

Articles

Single-crystal Structure of Fully Dehydrated and Largely NH₄⁺-exchanged Zeolite Y (FAU, Si/Al = 1.70), [(NH₄)₆₀Na₁₁][Si₁₂₁Al₇₁O₃₈₄]-FAU

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The single-crystal structure of largely ammonium-exchanged zeolite Y dehydrated at room temperature (293 K) and 1×10^{-5} Torr, has been determined using synchrotron X-radiation in the cubic space group $Fd\bar{3}m$ ($a = 24.9639(2)$ Å) at 294 K. The structure was refined to the final error index $R_1 = 0.0429$ with 926 reflections where $F_o > 4\sigma(F_o)$; the composition (best integers) was identified as [(NH₄)₆₀Na₁₁][Si₁₂₁Al₇₁O₃₈₄]-FAU. The 11 Na⁺ ions per unit cell were found at three different crystallographic sites and 60 NH₄⁺ ions were distributed over three sites. The 3 Na⁺ ions were located at site I, the center of the hexagonal prism (Na-O = 2.842(5) Å and O-Na-O = 85.98(12)^o). The 4 Na⁺ and 22 NH₄⁺ ions were found at site I' in the sodalite cavity opposite the double 6-rings, respectively (Na-O = 2.53(13) Å, O-Na-O = 99.9(7)^o, N-O = 2.762(11) Å, and O-N-O = 89.1(5)^o). About 4 Na⁺ ions occupied site II (Na-O = 2.40(4) Å and O-Na-O = 108.9(3)^o) and 29 NH₄⁺ ions occupy site II (N-O = 2.824(9) Å and O-N-O = 87.3(3)^o) opposite to the single 6-rings in the supercage. The remaining 9 NH₄⁺ ions were distributed over site III (N-O = 2.55(3), 2.725(13) Å and O-N-O = 94.1(13), 62.16(15), 155.7(14)^o).

Key Words: Zeolite Y, Ammonium-exchange, Single-crystal X-ray diffraction, Crystal structure

Introduction

Zeolite has a wide range of industrial applications as an ion exchanger, a sorption agent, a molecular sieve, and a catalyst due to its excellent structural stability, large and accessible pore volume, high activity, and high regenerability.¹ The thermal stability, the sorption properties, and catalytic characteristics of zeolites heavily depend on the kind, number, and distribution of exchangeable cations.^{2,3} The information of exchangeable cations, adsorbate, and framework in zeolites has been comprehensively studied using the single-crystal X-ray diffraction method,⁴⁻⁶³ one of the most frequently used and informative techniques for characterization of cations in a zeolite framework. The large single crystals of zeolite should be grown to minimum of *ca.* 60 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 information on the exchangeable cations, and the adsorbate. For instances, large single crystals of synthetic sodium zeolites A (*ca.* 80 μm) and X (*ca.* 200 μm), stoichiometry of Na₉₂Al₉₂Si₁₀₀O₃₈₄, were prepared by Charnell⁶⁴ and Petrakovskii *et al.*,⁶⁵ respectively. Sacco *et al.*⁶⁶⁻⁶⁸ 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, triethanolamine (TEA), and/or bis(2-hydroxyethyl)dimethyl-

ammonium chloride (TCl). They reported that their synthesized single crystals were suitable for single-crystal X-ray diffraction experiments.

By using these single crystals, the 3-dimensional structures of K⁺,^{5,6} Rb⁺,^{7,8} Cs⁺,^{9,10} Tl⁺,^{11,12} Ag⁺,¹³⁻¹⁶ Ca²⁺,¹⁷ Sr²⁺,¹⁷ Mn²⁺,^{18,19} Co²⁺,^{20,21} Ni²⁺,^{22,23} Cu²⁺,^{24,25} Zn²⁺,^{26,27} Cd²⁺,^{28,32} Pb²⁺,^{33,34} Eu²⁺-exchanged zeolite A,^{35,36} Na⁺,^{37,38} K⁺,³⁹ Rb⁺,⁴⁰ Cs⁺,⁴¹ Tl⁺,^{42,43} Ag⁺,^{44,45} Mg²⁺,⁴⁶ Ca²⁺,⁴⁶ Ba²⁺,⁴⁶ Sr²⁺,⁴⁷ Mn²⁺,⁴⁸ Co²⁺,⁴⁹ Ni²⁺,⁵⁰ Zn²⁺,^{51,52} Cd²⁺,^{53,54} Pb²⁺,^{55,56} Pd²⁺,⁵⁷ La³⁺-exchanged zeolite X,⁵⁸ and Na⁺,⁵⁹ K⁺,⁶⁰ Tl⁺,^{61,62} Cd²⁺-exchanged zeolite Y⁶³ were studied by the single crystal X-ray diffraction method.

Proton-exchanged zeolite Y (H⁺-Y) catalyst is used crucial processes for producing valuable petroleum products from crude oil because it has both Bronsted and Lewis acid sites.⁶⁹ The market of H⁺-Y zeolite exceeds US \$2 billion annually.⁷⁰ Bronsted and Lewis acid are provided by proton ions that are produced from the deamination (loss of NH₃) of NH₄⁺ ions in the NH₄⁺-exchanged zeolite and by aluminum ions that leave the zeolite framework (dealumination) by steaming at higher temperatures, respectively.

