Synthesis and Characterization of the Large Single Crystal of Fully K⁺-exchanged Zeolite X (FAU), |K₈₀|[Si₁₁₂Al₈₀O₃₈₄]-FAU (Si/Al = 1.41)

Woo Taik Lim,[1,*] **Gyo Cheol Jeong,**[2] **Chang Kun Park,**[3] **Jong Sam Park,**[4] and **Young Hun Kim**[5,*]

[1]*Department of Applied Chemistry, Andong National University, Andong 760-749, Korea.* *E-mail: wtlim@andong.ac.kr
[2]Department of Earth and Environmental Sciences, Andong National University, Andong 760-749, Korea
[3]Department of Civil Engineering, Kwandong University, Yangyang 215-802, Korea
[4]Department of Radiologic Technology, Daegu Health College, Daegu 702-722, Korea
[5]Department of Environmental Engineering, Andong National University, Andong 760-749, Korea*
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Large colorless single crystals of sodium zeolite X, stoichiometry |Na₈₀|[Si₁₁₂Al₈₀O₃₈₄]-FAU, with diameters up to 200 μm and Si/Al = 1.41 have been synthesized from gels with the composition of 2.40SiO₂ : 2.00NaAlO₂ : 7.52NaOH : 454H₂O : 5.00TEA. One of these, a colorless octahedron about 200 μm in cross-section has been treated with aqueous 0.1 M KNO₃ for the preparation of K⁺-exchanged zeolite X. The crystal structure of |K₈₀|[Si₁₁₂Al₈₀O₃₈₄]-FAU per unit cell, a = 24.838(4) Å, dehydrated at 673 K and 1×10^{-6} Torr, has been determined by single-crystal X-ray diffraction techniques in the cubic space group $Fd\bar{3}$ at 294 K. The structure was refined using all intensities to the final error indices (using only the 707 reflections for which $F_o > 4\sigma(F_o)$) R_1 = 0.075 (based on F) and R_2 = 0.236 (based on F^2). About 80 K⁺ ions per unit cell are found at an unusually large number of crystallographically distinct positions, eight. Eleven K⁺ ions are at the centers of double 6-rings (D6Rs, site I; K-O = 2.492(6) Å and O-K-O (octahedral) = 88.45(22)° and 91.55(22)°). Site-I' position (in the sodalite cavities opposite D6Rs) is occupied by five K⁺ ions per unit cell; these K⁺ ions are recessed 1.92 Å into the sodalite cavities from their 3-oxygen planes (K-O = 2.820(19) Å, and O-K-O = 78.6(6)°). Twety-three K⁺ ions are found at three nonequivalent site II (in the supercage) with occupancies of 5, 9, and 9 ions; these K⁺ ions are recessed 0.43 Å, 0.75 Å, and 1.55 Å, respectively, into the supercage from the three oxygens to which it is bound (K-O = 2.36(13) Å, 2.45(13) Å, and 2.710(13) Å, O-K-O = 116.5(20)°, 110.1(17)°, and 90.4(6)°, respectively). The remaining sixteen, thirteen, and twelve K⁺ ions occupy three sites III' near triple 4-rings in the supercage (K-O = 2.64(3) Å, 2.94(3) Å, 2.73(5) Å, 2.96(6) Å, 3.06(4) Å, and 3.08(3) Å).

Key Words : Zeolite, Crystal structure, Ion exchange, Potassium, Dehydrated

Introduction

One of the most frequently used and informative techniques for characterization of cations in zeolite framework is single-crystal X-ray diffraction. The large single crystals of zeolite should be grown to minimum of 80 μm to be examined in the single-crystal X-ray diffractometer. The growth of large single crystals of zeolite is of interest in order to obtain the 3-dimensional structural parameters of the framework, and the information on the exchangeable cations, and the adsorbate. For example, Sacco *et al.*[1-3] synthesized the large single crystals of faujasite-type zeolites (Si/Al = 1.35~1.45, 1.71, and 1.90) with diameters of 95 to 340 μm from a reaction mixture composed of Na₂O, Al₂O₃, SiO₂, H₂O, TEA, and/or TCl. They reported their synthesized single crystals were suitable for single-crystals X-ray diffraction experiments.

The properties of zeolites are contingent on their cation content. The thermal stability, the sorption properties, and catalytic characteristics are dependant on the kind, number, and distribution of exchangeable cations.[4] The kind, number, and distribution of exchangeable cations in zeolites has been comprehensively studied using X-ray diffraction method.[5-9]

The exchangeable K⁺ ions in faujasite-type zeolites have

been widely studied by single-crystal X-ray diffraction methods.[5-9] Smith *et al.*[5] investigated a dehydrated K⁺-exchanged natural faujasite (Si/Al = 2.3) by single-crystal X-ray diffraction. Using single-crystal X-ray diffraction techniques in the cubic space group $Fd\bar{3}$ at 24(1) °C, Kim *et al.*[6] determined the structure of fully dehydrated, fully K⁺-exchanged zeolite X (Si/Al = 1.09). This crystal was prepared by the flow method with a 0.05 M aqueous exchange solution 0.025 M in KNO₃ and 0.025 M in KOH at 24(1) °C for 5 days. Seff *et al.*[7] prepared fully dehydrated fully K⁺-exchanged zeolite X using flowing aqueous 0.1 M KNO₃, with pH adjusted to 12 using KOH, at 353 K, and determined its structure through single-crystal X-ray diffraction methods in the cubic space group $Fd\bar{3}m$ at 21 °C. Both Kim *et al.*[6] and Seff *et al.*[7] noted that there are many more K⁺ equipoints in dehydrated K₉₂-X than there are Na⁺ equipoints in dehydrated |Na₉₂|[Si₁₀₀Al₉₂O₃₈₄]-FAU,[8] and suggested that complete K⁺-exchange is not readily achieved for large crystals. They also described some unusually close K⁺···K⁺ contacts as cation crowding. The K⁺ ions seemed to be trying to maximize their contact distances even though they must increase some or all of their distances to framework oxygens to do so. The above results were further confirmed by Lim *et al.* who studied fully dehydrated, fully

