>+</sup> ions should never occupy D6Rs.

However, Cs<sup>+</sup> ions were found in the sodalite cavities of fully anhydrous FAU and LTA in the following structures determined by single-crystal X-ray crystallography. The number of Cs<sup>+</sup> ions per unit cell in sodalite cavities are:

7.3(2) in  $\text{Mn}_{28}\text{Cs}_{36}\text{-X}$ ,<sup>13</sup> 5.6(1) in  $\text{Cd}_{32}\text{Cs}_{28}\text{-X}$ ,<sup>14</sup> 3.5(3) in  $\text{Ca}_{35}\text{Cs}_{22}\text{-X}$ ,<sup>15</sup> 5.7(3) in  $\text{Ca}_{29}\text{Cs}_{34}\text{-X}$ ,<sup>15</sup> 6.9(8) in  $\text{Cs}_{45}\text{Na}_{47}\text{-X}$ ,<sup>16</sup> 0.77(4) in  $\text{Ca}_{3.98}\text{Cs}_{4.04}\text{-A}$ ,<sup>17</sup> 0.70(4) in  $\text{Ca}_{3.37}\text{Cs}_{5.26}\text{-A}$ ,<sup>17</sup> 1.15(6) in  $\text{Ca}_3\text{Cs}_6\text{-A}$ ,<sup>17</sup> 1.02(4) in  $\text{Ca}_{2.8}\text{Cs}_{6.4}\text{-A}$ ,<sup>17</sup> 2.07(7) in  $\text{Ag}_2\text{Cs}_{10}\text{-A}$ ,<sup>18</sup> and 2.53(7) in  $\text{Ag}_{4.5}\text{Cs}_{13.5}\text{-A}$  (contains reduced cesium and silver clusters).<sup>19</sup>

On the other hand, XRD studies revealed that cesium cations are located inside the sodalite cages and hexagonal prisms of dehydrated cesium-exchanged faujasite,<sup>8,20,21</sup> and inside the sodalite cages of zeolite Cs-A.<sup>22,23</sup>

In spite of a number of attempts, fully  $\text{Cs}^+$ -exchanged zeolite for  $\text{Na}^+$  in zeolite X has not been achieved by conventional aqueous methods of ion exchange.<sup>12,16,24,25</sup>

This work was done to confirm the special cation site selectivity that  $\text{Cs}^+$  ions can occupy double six-rings. In addition, it was hoped that fully  $\text{Cs}^+$ -exchanged zeolite X could be prepared from the conventional ion exchange method using different solution.

### Experimental Section

Large single crystals of Na-zeolite X with the stoichiometry  $\text{Na}_{92}\text{Al}_{92}\text{Si}_{100}\text{O}_{384}$  were prepared in St. Petersburg, Russia.<sup>26</sup> The crystal which was a colorless octahedron about 0.20 mm in cross-section was lodged in a fine Pyrex capillary.

To prepare fully  $\text{Cs}^+$ -exchanged zeolite X, an exchange solution of CsOH (the purest available, Aldrich, 99.9%; impurities: 1000 ppm total metal (max), K 60 ppm, Na 30 ppm, S 6 ppm, Si 4 ppm, Rb 2 ppm, Sn 2 ppm, Al 1 ppm, Mo 1 ppm, Sb 1 ppm, Sr 0.6 ppm, Ba 0.4 ppm, B 0.2 ppm) and  $\text{CsNO}_3$  (Aldrich, 99.999%) in the molar ratio of 1 : 1 with total concentration of 0.05 M was used. Ion exchange was accomplished by flow methods; the solution was allowed to flow past the crystal at a velocity of approximately 1.5 cm/s for 5 days at 24(1) °C. The clear, colorless, hydrated  $\text{Cs}^+$ -exchanged zeolite X was dehydrated at 400 °C and  $2 \times 10^{-6}$  Torr for 2 days. While still under vacuum, the crystal was allowed to cool to room temperature and was sealed in its capillary by torch. Microscopic examination showed it to be light brownish-yellow in color. Subsequent diffraction experiments were performed at 24(1) °C.