The single-crystal structures of several NH₄⁺-exchanged zeolites A (LTA) and X (FAU) have been reported.^{25,71-73} McCusker *et al.* investigated fully dehydrated, fully NH₄⁺-exchanged zeolite A by single-crystal X-ray diffraction methods and reported the positions of the NH₄⁺ ions.⁷¹ Their single crystal was prepared by the flow method using 1.0 M

NH_4NO_3 for 72 hrs at 298 K, followed by evacuation at 298 K and 10^{-5} torr; this resulted in the complete dehydration of NH_4^+ -A with no NH_4^+ decomposition. Lee *et al.* studied the structures of NH_4^+ , hydrolyzed- Cu^{2+} forms of zeolite A to find the Cu^{2+} positions.²⁵ (They added ammonia to their ion-exchange solutions to avoid crystal damage from the protons arising from the hydrolysis of Cu^{2+} .) Patalinghug *et al.* reported a structure of Ni^{2+} - and NH_4^+ -exchanged zeolite A.⁷² Zhen *et al.* prepared anhydrous NH_4^+ -exchanged zeolite X, allowing it to react with HgCl_2 vapor at 388 K, and determined the resulting structure.⁷³

Even though NH_4^+ -Y is the important precursor of H^+ -Y zeolite, no crystallographic work has been done to determine the detailed catalytic active sites in zeolite Y. Our work presented here investigates the cation position and confirms the special cation site selectivity of NH_4^+ ions in the crystal structure of the fully dehydrated largely NH_4^+ -exchanged zeolite Y. The precise and selective positions of NH_4^+ and Na^+ ions within zeolite Y were determined crystallographically because the ionic radii of Na^+ and NH_4^+ ions are quite different. The new findings could lead to deeper understand crystallographically on the dehydration, deamination, and dealumination processes in NH_4^+ -exchanged zeolite Y without loss of the framework crystallinity.

Experimental Section

Ion-exchange of Zeolite Y (FAU). Large single crystals of synthetic sodium zeolite Y, stoichiometry of $\text{Na}_{71}\text{Si}_{121}\text{Al}_{71}\text{O}_{384}$, with diameters up to 200 μm were synthesized from gels of composition 3.58SiO_2 : 2.08NaAlO_2 : 7.59NaOH : $455\text{H}_2\text{O}$:

5.06TEA : 1.23TCl . A starting gel was prepared from fumed silica (99.8%, Sigma), sodium aluminate (technical, Wako), sodium hydroxide (96%, Wako), triethanolamine (TEA, 99+%, Acros), bis(2-hydroxyethyl)dimethylammonium chloride (TCl, 99%, Acros), and distilled water. Further description is available.⁶⁹

It is very difficult to achieve complete NH_4^+ -exchange of Na-Y without prior complete K^+ -exchange.⁷⁰ In this work, complete K^+ -exchange was not carried out in order to study the selectivity of NH_4^+ ions in the framework of largely NH_4^+ -exchanged zeolite Y. Crystals of hydrated $[(\text{NH}_4)_{60}\text{Na}_{11}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]$ -FAU were prepared by static ion-exchange of $[\text{Na}_{71}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]$ -FAU (or Na_{71} -Y) with aqueous 0.1 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, pH = 6.9 (Aldrich 99.999%).⁷³ 0.02 g of hydrated sodium zeolite Y was mixed with 15 mL of 0.1 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ in 15-mL conical tube and then the mixture was stirred on an orbital shaker (NB-101M, N-Biotek) for 4 hrs at 293 K. The NH_4^+ ion-exchange procedure was repeated 5 times with the fresh $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution. The product was then filtered and dried at room temperature for 1 day. The crystals were transparent.

Two of these, hydrated and largely NH_4^+ -exchanged zeolite Y crystals, clear and colorless octahedrons about 200 μm in cross-section, were lodged in fine Pyrex capillaries. The contiguous downstream lengths of the vacuum system and a sequential 17-cm U-tube of zeolite 5A beads were fully activated at 673 K for 1 day, and then cooled to ambient temperature to prevent the movement of water molecules from more distant parts of the vacuum system to the crystal. While these conditions were maintained, the largely NH_4^+ -exchanged zeolite Y was dehydrated at room temperature

Table 1. Summary of experimental and crystallographic data

| | first crystal | second crystal |
|---|---|-----------------|
| Crystal cross-section (μm) | 200 | 180 |
| Ion exchange T (K) | 293 | 293 |
| Ion exchange for NH_4^+ (day, mL) | 2, 75 | 2, 75 |
| Evacuation T (K) | 293 | 293 |
| Crystal color | colorless | colorless |
| Data collection T (K) | 294(1) | 294(1) |
| Space group, Z | $Fd\bar{3}m, 1$ | $Fd\bar{3}m, 1$ |
| X-ray source | Pohang Light Source, Beamline 4A MXW (PLS, 4A MXW BL) | |
| Wavelength (\AA) | 0.74999 | 0.74999 |
| Unit cell constant, a (\AA) | 24.9639(2) | 24.9693(1) |
| 2θ range in data collection (deg) | 60.60 | 60.58 |
| No. of unique reflections, <i>m</i> | 992 | 992 |
| No. of reflections with $F_o > 4\sigma(F_o)$ | 926 | 921 |
| No. of variables, <i>s</i> | 60 | 60 |
| Data/parameter ratio, <i>m/s</i> | 16.5 | 16.5 |
| Weighting parameters, <i>a/b</i> | 0.064/136.0 | 0.055/106.5 |
| Final error indices | | |
| R_1/R_2 ($F_o > 4\sigma(F_o)$) ^a | 0.0429/0.1507 | 0.0376/0.1295 |
| R_1/R_2 (all intensities) ^b | 0.0446/0.1507 | 0.0396/0.1297 |
| Goodness-of-fit ^c | 1.272 | 1.254 |

