

## Articles

Synthesis and Single-crystal Structure of Fully Dehydrated Fully  $\text{Ca}^{2+}$ -exchanged Zeolite Y (FAU),  $[\text{Ca}_{35.5}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]$ -FAUSung Man Seo, Sik Young Choi, Jeong Min Suh,<sup>†</sup> Ki Jin Jung,<sup>‡</sup> Nam Ho Heo,<sup>‡</sup> and Woo Taik Lim\*

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The single-crystal structure of  $[\text{Ca}_{35.5}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]$ -FAU,  $\text{Ca}_{35.5}\text{Si}_{121}\text{Al}_{71}\text{O}_{384}$  per unit cell,  $a = 24.9020(10)$  Å, dehydrated at 673 K and  $2 \times 10^{-6}$  Torr, has been determined by single-crystal X-ray diffraction techniques in the cubic space group  $Fd\bar{3}m$  at 294 K. The large single crystals of zeolite Y (Si/Al = 1.70) were synthesized up to diameters of 200  $\mu\text{m}$  and  $\text{Ca}^{2+}$ -exchanged zeolite Y were prepared by ion exchange in a batch method of 0.05 M aqueous  $\text{Ca}(\text{NO}_3)_2$  for 4 hrs at 294 K. The structure was refined using all intensities to the final error indices (using only the 971 reflections for which  $F_o > 4\sigma(F_o)$ )  $R_1 = 0.038$  (based on  $F$ ) and  $R_2 = 0.172$  (based on  $F^2$ ). About 35.5  $\text{Ca}^{2+}$  ions per unit cell are found at an unusually large number of crystallographically distinct positions, four. Nearly filling site I (at the centers of the double 6-rings), 14.5 octahedrally coordinated  $\text{Ca}^{2+}$  ions (Ca-O = 2.4194(24) Å and O-Ca-O = 87.00(8) and 93.00(8)°) are found per unit cell. One  $\text{Ca}^{2+}$  ion per unit cell is located at site II' in the sodalite cavity and extends 0.50 Å into the sodalite cavity from its 3-oxygen plane (Ca-O = 2.324(13) Å and O-Ca-O = 115.5(10)°). The remaining twenty  $\text{Ca}^{2+}$  ions are found at two nonequivalent sites II (in the supercages) with occupancies of 10 and 10 ions, respectively. Each of these  $\text{Ca}^{2+}$  ions coordinates to three framework oxygens, either at 2.283(3) or 2.333(5) Å, respectively, and extends either 0.24 or 0.54 Å, respectively, into the supercage from the three oxygens to which it is bound. In this crystal, site I is the most populated; sites II' and II are only sparsely occupied.  $\text{Ca}^{2+}$  appears to fit the octahedral site I best. No cations are found at sites III or III', which are clearly less favorable for  $\text{Ca}^{2+}$  ions in dehydrated zeolite Y.

**Key Words:** Zeolite Y, Ion exchange, Dehydrated, Structure, Calcium

## Introduction

Synthetic faujasite (FAU) with  $1.5 \leq \text{Si} / \text{Al} \leq 3.0$  is called zeolite Y. It was first synthesized in its sodium form in 1964 by Union Carbide.<sup>1</sup> Zeolite Y has a wide range of industrial applications due primarily to its excellent structural stability and its large and accessible pore volume. 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.<sup>1</sup>

One of the most importantly applied and an informative technique for characterization of cations in zeolite framework is single-crystal X-ray diffraction. So numerous investigations of the positions of the exchangeable cations in zeolite X (Si/Al = 1.09) have been conducted by single-crystal X-ray diffraction technique.<sup>2-4</sup> And the structures of sorption complexes that show how various guest molecules are held on the inner surfaces of zeolites are being obtained crystallographically.<sup>5,11</sup>

Smolin *et al.*<sup>2</sup> determined the crystal structures of Ca-X at various dehydration temperatures. In the partially dehydrated form,  $\text{Ca}^{2+}$  ions were located in sites I, I', II, and III. They confirmed that the occupancy at site III decreased with increasing dehydration temperature. Using single-crystal X-ray diffraction technique in the cubic space group  $Fd\bar{3}$  at