K$^+$-exchanged zeolite Y (FAU) using single-crystal X-ray diffraction techniques.[9] They were successfully prepared |K$_{71}$|[Si$_{121}$Al$_{71}$O$_{384}$]-FAU single crystals and determined the distribution of 71 K$^+$ ions. The sites about the D6Rs and the sodalite cavities were densely occupied as was seen in |K$_{92}$|[Si$_{100}$Al$_{92}$O$_{384}$]-FAU.[7] |K$_{71}$|[Si$_{121}$Al$_{71}$O$_{384}$]-FAU[9] had 20 fewer K$^+$ ions at III' sites than |K$_{92}$|[Si$_{100}$Al$_{92}$O$_{384}$]-FAU.[7]

Synthetic faujasite (FAU) with $1.0 \leq$ Si/Al ≤ 1.5 is called zeolite X. The chemical properties of zeolites and the Si-Al ordering at the tetrahedral sites are quite different because of their differing Si/Al ratios. The higher Si/Al ratio X-type zeolite has a wide range of industrial applications as catalysts and sorbents due primarily to its structural stability and its large and accessible pore volume as catalysts and sorbents. The adsorptive properties of zeolites also depend heavily on the size (charge density) of the cations in the lattice and on their distribution among sites.[10]

In this work, large single crystals of zeolite X (Si/Al = 1.41) were synthesized in order to determine and compare the cation positions of the K$^+$ ions in dehydrated |K$_{80}$|[Si$_{112}$Al$_{80}$O$_{384}$]-FAU (Si/Al = 1.41) with those of |K$_{92}$|-[Si$_{100}$Al$_{92}$O$_{384}$]-FAU (Si/Al = 1.09).[7] Fully K$^+$-exchanged zeolite X is particularly easy to study for a couple of reasons: (1) ion exchange of K$^+$ into zeolites is facile; (2) it is easy to distinguish K$^+$ from Na$^+$ because of the large difference in their atomic scattering factors (19 e$^-$ for K$^+$ and 11 e$^-$ for Na$^+$) and ionic radii (K$^+$ = 1.33 Å and Na$^+$ = 0.97 Å).[11] It was also done as a test of the suitability of these zeolite X crystals for further work.

Experimental Section

Synthesis of the Large Single Crystals of Zeolite X (FAU). Large colorless single crystals of sodium zeolite X, stoichiometry |Na$_{80}$|[Si$_{112}$Al$_{80}$O$_{384}$]-FAU, with diameters up to 200 μm were synthesized from gels with the composition 2.40SiO$_2$: 2.00NaAlO$_2$: 7.52NaOH : 454H$_2$O : 5.00TEA. A starting gel was prepared from fumed silica (99.8%, Sigma), sodium aluminate (technical, Wako), sodium hydroxide (96%, Wako), and triethanolamine (99+%, Acros), and distilled water.

First, a silica slurry was prepared by suspending 0.72 g of fumed silica in 18.57 g of distilled water in a 30-mL PTFE beaker, and the suspension was stirred in an orbital shaker (NB-101M, N-Biotek) at 200 RPM for 10 minutes. In a 250-mL PTFE beaker, 1.50 g of sodium hydroxide was dissolved in 22.30 g of distilled water, and then 0.82 g of sodium aluminate was added. This aluminate solutions was filtered through a 0.2-μm membrane filters (PTFE syringe, Whatman). After adding 3.73 g of TEA to the filtered sodium aluminate solution, the solution was filtered two more times through 0.2-μm membrane filters. Finally, the aluminate solution was slowly added to the silica slurry, which caused the mixture to become a very viscous gel. All these procedures were carried out at room temperature. After the TEA-aluminosilicate gel was charged in a 30-mL PTFE bottle, the bottle was placed in a convection oven at 368 K for 18 days. The product was filtered and washed with distilled water 10 times, and dried at 323 K for 2 days prior to characterization.
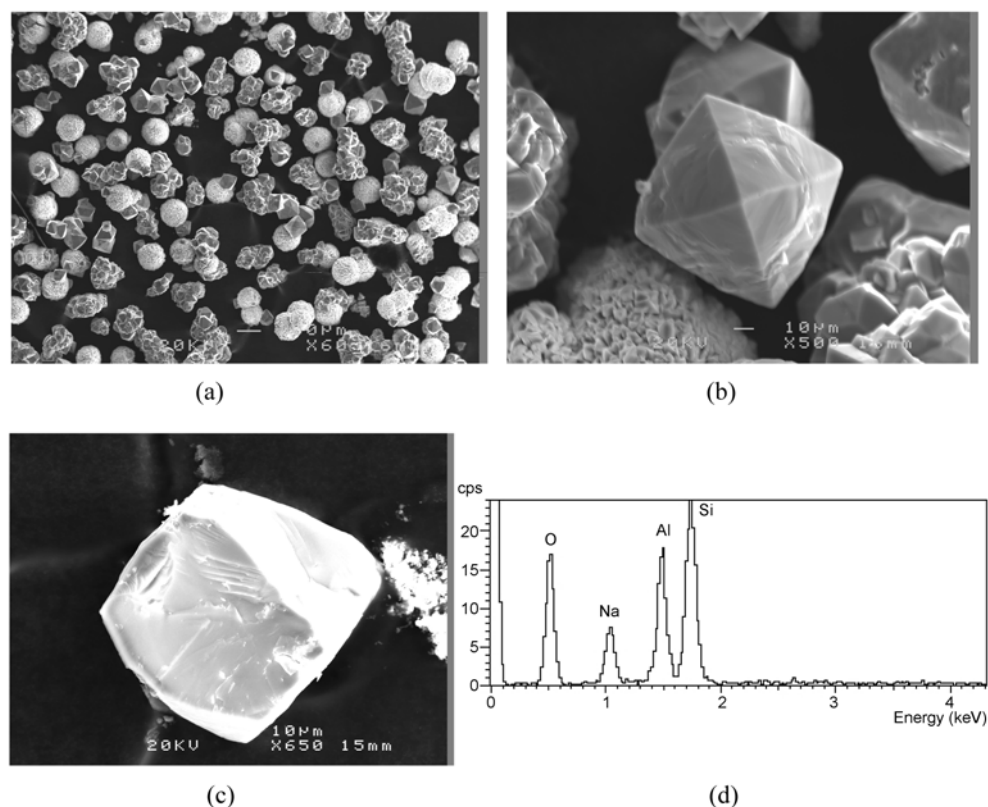