^a $R_1 = \sum F_o - F_c / \sum F_o$ and $R_2 = [\sum w(F_o - F_c)^2 / \sum w(F_c)^2]^{1/2}$. R_1 and R_2 are calculated using only the 926 and 921 reflections for which $F_o > 4\sigma(F_o)$. ^b R_1 and R_2 are calculated using all 992 unique reflections measured. ^cGoodness-of-fit = $(\sum w(F_o - F_c)^2 / (m-s))^{1/2}$, where *m* and *s* are the number of unique reflections and variables, respectively.

(293 K) for 90 hrs. Still under vacuum in their capillaries, the crystals were then sealed in their capillaries and removed from the vacuum line by torch. Microscopic examination showed that the resulting single crystals, still under vacuum in their capillaries, were colorless.

X-ray Diffraction Work. X-ray diffraction data for the two single crystals dehydrated at room temperature were collected at 294(1) K using an ADSC Quantum210 detector at Beamline 4A MXW at The Pohang Light Source. Crystal evaluation and data collection were carried out using $\lambda = 0.74999 \text{ \AA}$ radiation with a detector-to-crystal distance of 6.0 cm. Preliminary cell constants and an orientation matrix were determined from 36 sets of frames collected at scan intervals of 5° with an exposure time of 1 second per frame. The basic scale file was prepared using the program HKL2000.⁵⁴ The reflections were successfully indexed by the automated indexing routine of the DENZO program.⁵⁴ The total of 92,589 and 92,786 reflections for each crystal, respectively, were harvested by collecting 72 sets of frames with 5° scans with an exposure time of 1 second per frame. These highly redundant data sets were corrected for Lorentz and polarization effects; negligible corrections for crystal decay were also applied. The space group $Fd\bar{3}m$ was determined by the program XPREP.⁵⁵ A summary of the experimental and crystallographic data is presented in Table 1.

Structure Determination

Full-matrix least-squares refinement using SHELXL97⁵⁶ was carried out on F_o^2 using all data for each crystal. Each refinement began with the atomic parameters of the framework atoms [(Si,Al), O(1), O(2), O(3), and O(4)] in dehydrated $[\text{K}_{11}][\text{Si}_{121}\text{Al}_{17}\text{O}_{384}]\text{-FAU}$.⁶⁰ Each initial refinement used

anisotropic thermal parameters and converged to the error indices given in Table 1. See Table 2 for the steps of structure determination and refinements as new atomic positions were found on successive difference-Fourier electron-density functions.

Because crystal had been ion exchanged with NH_4^+ , it was expected that this cation would predominate; indeed the bond lengths from the predominant cation positions to framework oxygens supported this assignment (ionic radii for NH_4^+ and Na^+ are 1.43 and 0.97 \AA , respectively⁵⁷). When cations were seen at site I, these were identified as Na^+ because (1) Na^+ had been introduced earlier to this crystal even though their radii were not appropriate.^{38,40,41,59} (2) the error indices R_1 and R_2 were more decreased when Na^+ was introduced than NH_4^+ . In support of these assignments, the refined occupancies for all cations provide the correct charge to balance that of the anionic zeolite framework.

The final cycles of refinement, done with the anisotropic temperature factors for all atoms and with the final weighting-scheme parameters, converged to $R_1/R_2 = 0.043/0.151$. The largest peaks appeared on the final difference Fourier function but were not included in the final model because they were too far from framework oxygen atoms to be cations, or because their peak heights were negligible. Furthermore, they were featureless when they were included in the model.

All shifts in the final cycles of refinements 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 $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$, with $a/b = 0.064/136.0$ as refined parameters (see Table 1). Atomic scattering factors for N^0 ,

Table 2. Initial steps of structure refinement^a

| Step | Occupancy ^b at | | | | | | R_1 | R_2 |
|----------------|---------------------------|---------|---------|----------|----------|----------|--------|--------|
| | Na(I) | Na(I') | Na(II) | N(I') | N(II) | N(III') | | |
| first crystal | | | | | | | | |
| 1 ^c | | | | | | | 0.1398 | 0.5467 |
| 2 | | | | | 25.9(12) | | 0.1072 | 0.3140 |
| 3 | | | | 27.7(13) | 33.1(9) | | 0.0740 | 0.2076 |
| 4 | 3.4(3) | | | 29.8(11) | 33.2(8) | | 0.0551 | 0.1740 |
| 5 | 3.4(3) | | 3.5(5) | 31.5(10) | 29.8(9) | | 0.0498 | 0.1610 |
| 6 | 3.5(3) | 2.7(4) | 3.4(5) | 28.2(12) | 29.8(9) | | 0.0474 | 0.1569 |
| 7 | 3.3(2) | 1.8(6) | 3.4(5) | 25.9(12) | 29.9(9) | 10.2(14) | 0.0445 | 0.1531 |
| 8 | 3.3(2) | 4.0(29) | 4.1(11) | 22.0(52) | 28.6(17) | 9.4(14) | 0.0429 | 0.1507 |
| second crystal | | | | | | | | |
| 1 ^c | | | | | | | 0.1364 | 0.5378 |
| 2 | | | | | 24.4(11) | | 0.1055 | 0.3006 |
| 3 | | | | 26.4(14) | 30.2(11) | | 0.0805 | 0.2178 |
| 4 | 4.5(2) | | | 26.4(9) | 32.6(7) | | 0.0483 | 0.1494 |
| 5 | 4.6(2) | | 2.6(4) | 27.8(9) | 30.7(8) | | 0.0440 | 0.1394 |
| 6 | 4.7(2) | 2.0(5) | 2.7(4) | 25.7(11) | 30.8(8) | | 0.0421 | 0.1346 |
| 7 | 4.7(2) | 1.7(5) | 3.1(4) | 24.0(10) | 31.1(7) | 8.3(13) | 0.0390 | 0.1311 |
| 8 | 4.7(2) | 1.8(12) | 3.2(6) | 24.0(22) | 30.6(11) | 7.3(13) | 0.0376 | 0.1295 |