24(1) °C, Seff *et al.*<sup>3,4</sup> determined the structure of fully dehydrated, fully  $\text{Ca}^{2+}$ -exchanged zeolite X (Si/Al = 1.09) to learn the cation positions and the site selectivity. They also studied the crystal structures of ethylene,<sup>5</sup> acetylene,<sup>5</sup> hydrogen sulfide,<sup>6</sup> benzene,<sup>7</sup> ammonia,<sup>8</sup> cyclopropane,<sup>9</sup> mesitylene,<sup>10</sup> and methylamine<sup>11</sup> complexes of fully dehydrated fully  $\text{Ca}^{2+}$ -exchanged zeolite X (Si/Al = 1.09) to observe the geometry and chemistry of sorption in zeolites (*i.e.*, to determine shifts in cation and framework atomic positions, to observe cation-sorbate interactions, and to detect resultant changes in sorbed molecule geometry). They noted that there were some unusual two kinds of site-II  $\text{Ca}^{2+}$  ions in benzene,<sup>7</sup> mesitylene,<sup>10</sup> and methylamine<sup>11</sup> sorption complexes of  $\text{Ca}^{2+}$ -exchanged zeolite X. They described that the coordination of the sorption complexes such as benzene, mesitylene, and methylamine had caused  $\text{Ca}^{2+}$  ions to move along its 3-fold axis more deeply into the supercage from the three O(2) plane, compared to its position in dehydrated  $\text{Ca}_{46}\text{-X}$ .<sup>2-4</sup>

Zeolites X and Y are distinct zeolite species with characteristic differences, even though they have topologically similar aluminosilicate framework structure. Due to the high thermal stability and the selectivity, zeolite Y is very important catalyst or catalyst supports in various industrial reactions such as cracking, isomerization, and hydrocracking.

Sun *et al.*<sup>12</sup> used  $\text{Ca}^{2+}$ - and  $\text{Ba}^{2+}$ -exchanged Zeolites Y for the oxidation of toluene. They reported the first selective photo-oxidation of toluene to benzaldehyde by  $\text{O}_2$ . It was accomplished by photoexcitation of  $\text{C}_6\text{H}_5\text{CH}_2\text{O}_2$  complexes in the molecular-scale cages of alkaline-earth-exchanged faujasite zeolites with visible light. Fraissard *et al.*<sup>13</sup> dealuminated zeolite Y ( $\text{Si}/\text{Al} = 2.17$ ) by hexafluorosilicate ( $\text{Si}/\text{Al} = 3.13$ ) and exchanged calcium to study the effect of calcium on its behavior in acidic and basic media by using X-ray diffraction and solid-state NMR of  $^{29}\text{Si}$  and  $^{27}\text{Al}$ . They reported that the introduction of calcium improved the stability of the zeolite in acid and base. After the synthesis of the large single crystals of zeolite Y with diameters up to 210–245  $\mu\text{m}$  by David Vaughan, there were two crystallographic studies on the distribution of the cations in zeolite Y.<sup>14–15</sup> Kim *et al.*<sup>14</sup> reported the single crystal structure of fully dehydrated, excessively  $\text{Cd}^{2+}$ -exchanged zeolite Y. They found the eight additional molecules of  $\text{Cd}(\text{OH})_2$  imbedded per unit cell of zeolite Y at  $\text{pH} = 7$ . Lim *et al.*<sup>15</sup> successfully prepared and determined the structure of fully dehydrated fully  $\text{K}^+$ -exchanged zeolite Y by single-crystal X-ray diffraction technique to determine the cation positions of the  $\text{K}^+$  ions. They found the sites about the D6Rs and the sodalite cavities were densely occupied as was seen in  $\text{K}_{92}\text{-X}$ <sup>16</sup> and  $\text{K}_{96}\text{-LSX}$ .<sup>17</sup> They noted some unusually close  $\text{K}^+\cdots\text{K}^+$  contacts and described it as cation crowding.