Figure 1. The SEM images magnified 60 (a), magnified 500 (b), intentionally broken for EDS analysis (c), and EDS spectra (d) of the large single crystals of zeolite X.

The products were characterized through optical microscopy, XRD, and SEM-EDS analysis. Microscopic examination showed that the crystals were transparent (see Figures 1(a) and (b)). Ten of selected single crystals from the batch were intentionally broken to reveal a fresh crystal surface for examination, and were attached to the surface of carbon-attach tape for SEM-EDS analysis (see Figure 1(c)). Each single crystal was measured 3 times and resulted in a Si/Al mean value of 1.41. The SEM images and atomic concentrations of the crystals were identified using a JSM-6300 SEM (scanning electron microscope) and an EDS (Energy dispersive X-ray spectrometer) (294 K and 1×10^{-7} Torr) (see Figures 1(c) and (d)).

Ion-exchange of Zeolite X (FAU). One of crystals, a colorless octahedron about 200 μm in cross-section was lodged in a fine Pyrex capillary. Crystals of hydrated $|K_{80}|[Si_{112}Al_{80}O_{384}]$-FAU were prepared by the dynamic (flow) ion-exchange of $|Na_{80}|[Si_{112}Al_{80}O_{384}]$-FAU with aqueous 0.1 M KNO_3, pH $= 5.9$ (Aldrich 99.999%).[6,7] The solution was allowed to flow past the crystal at a velocity of approximately 1.5 cm/s for 5 days at 294 K. The resulting clear, colorless, hydrated K^+-exchanged zeolite X crystal was dehydrated at 653 K and 1×10^{-6} Torr for 3 days. While these conditions were maintained, the hot contiguous downstream lengths of the vacuum system, including a sequential 17-cm U-tube of zeolite 5A beads fully activated *in situ*, were cooled to ambient temperature to prevent the movement of water molecules from more distant parts of the vacuum system to the crystal. Still under vacuum in its capillary, the crystal was then allowed to cool and was sealed in its capillary and removed from the vacuum line by torch. Microscopic examination showed that the crystal had become brown.

X-ray Data Collection. The structure of the resulting crystal was determined by single-crystal X-ray diffraction techniques at 294(1) K using a Bruker SMART CCD diffractometer. The crystal evaluation and data collection were done using Mo Kα radiation with a sealed-tube X-ray source operating at 1.5 kW with a detector-to-crystal distance of 4.8 cm.

Preliminary cell constants and an orientation matrix were determined from three series of scans at different starting angles. Each series consisted of 20 frames collected at scan intervals of $0.3°$ with an exposure time of 10 seconds per frame. The reflections were successfully indexed by the automated indexing routine of the SMART program.[12] A total of 26,890 reflections were harvested by collecting four sets of frames with $0.3°$ scans with an exposure time of 10 seconds per frame. This highly redundant data set was corrected for Lorentz and polarization effects, and a (negligible) correction for crystal decay was also applied. The space group $Fd\bar{3}$ was determined by the program SAINT-plus.[12] A summary of the experimental and crystallographic data is presented in Table 1.

Structure Determination

Full-matrix least-squares refinement (SHELXL97)[13] was done on F_o^2 using all data. Refinement was initiated with the atomic parameters of the framework atoms [(Si,Al), O(1), O(2), O(3), and O(4)] in dehydrated $|K_{92}|[Si_{100}Al_{92}O_{384}]$-FAU.[7] The initial refinement using anisotropic thermal parameters for all positions converged to the error indices (defined in Table 1, footnote a) $R_1 = 0.24$ and $R_2 = 0.66$.

See Table 2 for the steps of structure determination and refinement as new atomic positions were found on successive difference Fourier electron-density functions.

The final cycles of anisotropic refinement, done with the occupancies at the framework atoms and K^+ ions fixed at their nearest integral values to facilitate the discussion (see Table 3) and with the final weighting-scheme parameters, converged to $R_1 = 0.075$ and $R_2 = 0.236$. On the final difference Fourier function, the largest peak appeared at (0.302, 0.302, 0.302) with height 0.84 e$^-$/Å^3. It was not included in the final model because it was too far from framework oxygen atoms to be a cation.

All shifts in the final cycles of refinement were less than 0.1% of their corresponding estimated standard deviations. The final structural parameters are given in Table 3. Selected interatomic distances and angles are given in Table 4.