^aIsotropic temperature factors were used for all Na^+ and NH_4^+ positions except for the last step. ^bThe occupancy is given as the number of Na^+ and NH_4^+ ions per unit cell. ^cOnly 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 | ^b U ₁₁ | U ₂₂ | U ₃₃ | U ₂₃ | U ₁₃ | U ₁₂ | ^c Occupancy | | | |
|--|------------------|-------------|----------|----------|----------|------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--|----------|-------|--|
| | | | | | | | | | | | | initial | varied | fixed | |
| [(NH ₄) ₆₀ Na ₁₁][Si ₁₂₁ Al ₇₁ O ₃₈₄]-FAU, first crystal | | | | | | | | | | | | | | | |
| Si,Al | 192(i) | | -542(1) | 1254(1) | 360(1) | 132(4) | 111(4) | 97(4) | -26(2) | 7(2) | -24(2) | 192 | | | |
| O(1) | 96(g) | | -1057(1) | 0 | 1057(1) | 267(9) | 289(15) | 267(9) | -91(8) | -38(12) | -91(8) | 96 | | | |
| O(2) | 96(g) | | -29(1) | -29(1) | 1424(1) | 261(9) | 261(9) | 225(14) | -39(8) | -39(8) | 137(12) | 96 | | | |
| O(3) | 96(g) | | -327(1) | 771(1) | 771(1) | 352(19) | 281(11) | 281(11) | 95(16) | 21(12) | 21(12) | 96 | | | |
| O(4) | 96(g) | | -707(1) | 709(1) | 1791(1) | 235(14) | 271(9) | 271(9) | -162(12) | -13(9) | 13(9) | 96 | | | |
| Na(I) | 16(c) | I | 0 | 0 | 0 | 9(40) | 9(40) | 9(40) | 32(27) | 32(27) | 32(27) | | 3.3(2) | 3 | |
| Na(I') | 32(e) | I' | 679(67) | 679(67) | 679(67) | 629(408) | 629(408) | 629(408) | 495(372) | 495(372) | 495(372) | | 4.0(29) | 4 | |
| Na(II) | 32(e) | II | 2351(26) | 2351(26) | 2351(26) | 638(325) | 638(325) | 638(325) | 555(306) | 555(306) | 555(306) | | 4.1(11) | 4 | |
| N(I') | 32(e) | I' | 780(4) | 780(4) | 780(4) | 340(45) | 340(45) | 340(45) | -30(65) | -30(65) | -30(65) | | 22.0(52) | 22 | |
| N(II) | 32(e) | II | 2555(3) | 2555(3) | 2555(3) | 290(23) | 290(23) | 290(23) | 11(26) | 11(26) | 11(26) | | 28.6(17) | 29 | |
| N(III') | 192(g) | III' | 595(8) | 1905(8) | 2868(16) | 46(101) | 46(101) | 401(197) | 7(83) | -7(83) | 219(105) | | 9.4(14) | 9 | |
| | | | | | | | | | | | | Σ(Na ⁺ +NH ₄ ⁺) = 71.4(21) | | | |
| [(NH ₄) ₆₁ Na ₁₀][Si ₁₂₁ Al ₇₁ O ₃₈₄]-FAU, second crystal | | | | | | | | | | | | | | | |
| Si,Al | 192(i) | | -541(1) | 1252(1) | 360(1) | 127(3) | 106(3) | 93(3) | -26(2) | 8(2) | -25(2) | 192 | | | |
| O(1) | 96(g) | | -1057(1) | 0 | 1057(1) | 259(8) | 285(13) | 259(8) | -94(7) | -42(10) | -94(7) | 96 | | | |
| O(2) | 96(g) | | -30(1) | -30(1) | 1425(1) | 255(8) | 255(8) | 218(12) | -41(7) | -41(7) | 134(10) | 96 | | | |
| O(3) | 96(g) | | -326(1) | 762(1) | 762(1) | 339(17) | 323(11) | 323(11) | 145(16) | 29(11) | 29(11) | 96 | | | |
| O(4) | 96(g) | | -704(1) | 716(1) | 1784(1) | 231(12) | 289(9) | 289(9) | -183(10) | -29(8) | 29(8) | 96 | | | |
| Na(I) | 16(c) | I | 0 | 0 | 0 | 21(25) | 21(25) | 21(25) | 21(16) | 21(16) | 21(16) | | 4.7(2) | 5 | |
| Na(I') | 32(e) | I' | 613(45) | 613(45) | 613(45) | 235(364) | 235(364) | 235(364) | 142(283) | 142(283) | 142(283) | | 1.8(12) | 2 | |
| Na(II) | 32(e) | II | 2329(17) | 2329(17) | 2329(17) | 475(213) | 475(213) | 475(213) | 354(197) | 354(197) | 354(197) | | 3.2(6) | 3 | |
| N(I') | 32(e) | I' | 778(7) | 778(7) | 778(7) | 336(33) | 336(33) | 336(33) | 16(44) | 16(44) | 16(44) | | 24.0(22) | 24 | |
| N(II) | 32(e) | II | 2549(2) | 2549(2) | 2549(2) | 292(19) | 292(19) | 292(19) | 7(19) | 7(19) | 7(19) | | 30.6(11) | 30 | |
| N(III') | 192(g) | III' | 588(8) | 1912(8) | 2870(15) | 1(104) | 1(104) | 340(191) | -36(74) | 36(74) | 265(106) | | 7.3(13) | 7 | |
| | | | | | | | | | | | | Σ(Na ⁺ +NH ₄ ⁺) = 71.6(11) | | | |