This work was initiated to investigate the ion exchange behavior of  $\text{Ca}^{2+}$  in zeolite Y, perhaps to find in possible Si-Al ordering at the tetrahedral sites, and to compare its structure with that of  $\text{Ca}_{46}\text{-X}$ .<sup>3,4</sup> It was hoped that something more could be learned about the Si/Al ordering within these crystals. Perhaps sharp differences in Si/Al ordering make various zeolite Y samples fundamentally nonequivalent so that work completed on these crystals would not be generally applicable to all zeolite Y samples of similar composition. It was also done as a preliminary to later studies of crystal structures of the zeolite Y absorbed with other guest molecules.

### Experimental Section

#### Synthesis of the Large Single Crystals of Zeolite Y(FAU).

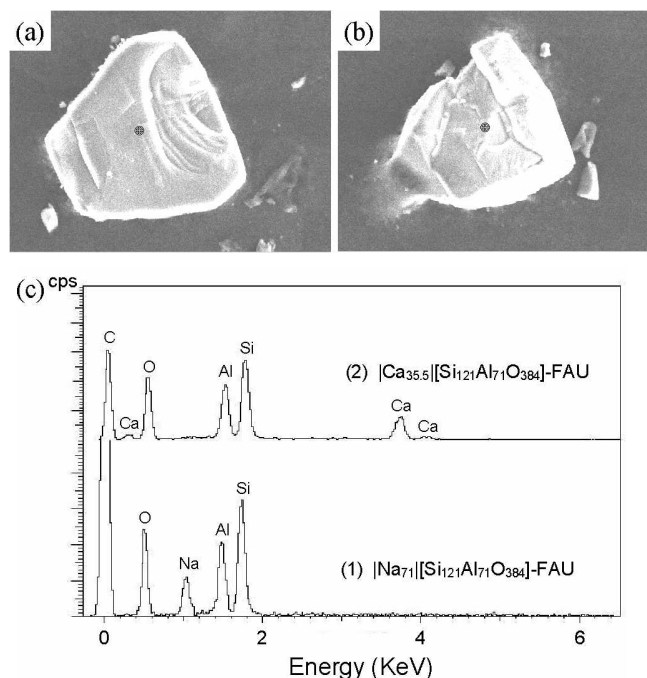
Large colorless single crystals of sodium zeolite Y, stoichiometry  $\text{Na}_{71}\text{Si}_{121}\text{Al}_{71}\text{O}_{384}$ , with diameters up to 200  $\mu\text{m}$  were synthesized from a gel with the composition 3.58 $\text{SiO}_2$  : 2.08  $\text{NaAlO}_2$  : 7.59 $\text{NaOH}$  : 455 $\text{H}_2\text{O}$  : 5.06 $\text{TEA}$  : 1.23 $\text{TCl}$ . A starting gel was prepared from fumed silica (99.8%, Sigma), sodium aluminate (technical, Wako), sodium hydroxide (96%, Wako), triethanolamine (99+%, Acros), bis(2-hydroxyethyl)dimethyl ammonium chloride (99%, Acros), and distilled water.

First, silica slurries were prepared by suspending 0.58 g of fumed silica in 10 g of distilled water in 30 mL PTFE beaker, and the suspension was stirred in orbital shaker (NB-101M, N-Biotek) with 200 RPM for 10 minutes. In another 250 mL PTFE beaker, 11.51 g of sodium hydroxide dissolved in 170.40 g of distilled water, and then 6.47 g of sodium aluminate was added. The resulting solution was filtered through a 0.1  $\mu\text{m}$  membrane filter (PTFE syringe, Whatman). After adding 15.19 g of TEA and 4.19 g of TCl to the filtered sodium aluminate solutions, it was filtered two times through 0.1  $\mu\text{m}$

membrane filters. Finally, the latter solution was added to the former slowly, which caused the mixture to be a very viscous gel. These steps were all done at room temperature (294 K). After the TEA/TCl-aluminosilicate gel was charged in 30 mL PTFE bottle, the bottle was placed in a convection oven at 368 K for 18 days. The product was filtered, washed with distilled water 10 times, and dried at 323 K for 2 days prior to characterization. Microscopic examination showed that the single crystals were transparent and colorless.