Fixed weights were used initially; the final weights were assigned using the formula $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$, with $a = 0.148$ and $b = 158.5$ as refined parameters (see Table 1). Atomic scattering

Table 1. Summary of experimental and crystallographic data

Formula	$K_{80}Si_{112}Al_{80}O_{384}$
Formula weight	13855.8
Crystal cross section (μm)	200
Ion exchange T (K)	294(1)
Ion exchange for K^+ (days, mL)	4, 12.0
Data collection T (K)	294(1)
Crystal system	Cubic
Space group, Z	$Fd\bar{3}$, 1
Scan technique	ω-scans
Radiation (Mo Kα) λ_1 (Å)	0.70930
λ_2 (Å)	0.71359
Unit cell constant, a (Å)	24.838(4)
2θ range in data collection (deg)	$2.82 < 2\theta < 56.6$
No. of unique reflections, m	1618
No. of reflections with $F_o > 4\sigma(F_o)$	707
No. of variables, s	97
Data/parameter ratio, m/s	16.8
Weighting parameters, a/b	0.148/158.5
Final error indices	
R_1/R_2 ($F_o > 4\sigma(F_o)$)[a]	0.075/0.236
R_1/R_2 (all intensities)[b]	0.187/0.314
Goodness-of-fit[c]	1.22
Structure determination	Direct methods (SHELXS-97)
Refinement	Full matrix least-squares (SHELX-97)

[a]$R_1 = \Sigma|F_o - |F_c||/\Sigma F_o$ and $R_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; R_1 and R_2 are calculated using only the 707 reflections for which $F_o > 4\sigma(F_o)$. [b]R_1 and R_2 are calculated using all 1618 unique reflections measured. [c]Goodness-of-fit $= (\Sigma w(F_o^2 - F_c^2)^2/(m-s))^{1/2}$, where m and s are the number of unique reflections and variables, respectively.

Table 2. Initial steps of structure refinement[a]

| Step | Occupancy[b] at | | | | | | | | R_1 | R_2 |
	K(I)	K(I')	K(IIa)	K(IIb)	K(IIc)	K(III'a)	K(III'b)	K(III'c)		
1[c]									0.24	0.66
2	9.8(5)								0.18	0.57
3	9.8(5)			9.6(7)					0.15	0.54
4	9.5(4)			7.1(6)	6.8(6)				0.13	0.50
5	10.5(4)	9.6(10)		8.4(6)	7.3(6)				0.11	0.48
6	10.1(3)	8.6(7)		9.1(6)	9.2(6)	15.5(12)			0.10	0.43
7	10.5(3)	5.5(6)		11.2(6)	9.6(6)	21.5(15)		10.7(11)	0.090	0.391
8	10.5(3)	4.8(5)	4.0(9)	8.6(9)	8.5(6)	22.2(14)		10.7(10)	0.087	0.371
9	10.5(3)	4.8(5)	4.6(9)	8.8(9)	9.0(6)	16.3(15)	13.2(18)	12.3(10)	0.083	0.367

[a]Isotropic temperature factors were used for all K^{+} positions. [b]The occupancy is given as the number of K^{+} ions per unit cell. [c]Only the atoms of zeolite framework were included in the initial structure model.

Table 3. Positional, thermal, and occupancy parameters[a]

| atom | Wyckoff position | Cation site | x | y | z | $^bU_{11}$ | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} | [c]Occupancy | | |
												initial	varied	fixed
Si	96(g)		−544(1)	1234(1)	354(1)	246(13)	251(13)	239(13)	−27(11)	11(10)	−11(11)	112		
Al	96(g)		−544(1)	354(1)	1234(1)	203(13)	169(12)	200(13)	−32(11)	−16(11)	11(10)	80		
O(1)	96(g)		−1098(3)	3(3)	1097(3)	317(37)	476(44)	334(38)	−76(30)	−10(29)	−82(31)	96		
O(2)	96(g)		−42(3)	−41(3)	1447(3)	356(38)	335(37)	249(33)	−19(28)	−24(28)	85(29)	96		
O(3)	96(g)		−662(3)	−666(3)	353(3)	318(36)	346(36)	347(39)	55(30)	51(30)	82(30)	96		
O(4)	96(g)		−687(3)	773(3)	1726(3)	372(37)	345(38)	296(36)	−134(29)	39(30)	−45(32)	96		
K(I)	16(c)	I	0	0	0	396(21)	396(21)	396(21)	46(21)	46(21)	46(21)		10.5(3)	11
K(I')	32(e)	I'	772(6)	772(6)	772(6)	405(60)	405(60)	405(60)	−12(65)	−12(65)	−12(65)		4.8(5)	5
K(IIa)	32(e)	II	2276(30)	2276(30)	2276(30)	672(313)	672(313)	672(313)	696(369)	696(369)	696(369)		4.6(9)	5
K(IIb)	32(e)	II	2353(17)	2353(17)	2353(17)	671(134)	671(134)	671(134)	88(91)	88(91)	88(91)		8.8(9)	9
K(IIc)	32(e)	II	2538(5)	2538(5)	2538(5)	431(54)	431(54)	431(54)	69(49)	69(49)	69(49)		9.0(6)	9
K(III'a)	96(g)	III'	750(17)	756(17)	4248(12)	1620(343)	1614(343)	426(131)	105(185)	70(190)	729(263)		16.3(15)	16
K(III'b)	96(g)	III'	443(34)	410(30)	4171(26)	3304(996)	2745(871)	1353(528)	1243(596)	1695(632)	1144(723)		13.2(18)	13
K(III'c)	96(g)	III'	1109(22)	1421(14)	4206(8)	2135(534)	1219(361)	169(98)	72(125)	−304(181)	156(284)		12.3(10)	12
													$\Sigma K^+ = 79.1 (9)$	

[a]Positional parameters $\times 10^4$ and thermal parameters $\times 10^4$ are given. Numbers in parentheses are the estimated standard deviations in the units of the least significant figure given for the corresponding parameter. [b]The anisotropic temperature factor is $\exp[-2\pi k^2 a^{-2}(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{23}kl + 2U_{13}hl + 2U_{12}hk)]$. [c]Occupancy factors are given as the number of atoms or ions per unit cell.

factors for K^{+}, O[−], and (Si,Al)[1.79+] were used.[14,15] The function describing (Si,Al)[1.79+] is the weighted mean of the Si[4+], Si[0], Al^{3+}, and Al[0] functions (Si/Al = 1.41). All scattering factors were modified to account for anomalous dispersion.[16,17]

Results and Discussion

Synthesis of the Large Single Crystals of Zeolite X (Si/Al = 1.41). Based on procedures in the literature for the synthesis of faujasite-type zeolites with the larger and well defined single crystals,[2] in this work, large single crystals of zeolite X (Si/Al = 1.41) were synthesized from gels with the composition $2.40SiO_2 : 2.00NaAlO_2 : 7.52NaOH : 454H_2O : 5.00TEA$. The produts contained the aggregated octahedral crystals and the polycrystalline spherical impurities (see Figures 1(a) and (b)). The optical microscopy, XRD, and SEM showed that the aggregated octahedral products were large transparent crystals of faujasite-type zeolite with dia-

meters up to *ca.* 200 μm and that the translucent polycrystalline spheres were gismondine. The spherical impurities were not to exceed 26% of the particulated product as counted from SEM images (see Figure 1(a)).