^aPositional parameters × 10⁴ and thermal parameters × 10⁴ are given. Numbers in parentheses are the estimated standard deviations in the units of the least significant figure given for the corresponding parameter. ^bThe anisotropic temperature factor is exp[-2π²a⁻²(U₁₁h² + U₂₂k² + U₃₃l² + 2U₂₃kl + 2U₁₃hl + 2U₁₂hk)]. ^cOccupancy factors are given as the number of atoms or ions per unit cell.

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

| | first crystal | second crystal | | first crystal | second crystal |
|---------------------|-------------------|-------------------|----------------------|----------------------|----------------------|
| (Si,Al)-O(1) | 1.6436(12) | 1.6448(10) | O(1)-(Si,Al)-O(4) | 109.65(14) | 109.89(12) |
| (Si,Al)-O(2) | 1.6624(10) | 1.6621(9) | O(2)-(Si,Al)-O(3) | 107.14(15) | 107.21(13) |
| (Si,Al)-O(3) | 1.6720(13) | 1.6706(11) | O(2)-(Si,Al)-O(4) | 107.05(14) | 107.20(12) |
| (Si,Al)-O(4) | 1.6514(11) | 1.6492(10) | O(3)-(Si,Al)-O(4) | 110.00(21) | 110.21(19) |
| Mean (Si,Al) | 1.6574(12) | 1.6567(10) | (Si,Al)-O(1)-(Si,Al) | 140.16(21) | 139.80(18) |
| Na(I)-O(3) | 2.842(5) | 2.812(5) | (Si,Al)-O(2)-(Si,Al) | 146.56(19) | 146.43(16) |
| Na(I')-O(3) | 2.53(13) | 2.4(7) | (Si,Al)-O(3)-(Si,Al) | 141.45(23) | 140.93(20) |
| Na(II)-O(2) | 2.40(4) | 2.366(22) | (Si,Al)-O(4)-(Si,Al) | 142.53(20) | 143.75(18) |
| N(I')-O(3) | 2.762(11) | 2.756(19) | | | |
| N(II)-O(2) | 2.824(9) | 2.809(6) | O(3)-Na(I)-O(3) | 85.98(12), 94.02(12) | 86.43(9), 93.57(9) |
| N(III')-O(1) | 2.55(3) | 2.54(3) | O(3)-Na(I')-O(3) | 99.9(7) | 106.2(5) |
| N(III')-O(2) | 2.725(13) | 2.733(13) | O(2)-Na(II)-O(2) | 108.9(3) | 111.1(15) |
| N(I')...N(I') | 3.32(3) | 3.34(5) | O(3)-N(I')-O(3) | 89.1(5) | 88.4(8) |
| | | | O(2)-N(II)-O(2) | 87.3(3) | 88.0(3) |
| O(1)-(Si,Al)-O(2) | 111.10(12) | 110.92(10) | O(1)-N(III')-O(1) | 94.1(13) | 94.4(13) |
| O(1)-(Si,Al)-O(3) | 111.76(17) | 111.29(16) | O(1)-N(III')-O(2) | 62.16(15), 155.7(14) | 62.06(15), 155.7(14) |

^aThe numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

Table 5. Displacements of Atoms (Å) from 6-ring Planes

| | position | site | first crystal | second crystal |
|----------------------|----------|------|---------------|----------------|
| | | | displacement | displacement |
| at O(3) ^a | Na(I) | I | 1.75 | 1.73 |
| | Na(I') | I' | -1.19 | -0.93 |
| | N(I') | I' | -1.62 | -1.64 |
| at O(2) ^b | Na(II) | II | 0.82 | 0.72 |
| | N(II) | II | 1.70 | 1.67 |

^aA positive displacement indicates that the ion lies within a D6R. A negative deviation indicates that the ion lies in a sodalite unit. ^bThe positive displacement indicates that the ion lies in the supercage.