**Ion-exchange of Zeolite Y(FAU).** Crystals of hydrated  $[\text{Ca}_{35.5}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]\text{-FAU}$  (or  $\text{Ca}_{35.5}\text{-Y}$ ) were prepared by static ion-exchange of  $[\text{Na}_{71}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]\text{-FAU}$ <sup>18</sup> with aqueous 0.05 M  $\text{Ca}(\text{NO}_3)_2$  (Aldrich 99.997%).<sup>7,12</sup> 0.1 g of hydrated sodium zeolite Y was mixed with 10 mL of 0.05 M  $\text{Ca}(\text{NO}_3)_2$  in 15 mL-conical tube and then the mixture was stirred on an orbital shaker (NB-101 M, N-Biotek) for 4 hrs at 294 K. The ion-exchange procedure was repeated 5 times with the fresh  $\text{Ca}(\text{NO}_3)_2$  solution. The product was then washed each time with 300 mL distilled water followed by filtration and oven-dried at 323 K for 1 day. These crystals may have contained the template cation, bis(2-hydroxyethyl)dimethyl ammonium, used in its synthesis.

One of these, a clear and colorless octahedron about 200  $\mu\text{m}$  in cross-section, hydrated  $\text{Ca}^{2+}$ -exchanged zeolite Y crystal was lodged in a fine Pyrex capillary and dehydrated at 673 K and  $2 \times 10^{-6}$  Torr for 2 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.



**Figure 1.** The SEM images of the intentionally broken single crystals of  $[\text{Na}_{71}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]\text{-FAU}$  (a) and  $[\text{Ca}_{35.5}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]\text{-FAU}$  (b), and EDX spectra of  $[\text{Na}_{71}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]\text{-FAU}$  (c, (1)) and  $[\text{Ca}_{35.5}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]\text{-FAU}$  (c, (2)).

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 was pale yellow.

**SEM-EDX Analysis.** The in-situ synthetic zeolite Y ([Na<sub>71</sub>] [Si<sub>121</sub>Al<sub>71</sub>O<sub>384</sub>]-FAU) and Ca<sup>2+</sup>-exchanged zeolite Y ([Ca<sub>35.5</sub>] [Si<sub>121</sub>Al<sub>71</sub>O<sub>384</sub>]-FAU) products were characterized by SEM-EDX analysis. Ten of selected single crystals from the batch were intentionally broken for using the fresh surface of the crystals, and were attached on the surface of carbon-attach tape for SEM-EDX analysis (see Figure 1(a)). Each single crystal was measured 3 times and resulted Si/Al = 1.70 of mean value. After diffraction data collection, the Ca<sup>2+</sup>-exchanged zeolites Y were removed from its capillaries for SEM-EDX analysis. This single crystal was also intentionally broken to expose fresh surface and was attached on the surface of carbon-attach tape for analysis (see Figure 1(b)). As shown in Figure 1(c), it was confirmed that Na-type zeolite Y was completely ion exchanged with Ca<sup>2+</sup>.

The SEM image and atomic concentration of the crystal were identified by JSM-6300 scanning electron microscope and Energy Dispersive X-ray spectrometer (EDX) both at 294 K and  $1 \times 10^{-7}$  Torr.

**Single-crystal X-ray Diffraction Work.** X-ray diffraction data of the resulting single-crystal was collected at 294(1) K on an ADSC Quantum210 detector at Beamline 4A MXW of Pohang Light Source. The crystal evaluation and data collection were done using 0.70 Å-wavelength 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.<sup>19</sup> The reflections were successfully indexed by the automated indexing routine of the DENZO

program.<sup>19</sup> A total of 112,973 reflections were harvested by collecting 72 sets of frames with 5° scans with an exposure time of 1 second 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 $\bar{3}m$*  was determined by the program XPREP.<sup>20</sup> A summary of the experimental and crystallographic data is presented in Table 1.

### Structure Determination

Full-matrix least-squares refinement (SHELXL97)<sup>21</sup> 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 [Na<sub>71</sub>][Si<sub>121</sub>Al<sub>71</sub>O<sub>384</sub>]-FAU.<sup>18</sup> The initial refinement using anisotropic thermal parameters for all positions converged to the error indices (defined in Table 1, footnote *b*)  $R_1 = 0.322$  and  $R_2 = 0.788$ .