Further EDS experiments using the fresh surface of an intentionally broken large single crystals of faujasite-type zeolite confirmed the mean value of Si/Al = 1.41 (see Figures 1(c) and (d)). This means that the molecular composition of the single crystals were $M_{80}Si_{112}Al_{80}O_{384}$, where $M = Na^+$ and/or H_3O^+. This result is consistent with the later more precise crystallographic determination of 79.1(9) K^{+} ions per unit cell.

Large, uniform, and well shaped octahedral single crystals of zeolite X (Si/Al = 1.41) have been synthesized using a highly reproducible synthetic method. These are suitable for single-crystal X-ray diffraction experiments.

Brief Description of FAU. The framework structure of faujasite is characterized by the double 6-ring (D6R, hexagonal prism), the sodalite cavity (a cubooctahedron), and the

Table 4. Selected interatomic distances (Å) and angles (deg)[a]

	Distances		Angles
Si-O(1)	1.670(7)	O(1)-Si-O(2)	111.5(3)
Si-O(2)	1.675(6)	O(1)-Si-O(3)	107.8(3)
Si-O(3)	1.687(7)	O(1)-Si-O(4)	108.0(3)
Si-O(4)	1.649(7)	O(2)-Si-O(3)	109.0(3)
average	**1.670(7)**	O(2)-Si-O(4)	107.3(3)
		O(3)-Si-O(4)	113.3(4)
Al-O(1)	1.665(7)	O(1)-Al-O(2)	112.0(3)
Al-O(2)	1.671(6)	O(1)-Al-O(3)	107.6(3)
Al-O(3)	1.674(7)	O(1)-Al-O(4)	107.7(3)
Al-O(4)	1.644(7)	O(2)-Al-O(3)	108.9(3)
average	**1.664(7)**	O(2)-Al-O(4)	107.3(3)
		O(3)-Al-O(4)	113.5(4)
K(I)-O(3)	2.492(6)		
K(I')-O(3)	2.820(19)	Si-O(1)-Al	127.8(4)
K(I')-O(2)	3.313(13)	Si-O(2)-Al	140.8(4)
K(IIa)-O(2)	2.26(3)	Si-O(3)-Al	133.9(4)
K(IIa)-O(4)	2.973(14)	Si-O(4)-Al	153.5(5)
K(IIb)-O(2)	2.35(3)		
K(IIb)-O(4)	3.020(16)	O(3)-K(I)-O(3)	88.45(22),
			91.55(22)
K(IIc)-O(2)	2.710(13)	O(3)-K(I')-O(3)	78.6(6)
K(IIc)-O(4)	3.273(11)	O(2)-K(IIa)-O(2)	116.5(20)
K(III'a)-O(4)	2.64(3)	O(2)-K(IIb)-O(2)	110.1(17)
K(III'a)-O(1)	2.94(3), 2.97(4)	O(2)-K(IIc)-O(2)	90.4(6)
K(III'b)-O(4)	2.73(5)	O(1)-K(III'a)-O(1)	113.1(10)
K(III'b)-O(1)	2.96(6), 3.05(7)	O(1)-K(III'a)-O(4)	57.0(6)
K(III'c)-O(4)	3.06(4)	O(1)-K(III'b)-O(1)	110.1(13)
K(III'c)-O(1)	3.08(3), 3.11(3)	O(1)-K(III'b)-O(4)	56.1(10)
		O(1)-K(III'c)-O(1)	76.6(7)
		O(1)-K(III'c)-O(4)	51.9(6)

[a]The numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

Figure 2. Stylized drawing of the framework structure of zeolite Y. Near the center of the each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1 to 4. There is no evidence in this work of any ordering of the silicon and aluminum atoms among the tetrahedral positions, although it is expected that Lowenstein's rule (ref. 21) would be obeyed. Extra-framework cation positions are labeled with Roman numerals.

supercage (see Figure 2). Each unit cell has 8 supercages, 8 sodalite cavities, 16 D6Rs, 16 12-rings, and 32 S6Rs (single 6-rings).

The exchangeable cations, which balance the negative charge of the faujasite framework, usually occupy some or all of the sites shown with Roman numerals in Figure 2. The maximum occupancies at the cation sites I, I', II, II', III, and III' in faujasite are 16, 32, 32, 32, 48, and 96, respectively. Further description is available.[7,9,18-20]