Na^+ , O^- , and $(\text{Si,Al})^{1.82+}$ were used.^{78,79} The function describing $(\text{Si,Al})^{1.82+}$ is the weighted mean of the Si^{4+} , Si^{δ} , Al^{3+} , and Al^{δ} functions assuming half formal charges. All scattering factors were modified to account for anomalous dispersion.^{80,81} The structure was determined again, using a second crystal prepared like the first. The second determination was done to check-reproducibility; only the result for first crystal is presented in this report except in Tables.

Results and Discussion

The framework structure of faujasite is characterized by the double 6-ring (D6R, hexagonal prism), the sodalite cavity (a cubooctahedron), and the supercage (see Figure 1). Each unit cell has 8 supercages, 8 sodalite cavities, 16 D6Rs, 16 12-rings, and 32 single 6-rings (S6Rs).

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 1. The maximum occupancies at the cation sites I, I', II, II', III, and III' in faujasite are 16, 32, 32, 32, 48, and (in $Fd\bar{3}m$) 192, respectively. Further description is available.^{4,69}

In this structure, The 11 Na^+ ions per unit cell are found at three different crystallographic sites and 60 NH_4^+ ions are distributed over three sites. Three Na^+ ions at Na(I) lie at site

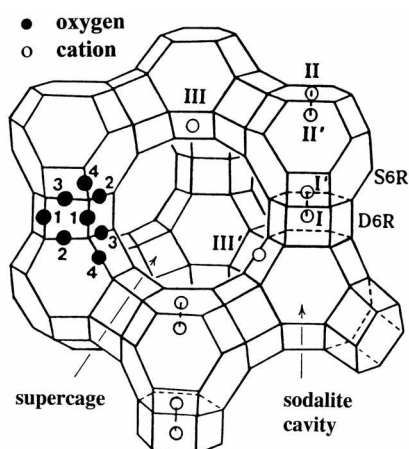


Figure 1. Stylized drawing of the framework structure of zeolite Y. Near the center of the each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1 to 4. There is no evidence in this work of any ordering of the silicon and aluminum atoms among the tetrahedral positions, although it is expected that Lowenstein's rule (ref. 82) would be obeyed. Extraframework cation positions are labeled with Roman numerals.

I in the center of a D6R (see Figure 2(a)). Each Na^+ ion at Na(I) is coordinated by the six O(3) oxygen atoms of its D6R at distance of 2.842(5) Å, which is longer than the sum of the ionic radii of Na^+ and O^{2-} , $0.97 + 1.32 = 2.29$ Å.⁷⁷ In the structure of $[\text{Na}_{38}][\text{Si}_{104}\text{Al}_{88}\text{O}_{384}]$ -FAU,³⁸ $[\text{Rb}_{71}\text{Na}_{21}][\text{Si}_{100}\text{Al}_{92}\text{O}_{384}]$ -FAU,⁴⁰ $[\text{Cs}_{45}\text{Na}_{47}][\text{Si}_{100}\text{Al}_{92}\text{O}_{384}]$ -FAU,⁴¹ and $[\text{Na}_{71}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]$ -FAU,³⁹ Na^+ ions were found at site I with occupancies of 3, 7, 14, and 5, respectively. The bonding distances between Na^+ ions at site I and framework oxygen