The cubic space group  $Fd\bar{3}$  was used throughout this work. Diffraction data were collected with an automated Enraf-Nonius four-circle computer controlled CAD-4 diffractometer equipped with a pulse-height analyzer and a graphite monochromator, using Mo  $K\alpha$  radiation ( $K\alpha_1$ ,  $\lambda = 0.70903$  Å;  $K\alpha_2$ ,  $\lambda = 0.71359$  Å). The unit cell constant,  $a = 24.9765(10)$  Å was determined by a least-squares refinement of 25 intense reflections for which  $14^\circ < 2\theta < 24^\circ$  for dehydrated  $\text{Cs}^+$ -exchanged zeolite X.

All unique reflections in the positive octant of an  $F$ -centered unit cell for which  $2\theta < 60^\circ$ ,  $l > h$ , and  $k > h$  were recorded at 21(1) °C. Of the 1118 reflections examined, only the 247 whose net counts exceeded three times their corresponding estimated standard deviations were used in structure solution and refinement.

The intensities were corrected for Lorentz and polarization effects. An absorption correction ( $\mu R = 0.361$ ,  $\rho_{\text{calc}} = 2.053$  g/cm<sup>3</sup>)<sup>27</sup> was made empirically using a  $\psi$  scan. The calculated transmission coefficients ranged from 0.981 to 0.995. This correction had little effect on the final  $R$  indices. The structures were solved by the direct method (SHELXS 97) and refined by full-matrix least squares technique (SHELXL 97).<sup>28</sup>

Further details of the crystal structure investigation(s) may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49)7247-808-666; e-mail: [crysdata@fiz-karlsruhe.de](mailto:crysdata@fiz-karlsruhe.de), [http://www.fiz-karlsruhe.de/ecid/Internet/en/DB/icsd/depot\\_anforderung.html](http://www.fiz-karlsruhe.de/ecid/Internet/en/DB/icsd/depot_anforderung.html)) on quoting the deposition number CSD-417467.

### Structure Determination

Full-matrix least-squares refinement was initiated with atomic thermal parameters of the framework atoms [Si, Al, O(1), O(2), O(3), and O(4)] in the  $\text{Mn}_{28}\text{Cs}_{36}\text{-X}$ .<sup>29</sup> Isotropic refinement of the framework atoms converged to an  $R_1$  index,  $(\sum F_o - F_c)/F_o$  of 0.41 and a weighted  $R_2$  index,  $(\sum w(F_o - F_c)^2 / \sum w F_o^2)^{1/2}$  of 0.77.

A difference fourier function revealed four large peaks at (0.4217, 0.125, 0.125), (0.0, 0.0, 0.0), (0.1698, 0.1698, 0.1698), and (0.2582, 0.2582, 0.2582) with height of 8.4, 5.3, 4.9, and 3.5 eÅ<sup>-3</sup>, respectively. These four peaks were stable in least-square refinement. The first peak was assigned to Cs(5) at site III. The second peak refinement was performed assuming only sodium inside the hexagonal prism (D6Rs). Because of this reason, Na(1) was assigned to (0.0, 0.0, 0.0) position at site I. And the next peak was refined as Cs(4) position at site II'. The last peak of (0.2582, 0.2582, 0.2582) was assigned to Cs(3) at site II because of the long distance between this position and the oxygen atoms of the framework (2.965(11) Å). Isotropic refinement including these positions converged to  $R_1 = 0.135$  and  $wR_2 = 0.356$ .

A subsequent fourier maps showed two large peaks remaining at positions (0.2259, 0.2259, 0.2259) (site II) and (0.4208, 0.1427, 0.1110) (site III') in the supercage, and (0.0906, 0.0906, 0.0906) with peaks height of 4.1, 2.3, and 1.4 eÅ<sup>-3</sup>, respectively. The first peak was assigned to Na(2) at site II. The next peak was assigned to Cs(2) at site III', and the last peak was refined as Cs(2) at site I'.

The Na(1) at (0.0, 0.0, 0.0) showed large multiplicity of 19.7(6). This indicates that additional scattering matter ( $\text{Cs}^+$  ion) is also present at site I. Refinement with both Cs(1) and Na(1) at site I, with their thermal parameters constrained to be equal and their occupancies constrained to sum to 15.0, converged with 14.0(2)  $\text{Na}^+$  and 1.0(2)  $\text{Cs}^+$  cations (see Table 2) with  $R_1 = 0.071$  and  $wR_2 = 0.146$ . Refinements were unsuccessful without constraint of Na(1) and Cs(1).