Space Group Considerations. If the Si/Al = 1.00, then Si and Al atoms would alternate in the FAU framework in obeyance of Lowenstein's rule (-Al-O-Al- sequences are forbidden).[21] The space group would then be $Fd\bar{3}$; one 96(g) equipoint, Si, would contain only Si atoms, another 96(g) equipoint, Al, would contain only Al atoms, and Si-O bond lengths would correctly be seen crystallographically to be shorter than Al-O. |Na$_{92}$|[Si$_{100}$Al$_{92}$O$_{384}$]-FAU[8] and |K$_{92}$|[Si$_{100}$Al$_{92}$O$_{384}$]-FAU[7] show these bond length differences and show the intensity inequalities of $Fm\bar{3}$, indicating that the excess Si atoms occupy Al sites. Except for this, long-range order is retained.
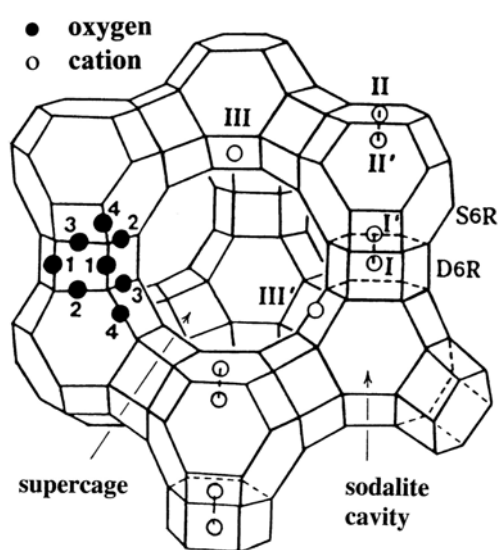
The crystal of |K$_{71}$|[Si$_{121}$Al$_{71}$O$_{384}$]-FAU[9] was refined using the space group $Fd\bar{3}m$ because it showed Si-O and Al-O bond length did not differ significantly and clearly showed mirror symmetry at (110) from the X-ray diffraction intensities, indicating that the Si and Al positions were not distinguishable.

In this work, the space group used is $Fd\bar{3}$, even when about 14% of the Al sites are occupied by Si atoms. This is confirmed by no showing mirror symmetry at (110) even though the average values of the Si-O and Al-O distances are not significantly different (see Tables 4 and 5). This is indicating that the Si and Al positions are distinguishable. Furthermore, when $Fd\bar{3}m$ was used, R_1 increased from 0.075 to 0.099 and R_2 from 0.187 to 0.394, again indicating that the Si and Al atoms are not disordered in the long range. Accordingly, the crystal in this work was refined using the space group $Fd\bar{3}$.

Framework and K$^+$ Ions. The total number of K$^+$ ions found per unit cell, 79.1(9), does not differ significantly from 80, the number required to balance the negative charge of the zeolite framework. It is possible that a minor amount of H$^+$ exchange has occurred as has been proposed for |K$_{92}$|[Si$_{100}$Al$_{92}$O$_{384}$]-FAU[6,7] and |K$_{71}$|[Si$_{121}$Al$_{71}$O$_{384}$]-FAU.[9]

In this structure, 80 K$^+$ ions have been found at eight equipoints. Eleven K$^+$ ions per unit cell are exactly at the centers of their D6Rs, at site I (see Figure 3). This 16-fold position is not fully occupied. Each K$^+$ ion at K(I) is coordinated by six O(3) oxygen atoms of hexagonal prism at distance of 2.492(6) Å, slightly shorter than the sum of the conventional ionic radii of K$^+$ and O^{2-}, 1.33 + 1.32 (respectively) = 2.65 Å.[11] This indicates that each K$^+$ ion coordinates strongly to its six O(3) oxygens. The K$^+$ ions are

Table 5. Selected comparison of F_o^2 for the pairs of *hkl* and *khl* reflections

h	k	l	$F_o^2{}_{,hkl}$	k	h	l	$F_o^2{}_{,khl}$	$F_o^2{}_{,hkl}/F_o^2{}_{,khl}$
2	0	10	9259.14	0	2	10	7378.65	**1.2549**
4	0	12	−762.67	0	4	12	477.37	**−1.5976**
5	1	9	503.68	1	5	9	71.07	**7.0871**
5	3	11	6759.95	3	5	11	5857.53	**1.1541**
5	3	13	2441.91	3	5	13	758.22	**3.2206**
6	0	10	17673.08	0	6	10	16412.05	**1.0768**
6	2	10	1573.01	2	6	10	1292.91	**1.2166**
6	2	12	17313.95	2	6	12	20151.25	**0.8592**
6	4	10	1112.07	4	6	10	2023.79	**0.5495**
6	4	12	320.78	4	6	12	−458.02	**−0.7004**
7	5	9	1766.47	5	7	9	2725.22	**0.6482**
8	4	10	−706.22	4	8	10	−94.11	**7.5042**
9	1	11	2998.56	1	9	11	2100.85	**1.4273**
9	3	13	11739.95	3	9	13	13103.54	**0.8959**
9	5	11	1208.98	5	9	11	1428.39	**0.8464**
10	2	12	3687.03	2	10	12	3211.83	**1.1480**
10	4	12	788.04	4	10	12	−134.23	**−5.8708**
10	8	12	434.75	8	10	12	−201.19	**−2.1609**

octahedral.

Five K^+ ions at K(I') are located at site I' in the sodalite cavity opposite D6Rs (see Figure 4). Each K^+ ion at K(I') is recessed *ca.* 1.92 Å into the sodalite cavity from its 6-ring plane. This 32-fold position is also not fully occupied (This indicates that K^+ ions at K(I') are not present at the every opposite D6Rs in the sodalite unit). The distance between K(I') and its nearest framework oxide ions, again at O(3), is 2.820(19) Å, which is a little longer than the sum of the conventional ionic radii of K^+ and O^{2-}, 1.33 + 1.32 (respectively) = 2.65 Å,[11] indicative of a good fit.

About 23 K^+ ions are located at three site II positions opposite S6Rs in the supercage (see Figure 4 and 5). These K^+ ions at site II do not fill the 32-fold site-II position perhaps because some S6Rs are severely deficient in Al atoms. Each of these ions at K(IIa), K(IIb), and K(IIc) lies inside the supercage, 0.43 Å, 0.75 Å, and 1.55 Å, respectively, from the plane of three O(2) framework oxygens of
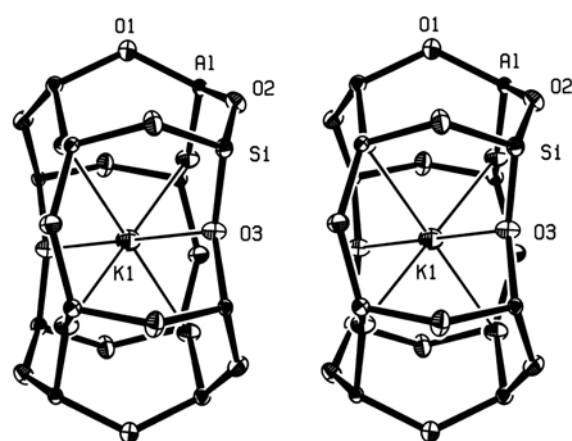