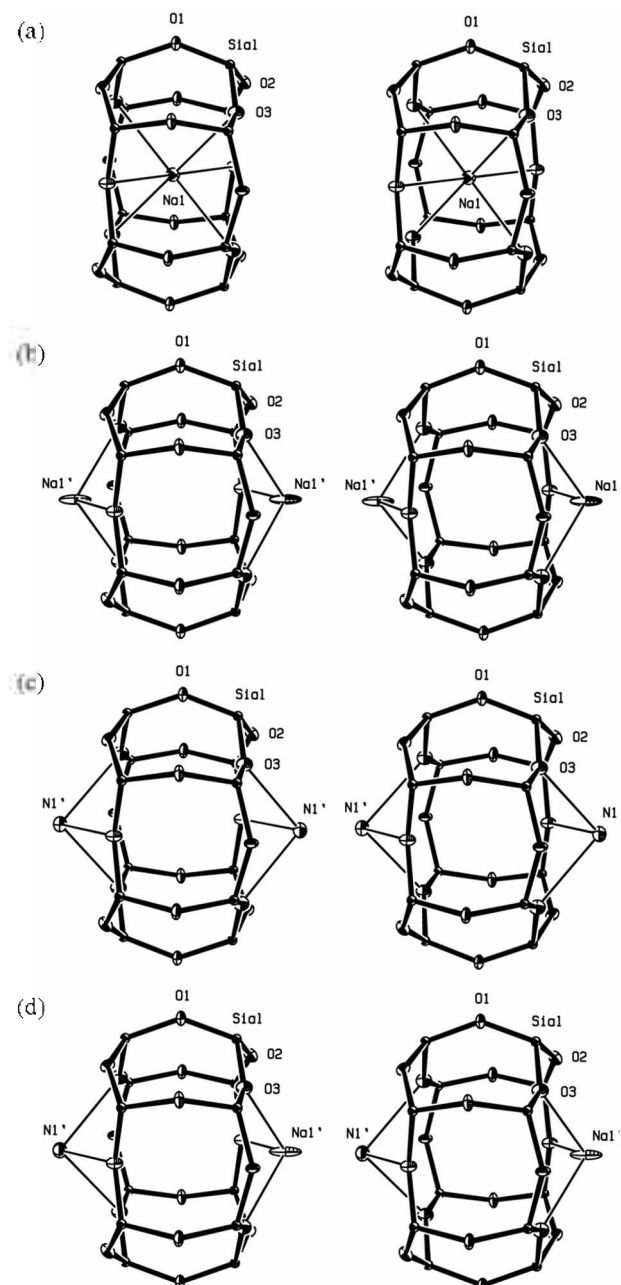


Figure 2. A stereoview of a representative double 6-ring (D6R) and sodalite unit in dehydrated $[(\text{NH}_4)_{60}\text{Na}_{11}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]$ -FAU. Of the 16 D6Rs per unit cell, about 3 Na^+ ions are occupied as shown in (a) and the arrangements of Na^+ and NH_4^+ ions (b), (c), and (d) are also possible. The zeolite Y framework is drawn with heavy bonds. The coordination of Na^+ and NH_4^+ ions to oxygens of the zeolite framework are indicated by light bonds. Ellipsoids of 25% probability are shown.

were 2.748(5), 2.578(12), 2.454(12), and 2.739(4) Å in the structures of $[\text{Na}_{88}][\text{Si}_{104}\text{Al}_{88}\text{O}_{384}]\text{-FAU}$,³⁸ $[\text{Rb}_{71}\text{Na}_{21}][\text{Si}_{100}\text{-Al}_{92}\text{O}_{384}]\text{-FAU}$,⁴¹ $[\text{Cs}_{45}\text{Na}_{47}][\text{Si}_{100}\text{Al}_{92}\text{O}_{384}]\text{-FAU}$,⁴¹ and $[\text{Na}_{71}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]\text{-FAU}$,⁵⁰ respectively. In this work, 3 Na^+ ions were also found at site I. It is interesting that Na^+ ions occupy site I with relatively long bonding distances to the closest framework oxygens in this structure. Perhaps this occurs because NH_4^+ ions preferentially occupy large-cavity sites, in particular sites I', II, and III', which Na^+ would otherwise occupy. The inability of the large cation, NH_4^+ , to approach into the small-cavity sites like as D6Rs makes it difficult for NH_4^+ to exchange completely for Na^+ in D6Rs. Size effect, therefore, appears to be responsible for the occupancy of site I by Na^+ ions in this structure. Furthermore, NH_4^+ ion has lower ionization tendency than Na^+ ion.

The 4 Na^+ ions at Na(I') and 22 NH_4^+ ions at N(I') lie at site I', on the 3-fold axis in the sodalite unit opposite D6Rs (see Figures 2(b), (c), (d), and 3). This is 32-fold position, but it is occupied by 26 cations. Each Na^+ and NH_4^+ ion lies relatively far inside the sodalite cavity, 1.19 and 1.62 Å, respectively, from the plane of the three O(3) framework oxygens of the D6R which it is bound (see Table 5). The Na(I')-O(3) distance is 2.53(13) Å, longer than the sum of the corresponding ionic radii, $0.97 + 1.32 = 2.29$ Å.⁷⁷ This indicates that Na^+ ions coordinate weakly to their three O(3) oxygens. The NH_4^+ ions at site I' bond to three O(3)s at 2.762(11) Å, which is almost the same with the sum of the conventional ionic radii of NH_4^+ and O^{2-} , $1.43 + 1.32 = 2.75$ Å,⁷⁷ indicative of a good fit (see

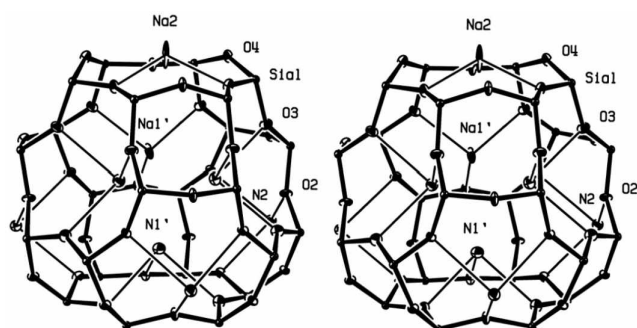


Figure 3. A stereoview of a representative sodalite in dehydrated $[(\text{NH}_4)_{60}\text{Na}_{11}][\text{Si}_{104}\text{Al}_{88}\text{O}_{384}]\text{-FAU}$. See the caption to Figure 2 for other details.

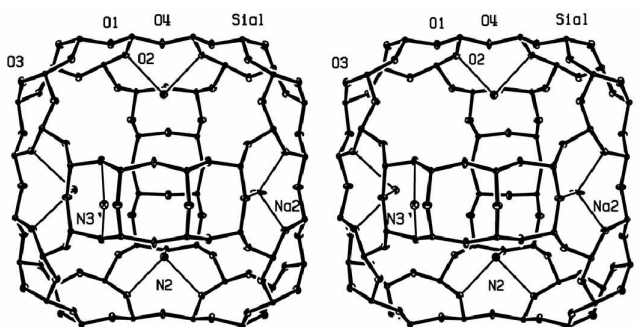


Figure 4. A stereoview of a representative supercage in dehydrated $[(\text{NH}_4)_{60}\text{Na}_{11}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]\text{-FAU}$. See the caption to Figure 2 for other details.

Table 4 and Figure 3).