The results of positional and thermal parameter refinement with varied occupancy numbers converged to the error indices,  $R_1 = 0.051$  and  $wR_2 = 0.093$ . The occupancy numbers of Na(1), Na(2), Cs(1), Cs(2), Cs(3), Cs(4), Cs(5), and Cs(6)

**Table 1.** Summary of Experimental Data

Empirical formula	Cs <sub>52</sub> Na <sub>40</sub> Al <sub>92</sub> Si <sub>100</sub> O <sub>384</sub>
Formula weight	19266.08
Ion exchange T (°C)	21(1)
Ion exchange t (h)	120
Data collection T (°C)	21(1)
Volume	15581.9(11) Å <sup>3</sup>
Z, Calculated density	1, 2.053 Mg/m <sup>3</sup>
Absorption coefficient	3.441 mm <sup>-1</sup>
F(000)	8968
Scan technique	θ-2θ
Radiation (Mo Kα) λ <sub>1</sub> (Å)	0.70930
λ <sub>2</sub> (Å)	0.71359
Unit cell constant, a (Å)	24.9765(10)
2θ range for a (deg)	14-24
No. of reflections for a	25
2θ range in data collection (deg)	3 < 2θ < 60
No. of unique reflections (m)	1118
No. of reflections with F <sub>o</sub> > 4σ(F <sub>o</sub> )	247
No. of parameters (s)	83
Data/parameter ratio (m/s)	13.5
Weighting parameters: a/b	0.0236/1626.9
R <sub>1</sub> <sup>a</sup> /wR <sub>2</sub> <sup>b</sup> (F <sub>o</sub> > 4σ(F <sub>o</sub> ))	0.052/0.094
R <sub>1</sub> <sup>a</sup> /wR <sub>2</sub> <sup>b</sup> (all data)	0.148/0.412
Goodness of fit <sup>c</sup>	0.960
Largest diff. peak and hole	0.987 and -0.617 e. Å <sup>-3</sup>

<sup>a</sup>R<sub>1</sub> = Σ|F<sub>o</sub> - |F<sub>c</sub>|| / ΣF<sub>o</sub>, <sup>b</sup>wR<sub>2</sub> = [Σw(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)<sup>2</sup> / Σw(F<sub>o</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup> (based on F<sup>2</sup>).  
<sup>c</sup>Goodness-of-fit = [Σw(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)<sup>2</sup> / (m - s)]<sup>1/2</sup>.

per unit cell were refined to 14.0(2), 26.2(2), 1.0(2), 2.2(4), 5.8(2), 5.5(4), 35.1(5), and 1.2(5), respectively. These were fixed at 14.0, 26.0, 1.0, 2.0, 6.0, 6.0, 36.0, and 1.0, respectively, because the cationic charge should not be exceeded 92<sup>+</sup> per Fd $\bar{3}$  unit cell as in the last column of Table 2.