A difference Fourier function revealed two large peaks, at (0.0, 0.0, 0.0) and (0.224, 0.224, 0.224), with heights of 39.9 and 20.7 e<sup>-</sup>/Å<sup>3</sup>, respectively. Refinement including them as Ca<sup>2+</sup> ions with isotropic thermal parameters at Ca(I) and Ca(IIb) converged to  $R_1 = 0.056$  and  $R_2 = 0.204$  with occupancies of 15.33(19) and 21.7(3), respectively.

On an ensuing difference Fourier function, a peak of height 2.8 e<sup>-</sup>/Å<sup>3</sup> appeared at (0.238, 0.238, 0.238). Least-squares refinement including this peak isotropically as Ca(IIa) converged to  $R_1 = 0.043$  and  $R_2 = 0.181$  with occupancies of 10.5(11).

From a subsequent difference Fourier function, a peak of height 2.1 e<sup>-</sup>/Å<sup>3</sup> was found at (0.202, 0.202, 0.202). This refined as Ca(II'). Simultaneous positional, occupancy and isotropic thermal parameter refinement for all atoms, except framework atoms which were refined anisotropically, converged to  $R_1 = 0.038$  and  $R_2 = 0.173$  with occupancies of 15.19(14), 1.6(3), 10.9(11), and 10.5(11) for Ca(I), Ca(II'), Ca(IIa), and Ca(IIb), respectively. The occupancy numbers at Ca(I), Ca(II'), Ca(IIa), and Ca(IIb) were reset and fixed at 14.5, 1, 10, and 10 Ca<sup>2+</sup> ions, respectively, because the cationic charge should sum to 71+ per unit cell.<sup>18,22</sup>

The final cycles of refinement, done with the anisotropic temperature factors for all atoms and with the final weighting-scheme parameters, converged to  $R_1 = 0.038$  and  $R_2 = 0.172$ . On the final difference Fourier function, the largest peak appeared at (0.009, 0.009, 0.009), a special position, with

**Table 1.** Summary of experimental and crystallographic data

|   |                              |
|---|------------------------------|
| Crystal cross section (μm)                      | 200                          |
| Ion exchange T (K)                              | 294                          |
| Ion exchange for Ca <sup>2+</sup> (mL)          | 50.0                         |
| Data collection T (K)                           | 294(1)                       |
| Scan technique                                  | ω-scans                      |
| X-ray source                                    | PLS (4A MXW BL) <sup>a</sup> |
| Wavelength (Å)                                  | 0.700                        |
| Unit cell constant, <i>a</i> (Å)                | 24.9020(10)                  |
| 2θ range in data collection (deg)               | 2.8 < 2θ < 60.4              |
| No. of unique reflections, <i>m</i>             | 1197                         |
| No. of reflections with $F_o > 4\sigma(F_o)$    | 971                          |
| No. of variables, <i>s</i>                      | 45                           |
| Data/parameter ratio, <i>m/s</i>                | 26.6                         |
| Weighting parameters, <i>a/b</i>                | 0.062/133.5                  |
| Final error indices                             |                              |
| $R_1/R_2$ ( $F_o > 4\sigma(F_o)$ ) <sup>b</sup> | 0.038/0.172                  |
| $R_1/R_2$ (all intensities) <sup>c</sup>        | 0.062/0.196                  |
| Goodness-of-fit <sup>d</sup>                    | 1.53                         |

<sup>a</sup>Beamline 4A MXW of Pohang Light Source. <sup>b</sup> $R_1 = \sum |F_o - F_c| / \sum F_o$  and  $R_2 = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$ .  $R_1$  and  $R_2$  are calculated using only the 971 reflections for which  $F_o > 4\sigma(F_o)$ . <sup>c</sup> $R_1$  and  $R_2$  are calculated using all 1197 unique reflections measured. <sup>d</sup>Goodness-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.