Figure 3. Stereoview of a representative double 6-ring (D6R) in dehydrated $|K_{80}|[Si_{112}Al_{80}O_{384}]$-FAU. The K^+ ion at K(1) is shown at site I. The zeolite X framework is drawn with heavy bonds. The coordination of K^+ ions to oxygens of the zeolite framework are indicated by light bonds. Ellipsoids of 25% probability are shown.

the S6R to which each is bound. The five, nine, and nine K(IIa), K(IIb), and K(IIc) ions bond to three O(2)s at 2.36(13) Å, 2.45(13) Å, and 2.710(13) Å, respectively (see Table 4 and Figure 4). The distances between K^+ ions at sites II and the framework oxide ions, 2.36(13) Å and 2.45(13) Å, are slightly shorter than the sum of the conventional ionic radii of K^+ and O^{2-}, 1.33 + 1.32 (respectively) = 2.65 Å.[11] This indicates that each K^+ ioin coordinates strongly to its three O(2) oxygens, as would be expected by the low coordination number. The three different 3-fold axis K^+ positions (in the supercage opposite S6Rs) are due (perhaps) to the different kinds of 6-rings which are 3Si3Al, 4Si2Al, and 5Si1Al.

The remaining 16.3(15), 13.2(18), and 12.3(10) K^+ ions at K(III'a), K(III'b), and K(III'c), respectively, occupy three site-III' positions near triple 4-rings in the supercage (see Figure 5). These positions are close to one O(4) and two O(1) framework oxygens. The site-III' cations at K(III'a), K(III'b), and K(III'c), with occupancies of 16.3(15), 13.2(18), and 12.3(10) K^+ ions per unit cell, respectively, are 2.64(3) Å and 2.94(3) Å (K(III'a)), 2.73(5) Å and 2.96(6) Å
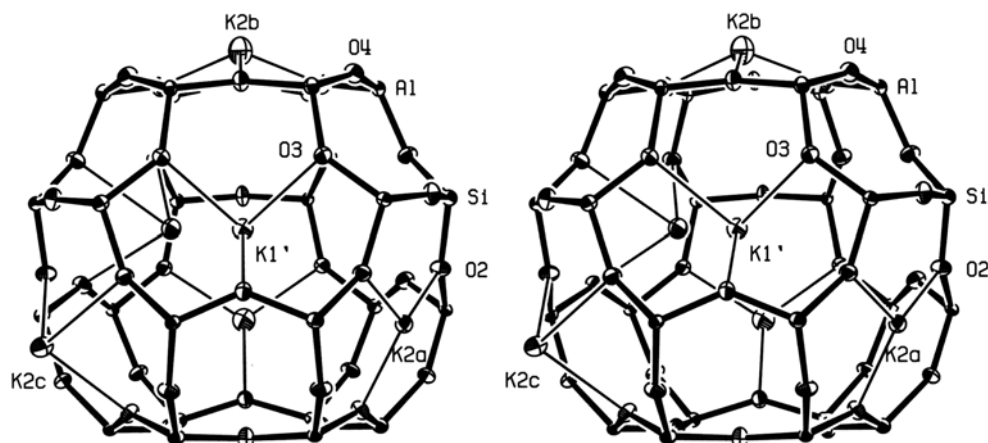

Figure 4. A stereoview of a representative sodalite unit in dehydrated $|K_{80}|[Si_{112}Al_{80}O_{384}]$-FAU. See the caption to Figure 3 for other details.
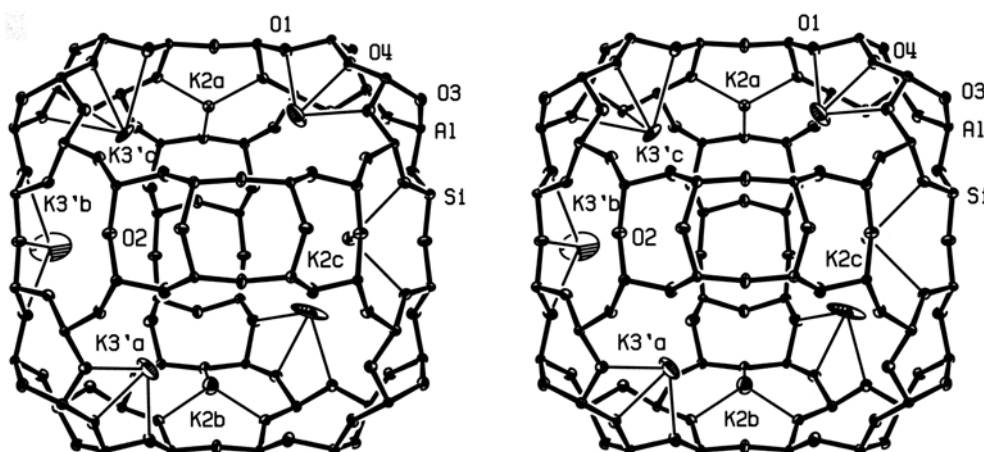
Figure 5. A stereoview of a representative supercage in dehydrated $|K_{80}|[Si_{112}Al_{80}O_{384}]$-FAU. See the caption to Figure 3 for other details.