**Table 2.** Positional<sup>a</sup>, Thermal, and Occupancy Parameters

Atom	Wyc. Pos.	Site	x	y	z	U <sub>11</sub> <sup>b</sup> U <sub>iso</sub> <sup>e</sup>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>	Occupancy <sup>c</sup>	
												varied	fixed
Si	96(g)		-545(4)	1243(5)	340(3)	127(45) <sup>b</sup>	198(44)	113(51)	16(54)	62(45)	51(57)		96 <sup>d</sup>
Al	96(g)		-542(3)	358(3)	1217(5)	159(47)	26(48)	59(45)	5(44)	-72(53)	-27(48)		96
O(1)	96(g)		-1125(8)	-13(9)	1087(8)	284(162)	520(136)	111(122)	-283(128)	-29(89)	57(104)		96
O(2)	96(g)		-36(8)	-57(8)	1440(7)	54(110)	146(116)	211(112)	77(87)	4(88)	36(101)		96
O(3)	96(g)		-353(9)	686(8)	643(7)	309(126)	178(139)	0(123)	126(115)	133(119)	75(88)		96
O(4)	96(g)		-663(7)	786(8)	1719(8)	310(130)	87(122)	150(127)	-77(121)	95(128)	-14(88)		96
Na(1)	16(c)	I	0	0	0	121(74) <sup>e</sup>						14.0(2)	14.0
Na(2)	32(e)	II	2261(9)	2261(9)	2261(9)	573(87)	573(87)	573(87)	166(125)	166(125)	166(125)	26.2(2)	26.0
Cs(1)	16(c)	I	0	0	0	121(74) <sup>e</sup>						1.0(2)	1.0
Cs(2)	32(e)	I'	902(21)	902(21)	902(21)	927(425)	927(425)	927(425)	-68(283)	-68(283)	-68(283)	2.2(4)	2.0
Cs(3)	32(e)	II	2621(5)	2621(5)	2621(5)	264(63)	264(63)	264(63)	-25(56)	-25(56)	-25(56)	5.8(2)	6.0
Cs(4)	32(e)	II'	1652(7)	1652(7)	1652(7)	639(142)	639(142)	639(142)	-143(98)	-143(98)	-143(98)	5.5(4)	6.0
Cs(5)	48(f)	III	4194(2)	1250	1250	204(25)	837(49)	892(57)	0	0	-226(42)	35.1(5)	36.0
Cs(6)	96(g)	III'	4375(46)	1701(55)	875(59)	32(467) <sup>f</sup>						1.2(5)	1.0

<sup>a</sup>Positional and anisotropic thermal parameters are given × 10<sup>4</sup>. Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. <sup>b</sup>The anisotropic temperature factor = exp[-(2π<sup>2</sup>/a<sup>2</sup>)(U<sub>11</sub>h<sup>2</sup> + U<sub>22</sub>k<sup>2</sup> + U<sub>33</sub>l<sup>2</sup> + U<sub>12</sub>hk + U<sub>13</sub>hl + U<sub>23</sub>kl)]. <sup>c</sup>Occupancy factors are given as the number of atoms or ions per unit cell. <sup>d</sup>Occupancy for Si = 96. <sup>e</sup>Constrained to be equal. <sup>f</sup>U<sub>iso</sub> (Å<sup>2</sup> × 10<sup>4</sup>).

**Table 3.** Selected Interatomic Distances (Å) and Angles (deg)<sup>a</sup> of Cs<sub>52</sub>Na<sub>40</sub>X

Si-O(1)	1.618(13)	O(2)-Si-O(3)	107.3(6)
Si-O(2)	1.609(13)	O(2)-Si-O(4)	108.7(6)
Si-O(3)	1.662(13)	O(3)-Si-O(4)	110.9(6)
Si-O(4)	1.638(14)	O(1)-Al-O(2)	111.7(7)
<b>Mean</b>	<b>1.632</b>	O(1)-Al-O(3)	108.5(7)
Al-O(1)	1.738(13)	O(1)-Al-O(4)	108.8(6)
Al-O(2)	1.724(13)	O(2)-Al-O(3)	109.7(6)
Al-O(3)	1.722(13)	O(2)-Al-O(4)	106.5(6)
Al-O(4)	1.683(14)	O(3)-Al-O(4)	111.7(5)
<b>Mean</b>	<b>1.717</b>	Si-O(1)-Al	125.4(7)
Na(1)-O(3)	2.498(10)	Si-O(2)-Al	141.5(7)
Na(2)-O(2)	2.288(10)	Si-O(3)-Al	134.1(7)
Cs(1)-O(3)	2.498(10)	Si-O(4)-Al	157.9(7)
Cs(2)-O(3)	3.17(4)		
Cs(3)-O(2)	2.965(11)	O(3)-Na(1)-O(3)	91.3(4)/88.7(4)
Cs(4)-O(2)	3.211(16)	O(2)-Na(2)-O(2)	117.7(3)
Cs(5)-O(4)	3.058(11)	O(3)-Cs(1)-O(3)	91.3(4)/88.7(4)
Cs(6)-O(1)	2.88(4)	O(3)-Cs(2)-O(3)	68.6(9)
Cs(6)-O(2)	2.94(8)	O(2)-Cs(3)-O(2)	82.7(4)
		O(2)-Cs(4)-O(2)	75.2(4)
O(1)-Si-O(2)	112.7(6)	O(4)-Cs(5)-O(4)	65.4(4)
O(1)-Si-O(3)	109.4(7)	O(1)-Cs(6)-O(1)	83.0(16)
O(1)-Si-O(4)	108.8(6)	O(1)-Cs(6)-O(2)	53.7(12)

<sup>a</sup>Numbers in parentheses are the estimated standard deviations in the least significant digit given for the corresponding value.