The Na(II) and N(II) occupy site II in the supercage with occupancies of 4 and 29, respectively, filling the 32-fold equipoint. Na(II)-O(2) is 2.40(4) Å, which is slightly longer than the sum of the ionic radii of Na^+ and O^{2-} , $0.97 + 1.32 = 2.29$ Å,⁷⁷ and O(2)-Na(II)-O(2) is $108.9(3)^\circ$; N(II)-O(2) is 2.824(9) Å which is a little longer than the sum of the ionic radii of NH_4^+ and O^{2-} , 2.75 Å,⁷⁷ and O(2)-N(II)-O(2) is $87.3(3)^\circ$. The 4 Na^+ ions at Na(II) are only 0.82 Å from the plane of the single 6-ring; 29 NH_4^+ ions at N(II) are much further, 1.70 Å from the corresponding plane (see Table 5). Plausible ionic arrangements for a sodalite unit and a supercage are shown in Figures 3 and 4, respectively.

The final 3 NH_4^+ ions at N(III') lie in 12-rings. They bind strongly to one O(1) at 2.55(3) Å and to one O(4) at 2.725(13) Å (see Figure 4). Such short bonding distances between cation at site III' and framework oxygen have been reported before in several references.^{42,83}

McCusker *et al.* readily accomplished the complete NH_4^+ -exchange into zeolite A. After evacuation at room temperature, a single crystal-structure determination showed that complete dehydration had been achieved. To avoid severe damage in the framework of zeolite A by protons arising from the hydrolysis of Cu^{2+} and Ni^{2+} ions, Lee *et al.*²⁵ and Patalinghug *et al.*⁷² added ammonia to the ion-exchange solutions. Their structures were revealed Cu^{2+} , NH_4^+ -exchanged and Ni^{2+} , NH_4^+ -exchanged zeolite A, respectively.^{25,72} Zhen *et al.* prepared anhydrous NH_4^+ -exchanged zeolite X, allowed it to react with HgCl_2 vapor at 388 K, and determined the resulting structure, $[\text{Hg}_{44}\text{Cl}_{64}(\text{NH}_4)_{58}][\text{Si}_{100}\text{Al}_{92}\text{O}_{384}]\text{-FAU}$.⁷³ At this structure, 8 and 30 NH_4^+ ions per unit cell at site I' and II, respectively, coordinated to oxygens of the zeolite framework. The 8 NH_4^+ ions at site I' each coordinated trigonally to three O(3) oxygens at 2.98(10) Å and the 30 NH_4^+ ions at site II each coordinated trigonally to three O(2) oxygens at 2.89(4) Å. These positions and bonding distances to the framework oxygens of NH_4^+ ions are similar with our findings.

The reproducibility of structural information was double checked using a second crystal prepared from exactly the same conditions as the first one. No significant differences were seen between the two crystal structures except for the distributions of cations (see Table 3). It appears that the difference in the amount of NH_4^+ ion could be attributed to the usage of the batch method for ion exchange. The total number of Na^+ and NH_4^+ ions in two single crystals was found to be 71.4(21) and 71.6(11) per unit cell, respectively. It means that the Si/Al ratio of the single crystals of FAU-type zeolite is 1.70.

Summary

The single crystal structure of largely NH_4^+ -exchanged zeolite Y has been determined using synchrotron X-radiation in the cubic space group $Fd\bar{3}m$ ($a = 24.9639(2)$ Å) at 294 K. The composition (best integers) is seen to be $(\text{NH}_4)_{60}\text{Na}_{11}[\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]\text{-FAU}$. The 11 Na^+ ions per unit cell are found at three different crystallographic sites and 60 NH_4^+ ions are distributed over three sites. The 3 Na^+ ions are located at site

I, the center of the hexagonal prism (Na(I)-O(3) = 2.842(5) Å and O(3)-Na(I)-O(3) = 85.98(12)°). The 4 Na⁺ and 22 NH₄⁺ ions are found at site I' in the sodalite cavity opposite the double 6-rings, respectively (Na(I')-O(3) = 2.53(13) Å, O(3)-Na(I')-O(3) = 99.9(7)°, N(I')-O(3) = 2.762(11) Å, and O(3)-N(I')-O(3) = 89.1(5)°). About 4 Na⁺ ions occupy site II (Na(II)-O(3) = 2.40(4) Å and O(3)-Na(II)-O(3) = 108.9(3)°) and 29 NH₄⁺ ions occupy site II (N(II)-O(3) = 2.824(9) Å and O(3)-N(II)-O(3) = 87.3(3)°) opposite to the single 6-rings in the supercage. The remaining 9 NH₄⁺ ions are distributed over site III' (N(III')-O(1) = 2.55(3), N(III')-O(2) = 2.725(13) Å, O(1)-N(III')-O(1) = 94.1(13), and O(1)-N(III')-O(2) = 62.16(15), 155.7(14)°).

The fully NH₄⁺-exchanged zeolite Y was not achieved due to the bigger size and lower ionization tendency of NH₄⁺ than Na⁺ ion in this work. The total number of Na⁺ and NH₄⁺ ions in two single crystals was found to be 71.4(21) and 71.6(11) per unit cell, respectively, which corresponds to the Si/Al ratio of 1.70 for the single crystals of FAU-type zeolite.

Supporting Information. Tables of calculated and observed structure factors (23 pages). The supporting materials are available at <http://www.kcsnet.or.kr/bkcs> or upon your request to a corresponding author.

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