Table 6. Distribution of K^+ ions over sites in $|K_{92}|[Si_{100}Al_{92}O_{384}]$-FAU[a,b] and $|K_{80}|[Si_{112}Al_{80}O_{384}]$-FAU[c]

Site	I		I'			II	III	III'		
Maximum occupancy	16		32			32	48	96		
Position	K(Ia)	K(Ib)	K(I'a)	K(I'b)	K(I'c)	K(II)	K(III)	K(III'a)	K(III'b)	K(III'c)
Structure	Occupancies									
$\|K_{92}\|[Si_{100}Al_{92}O_{384}]$-FAU[a]	6	8	4	4	4[d]	28.4(4)	12.2(9)	10.7(18)	12.8(21)	–
$\|K_{92}\|[Si_{100}Al_{92}O_{384}]$-FAU[b]	15.3(5)		12.5(8)[e]			29.9(7)	21.2(10)	8.6(18)		
$\|K_{80}\|[Si_{112}Al_{80}O_{384}]$-FAU[c]	10.5(3)		4.8(9)[e]		4.6(9)[f]	8.8(9)[f] 9.0(6)[f]	–	16.3(15)[f]	13.2(18)[f]	12.3(10)[f]

[a]Ref. 7, space group $Fd\bar{3}m$. [b]Ref. 6, space group $Fd\bar{3}$. [c]This work, space group $Fd\bar{3}$. [d]This I' position lies off the 3-fold axis at (x, x, z), x < z. [e]This I' position could not be resolved in least-squares refinement into two others as had been done in reference 7. Instead it occupies a 3-fold-axis position between those of K(I'a) and K(I'b) in reference 7. [f]These II and III' positions are resolved in least-squares refinement into three others due (perhaps) to the different kinds of 6-rings.

(K(III'b)), and 3.06(4) Å and 3.08(3) Å (K(III'c)) from the framework oxygens at O(4) and O(1), respectively (see Table 4 and Figure 5). The occupation of the three positions at sites III' may be a consequence of the nonequivalent environments generated by the partial occupancy of the K^+ ions at the sites I, I', II, or it may be due to the local Si/Al order among the T atoms. In this structure, the K^+ ions are not found at the 96-fold site III.

There is no indication that the structure contains the template, triethanolamine (TEA), in the synthesis. If it was present in the starting crystal, it was washed away by the intensive K^+-exchange process.

Comparison of $|K_{80}|[Si_{112}Al_{80}O_{384}]$-FAU with $|K_{92}|[Si_{100}Al_{92}O_{384}]$-FAU. Seff *et al.*[7] investigated a dehydrated zeolite X with unit-cell composition $K_{92}Si_{100}Al_{92}O_{384}$ (Si/Al = 1.09) by single-crystal X-ray diffraction. In its structure, K^+ ions were found at nine different crystallographic sites with the occupancies 6, 8, 4, 4, 4, 28.4(4), 12.2(9), 10.7(18), and 12.8(21) per unit cell at sites I, I', II, III, and III', respectively (see Table 6).

When the fully dehydrated structures of $|K_{80}|[Si_{112}Al_{80}O_{384}]$-FAU and $|K_{92}|[Si_{100}Al_{92}O_{384}]$-FAU[6,7] are compared, it can be seen that there are no unusually close $K^+ \cdots K^+$ contacts in $|K_{80}|[Si_{112}Al_{80}O_{384}]$-FAU as can be seen from Kim's study.[6] In the structure of $|K_{80}|[Si_{112}Al_{80}O_{384}]$-FAU, 23 K^+ ions are found at three nonequivalent site II (in the supercage) with

occupancies of 4.6(9), 8.8(9), and 9.0(6) ions. In two structures of $K_{92}|[Si_{100}Al_{92}O_{384}]$-FAU,[6,7] however, 28.4(4) and 29.9(7) K^+ ions were found at only one site II, respectively (see Table 6). The three different K^+ positions at sites II (in the supercage opposite S6Rs) are due (perhaps) to the different kinds of 6-rings in the structure of $|K_{80}|[Si_{112}Al_{80}O_{384}]$-FAU: 3Si3Al, 4Si2Al, and 5Si1Al. About 41 K^+ ions in the structure of $|K_{80}|[Si_{112}Al_{80}O_{384}]$-FAU are found at three sites III' near triple 4-rings in the supercage, but the K^+ ions exist at two or only one site III' in two structures of $K_{92}|[Si_{100}Al_{92}O_{384}]$-FAU[6,7] (see Table 6). This is perhaps due to the different kinds of 4-rings in the structure of $|K_{80}|[Si_{112}Al_{80}O_{384}]$-FAU: 2Si2Al and 3Si1Al.

Summary

Large single crystals of zeolite X (Si/Al = 1.41) were successfully prepared from gels with the composition $2.40SiO_2 : 2.00NaAlO_2 : 7.52NaOH : 454H_2O : 5.00TEA$ and the structure of fully K^+-exchanged zeolite X was determined by single-crystal X-ray diffraction methods. The synthetic produts are consisted of the large transparent crystals of faujasite-type zeolite with diameters up to *ca.* 200 μm and the translucent polycrystalline spheres of gismondine. In the SEM-EDS anaysis, the Si/Al ratio of the synthetic faujasite-type zeolite is 1.41 which is well con-

sistent with the crystallographic study.

In the crystallographic studies, it was determined about 80 K^+ ions are distributed over the eight sites much like those in $|K_{92}|[Si_{100}Al_{92}O_{384}]$-FAU[7] and $|K_{71}|[Si_{121}Al_{71}O_{384}]$-FAU.[9] Surprisingly, three site-II positions (in the supercage opposite S6Rs) and three site-III' positions (in the supercage near triple 4-rings) are occupied by K^+ ions which was not seen in $|K_{92}|[Si_{100}Al_{92}O_{384}]$-FAU[6,7] and $|K_{71}|[Si_{121}Al_{71}O_{384}]$-FAU.[9] The three different K^+ positions (in the supercage opposite S6Rs and near triple 4-rings) are due (perhaps) to the different kinds of 6-rings (3Si3Al, 4Si2Al, and 5Si1Al) and 4-rings (2Si2Al and 3Si1Al).

Supporting Information: Tables of calculated and observed structure factors (18 pages). The supporting materials are available *via* the Internet *http://www.kcsnet. or.kr/bkcs*.

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