All shifts in the final cycle of least-squares refinement were less than 0.1% of their corresponding standard deviations. The final error indices converged to R<sub>1</sub> = 0.052 and wR<sub>2</sub> = 0.094.

Atomic scattering factors<sup>30,31</sup> were modified to account for anomalous dispersion.<sup>32</sup> The final structural parameters and selected interatomic distances and angles are presented in Tables 2 and 3, respectively.

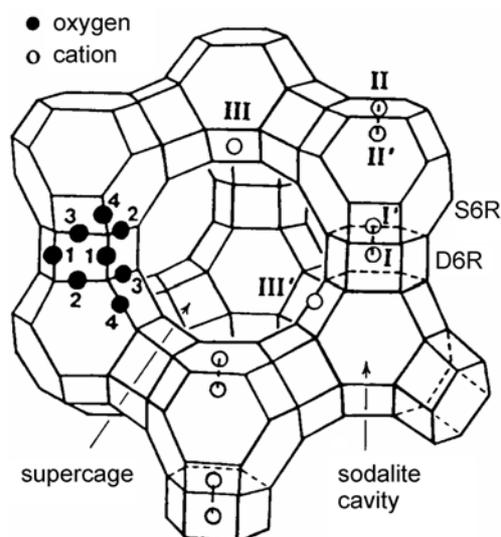
## Discussion

In the crystal structure of the dehydrated  $\text{Cs}_{52}\text{Na}_{40}\text{-X}$ , the structural data of framework show that Si-O distances are 1.609(13)-1.662(13) Å and Al-O distances 1.683(14)-1.738(13) Å; the mean values of the Si-O and Al-O bond lengths are 1.632 Å and 1.717 Å, respectively. The O-Si-O bond angles range from 107.3(6)° to 112.7(6)° and O-Al-O bond angles also range from 106.5(6)° to 111.7(7)° (see Table 3). Otherwise, the large difference between the smallest (125.4(7)°) and the largest (157.9(7)°) Si-O-Al angle indicates a distortion of the flexible framework by the cation coordination in the dehydrated zeolite X.

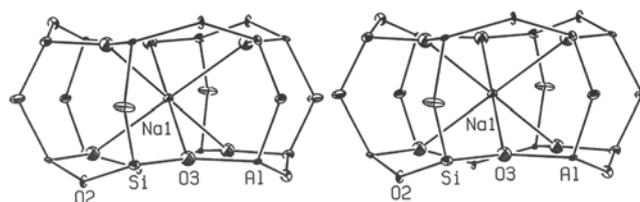
The extra-framework cations that compensate for the negative charge of the framework occupy the various positions, called the site I, I', II, II', III, and III' (see Figure 1). The site I is in the center of hexagonal prism (D6R). The site I' in the sodalite ( $\beta$ ) cavity on the opposite side of one of the D6Rs from site I. The site II is in the supercage adjacent to the single six-oxygen ring. The site II' is inside the sodalite cavity near a S6R entrance to the supercage. The site III lies in supercage opposite 4-ring and the site III' lies at a little bit off the site III.

In this structure, fifty-two  $\text{Cs}^+$  ions per unit cell are located at six different crystallographic sites and forty  $\text{Na}^+$  ions per unit cell are found at two different crystallographic sites.

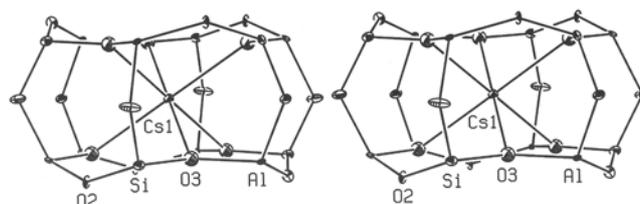
The site I position in the hexagonal prism is occupied by  $\text{Na}^+$  ions (Na(1)) and  $\text{Cs}^+$  ion (Cs(1)) (see Table 1). The occupancy parameter of the site I cannot be determined with high accuracy because a slight increase of the occupancy parameter of Cs(1) leads to a large decrease in the occupancy parameter of Na(1). Therefore, the occupancy and isotropic thermal parameter of Cs(1) was constrained to those of



**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. Si substitutes for about 4% of the Al's at the Al position. Extra-framework cation positions are labeled with Roman numerals.



**Figure 2.** A stereoview of the double 6-ring (D6R). One  $\text{Na}^+$  ion at Na(1) lie at site I. About 88% of the D6R may have this arrangement. Ellipsoids of 20% probability are shown.



**Figure 3.** A stereoview of the double 6-ring (D6R). One  $\text{Cs}^+$  ion at Cs(1) lie at site I. About 6.3% of the D6R may have this arrangement. Ellipsoids of 20% probability are shown.

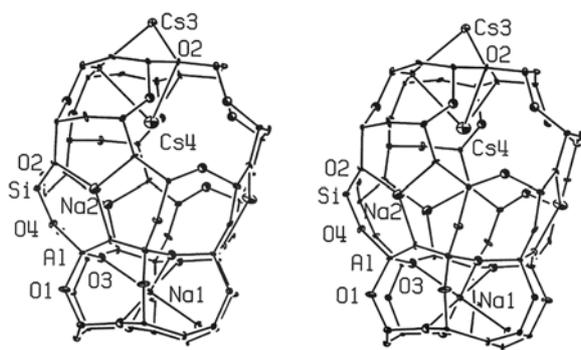
Na(1). Because of two site I'  $\text{Cs}^+$  ions at Cs(2) per unit cell with a Cs(2)-O(3) distance of 3.17(4) Å, only 15 sites I are available for cations. The two  $\text{Cs}^+$  ions at Cs(2) must occupy site I', about one double six-ring per unit cell which is empty of  $\text{Na}^+$  ion (Na(1)). According to the population refinement, the site I is occupied by about fourteen  $\text{Na}^+$  ions and about one  $\text{Cs}^+$  ion (see Figures 2 and 3). The distance of Na(1) and Cs(1) to the framework oxygen atoms are 2.498(10) Å as shown in Table 3. The distance is reasonably a little longer than the sum of the conventional  $\text{Na}^+$  and  $\text{O}^{2-}$ ,  $0.97 + 1.32 = 2.29$  Å.<sup>9</sup> The Cs(1)-O(3) distance is somewhat shorter than the sum of the ionic radii of  $\text{Cs}^+$  and  $\text{O}^{2-}$ ,  $3.01$  Å.<sup>9</sup> If Cs(1) is omitted in this structure, the *R* value is significantly higher.

The Cs(4) position is at site II' on a threefold axis in the sodalite cavity. Each  $\text{Cs}^+$  ion at Cs(4) lies 2.28 Å from the plane of the three O(2) framework oxygens (Table 4). The Cs(4)-O(2) distances are 3.211(16) Å, somewhat longer than the sum of the corresponding ionic radii of  $\text{Cs}^+$  and  $\text{O}^{2-}$ ,  $1.69 + 1.32 = 3.01$  Å<sup>9</sup> (see Figure 4 and Table 3).  $\text{Cs}^+$  ions at site I, I', and II' must have passed through six-rings. The site II of 32-fold positions in the supercage are fully occupied by twenty-six  $\text{Na}^+$  ions (Na(2) and six  $\text{Cs}^+$  ions (Cs(3)), which

**Table 4.** Deviations (Å) of Cations from 6-ring Planes

$\text{Cs}_{52}\text{Na}_{40}\text{-X}$		
at O(3) <sup>a</sup>	Na(1)	-1.40
	Cs(1)	-1.40
	Cs(2)	2.50
at O(2) <sup>b</sup>	Na(2)	0.35
	Cs(3)	1.92
	Cs(4)	-2.28

<sup>a</sup>A positive deviation indicates that the atom lies in the sodalite cavity and a negative deviation indicates that the atom lies in the D6R. <sup>b</sup>A positive deviation indicates that the atom lies in the supercage and a negative deviation indicates that the atom lies in the sodalite cavity.



**Figure 4.** A stereoview of the sodalite cavity and D6R of dehydrated Cs<sub>52</sub>Na<sub>40</sub>-X. Three Na<sup>+</sup> ions at Na(2) and one Cs<sup>+</sup> ion at Cs(3) lie at site II. One Cs<sup>+</sup> ion at Cs(4) lie at site II'. About 75% of the sodalite cavities may have this arrangement. The remaining 25% may have only four Na<sup>+</sup> at Na(2). Ellipsoids of 20% probability are shown.

are found at two different positions. The distances of Na(2)-O(2) are 2.288(10) Å, which is the same distance as the sum of the ionic radii, 0.95 + 1.32 = 2.27 Å.<sup>9</sup> The distances of Cs(3)-O(2) are 2.965(11) Å, shorter than the sum of corresponding ionic radii (3.01 Å)<sup>9</sup> (Table 3). This indicates that each Cs<sup>+</sup> ion at Cs(3) coordinates somewhat tightly to its three O(2) oxygens. Each Na<sup>+</sup> ion at Na(2) is recessed *ca.* 0.35 Å and each Cs<sup>+</sup> ion at Cs(3) is recessed *ca.* 1.92 Å into the supercage from its 6-ring plane (see Figure 4 and Table 4).

Thirty-six Cs<sup>+</sup> ions at Cs(5) lie in the supercage at site III. This is 48-fold position, but this is occupied by only 36 Cs<sup>+</sup> ions (see Figure 6). These large ions are located mainly in site III. The distances of Cs(5)-O(4) are 3.058(11) Å, which are nearly the same distance as the sum of ionic radii (Table 3).

One Cs<sup>+</sup> ion at Cs(6) of 96-fold position lies in the supercage at site III'. The Cs<sup>+</sup> ion at Cs(6) binds tightly to framework oxygens (O(1)/O(2)) at 2.88(4)/2.94(8) Å. These distances are much shorter than the sum of the ionic radii as previous work.<sup>14</sup>

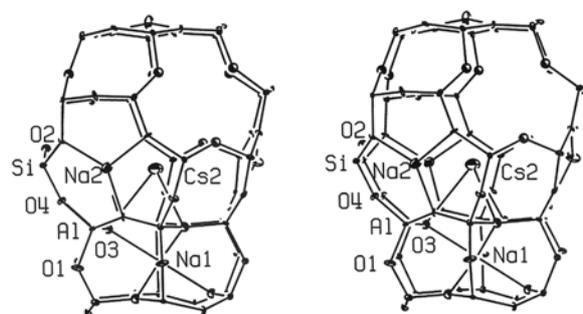
The first interesting feature of the cation distribution is a migration of unexchanged sodium ions into the hexagonal prism (D6R) during the dehydration. Because Cs<sup>+</sup> ions preferentially occupy large cavity, particularly site III, Na<sup>+</sup> ions occupy site I. The occupancy of site I by Na<sup>+</sup> ion appears to be a consequence of cation crowding,<sup>33</sup> the inability of large cations to fit into six-rings leads to shorter intercationic distances. It is this cation crowding that is responsible for the reluctance of Cs<sup>+</sup> to exchange completely for Na<sup>+</sup> into FAU from aqueous solution, not the inability of Cs<sup>+</sup> to enter sodalite cavities and D6Rs.<sup>12</sup> Compared with other structure refinement,<sup>14</sup> this result indicates close similarities of the cation distribution in site I. Yu. F. Shepelev *et al.* assumed that about one Cs<sup>+</sup> ion is located at site I.<sup>21</sup>

In CsNaY zeolites, H. Koller *et al.* revealed that both Cs<sup>+</sup> and Na<sup>+</sup> ions were found at site I. Furthermore, Na<sup>+</sup> ions at site I are replaced by Cs<sup>+</sup> ions at high cesium exchange

**Table 5.** Distribution of Nonframework Atoms in Cs<sub>52</sub>Na<sub>40</sub>-X

Site	Atoms	Number
I	Na(1)	14 <sup>a</sup>
	Cs(1)	1 <sup>a</sup>
I'	Cs(2)	2 <sup>a</sup>
II	Na(2)	26 <sup>b</sup>
	Cs(3)	6
II'	Cs(4)	6 <sup>c</sup>
III	Cs(5)	36
III'	Cs(6)	1

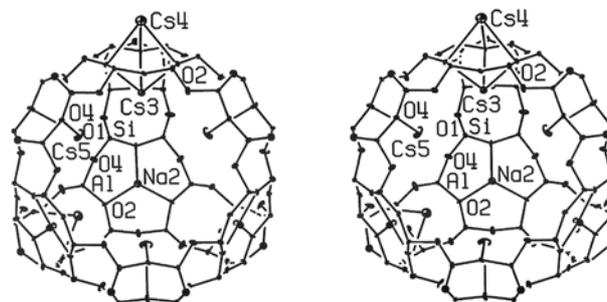
<sup>a</sup>Sum of occupancies is 16 ((14+1) at site I + 1/2(2) at site I'). <sup>b</sup>Site II is fully occupied with 26 + 6 = 32 cations. <sup>c</sup>Because the Cs(4)-Na(2) distance (2.63(5) Å) would be too short, the ions at Cs(4) and Cs(3) must share the same six-ring. This is shown in Figures 3 and 4.



**Figure 5.** A stereoview of the sodalite cavity and D6R of dehydrated Cs<sub>52</sub>Na<sub>40</sub>-X. Four Na<sup>+</sup> ions at Na(2) and one Cs<sup>+</sup> ion at Cs(2) lie at site I'. About 25% of the sodalite cavities may have this arrangement. Ellipsoids of 20% probability are shown.

levels. Upon increasing the calcination temperature of the 72% cesium-exchanged sample from 473 K to 773 K, further migration of Cs<sup>+</sup> and Na<sup>+</sup> to site I is observed. Consequently, cesium exchange levels up to 90% were achieved by a three-fold exchange-calcination cycle of the 72% cesium-exchanged sample without damage of the zeolite structure.<sup>34</sup>

In addition, the Cs<sup>+</sup> ions get through all 6-ring windows and are located at all different crystallographic sites. The site I' and II' positions in the sodalite cavities are occupied by only cesium cations (Cs(2) and Cs(4)) (see Figures 4 and 5). When water is present, including at room temperature, ring-



**Figure 6.** A stereoview of the supercage of dehydrated Cs<sub>52</sub>Na<sub>40</sub>-X. Four Cs<sup>+</sup> ions at Cs(5) and three Na<sup>+</sup> ions at Na(2) lie at site III and II. One Cs<sup>+</sup> ion at Cs(3) and one Cs<sup>+</sup> ion at Cs(4) lie at site II and II'. About 62.5% of the supercages may have this arrangement. About 25% may have six Cs<sup>+</sup> ions at Cs(5). The remaining 12.5% one Cs<sup>+</sup> ion at Cs(6) lie at site III'. Ellipsoids of 20% probability are shown.

opening to give Al-OH and HO-Si may occur. In hydrated Cs<sub>7</sub>Na<sub>5</sub>-A, each sodalite cavity contains a Cs<sup>+</sup> ion even though elevated temperature were not used.<sup>35</sup> In the structure of NaX·nNaI, D. H. Olson hypothesized that a ring-opening mechanism facilitated by the presence of H<sup>+</sup> ions (to give terminal -OH groups) had allowed the passage of these large anions through six-rings.<sup>36</sup> It shows that Cs<sup>+</sup> ion can also pass through double six-rings with ring-flexing and ring-opening. Because of the large size of cesium ion and occupation, Cs(4) cations lie at the opposite site of Cs(2) position. It was also proved that Cs<sup>+</sup> ions in the sodalite cavity could pass through the six-rings.

The second important result is the highest Cs<sup>+</sup> ion-exchanged level in dehydrated zeolite X. As the previous work,<sup>21</sup> the present study proved that achievement of fully exchanged dehydrated Cs<sub>92</sub>-X was impossible by the conventional method of ionic exchange solution. But, the highest Cs<sup>+</sup> ion-exchanged level (57%) in zeolite X was achieved by conventional aqueous solution methods at room temperature.

**Supporting Information Available:** Tables of calculated and observed structure factors (3 pages). The supporting materials are available *via* the Internet <http://www.kcsnet.or.kr/bkcs>.

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