**Table 2.** Steps of structure refinement<sup>a</sup> as atom positions are found

| Step           | Occupancy <sup>b</sup> at |         |          |          | $R_1$ | $R_2$ |
|----------------|---------------------------|---------|----------|----------|-------|-------|
|                | Ca(I)                     | Ca(II') | Ca(IIa)  | Ca(IIb)  |       |       |
| 1 <sup>c</sup> |                           |         |          |          | 0.322 | 0.788 |
| 2              | 15.33(19)                 |         |          | 21.7(3)  | 0.056 | 0.204 |
| 3              | 15.26(16)                 |         | 10.5(11) | 11.1(11) | 0.043 | 0.181 |
| 4              | 15.19(14)                 | 1.3(3)  | 10.9(11) | 10.5(11) | 0.038 | 0.173 |
| 5              | 14.5                      | 1.0     | 10.0     | 10.0     | 0.038 | 0.172 |

<sup>a</sup>Isotropic thermal parameters were used for all Ca<sup>2+</sup> positions except for final step. <sup>b</sup>The occupancy is given as the number of Ca<sup>2+</sup> ions per unit cell. <sup>c</sup>Only the atoms of zeolite framework were included in the initial structure model.

**Table 3.** Positional, thermal, and occupancy parameters<sup>a</sup>

| atom    | Wyckoff position | Cation site | x        | y        | z        | <sup>b</sup> U <sub>11</sub> | U <sub>22</sub> | U <sub>33</sub> | U <sub>23</sub> | U <sub>13</sub> | U <sub>12</sub> | Occupancy |           |       |
|---------|------------------|-------------|----------|----------|----------|------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------|-----------|-------|
|         |                  |             |          |          |          |                              |                 |                 |                 |                 |                 | initial   | varied    | fixed |
| Si,Al   | 192(i)           |             | -552(1)  | 1227(1)  | 350(1)   | 105(3)                       | 74(3)           | 83(3)           | -27(2)          | -2(2)           | -8(2)           | 192       |           |       |
| O(1)    | 96(h)            |             | -1099(1) | 0        | 1099(1)  | 172(8)                       | 188(12)         | 172(8)          | -52(7)          | 25(9)           | -52(7)          | 96        |           |       |
| O(2)    | 96(g)            |             | -39(1)   | -39(1)   | 1423(1)  | 157(7)                       | 157(7)          | 149(12)         | -17(6)          | -17(6)          | 54(9)           | 96        |           |       |
| O(3)    | 96(g)            |             | -358(1)  | 639(1)   | 639(1)   | 153(12)                      | 116(7)          | 116(7)          | -9(9)           | 7(6)            | 7(6)            | 96        |           |       |
| O(4)    | 96(g)            |             | -620(1)  | 787(1)   | 1714(1)  | 309(16)                      | 195(8)          | 195(8)          | -92(11)         | 65(8)           | -65(8)          | 96        |           |       |
| Ca(I)   | 16(e)            | I           | 0        | 0        | 0        | 81(3)                        | 81(3)           | 81(3)           | 17(3)           | 17(3)           | 17(3)           |           | 15.19(14) | 14.5  |
| Ca(II') | 32(e)            | II'         | 2052(14) | 2052(14) | 2052(14) | 82(87)                       | 82(87)          | 82(87)          | 220(122)        | 220(122)        | 220(122)        |           | 1.3(3)    | 1     |
| Ca(IIa) | 32(e)            | II          | 2222(4)  | 2222(4)  | 2222(4)  | 134(24)                      | 134(24)         | 134(24)         | 11(25)          | 11(25)          | 11(25)          |           | 10.9(11)  | 10    |
| Ca(IIb) | 32(e)            | II          | 2292(5)  | 2292(5)  | 2292(5)  | 216(36)                      | 216(36)         | 216(36)         | 42(33)          | 42(33)          | 42(33)          |           | 10.5(11)  | 10    |

<sup>a</sup>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. <sup>b</sup>The anisotropic temperature factor is  $\exp[-2\pi^2 a^2(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{23}kl - 2U_{13}hl + 2U_{12}hk)]$ . <sup>c</sup>Occupancy factors are given as the number of atoms or ions per unit cell.

height 1.08 e<sup>-</sup>/Å<sup>3</sup>. It was not included in the final model because it was featureless.

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  $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$ , with  $a = 0.062$  and  $b = 133.5$  as refined parameters (see Table 1). Atomic scattering factors for Ca<sup>2+</sup>, O<sup>-</sup>, and (Si,Al)<sup>1.82+</sup> were used.<sup>23,24</sup> The function describing (Si,Al)<sup>1.82+</sup> is the weighted mean of the Si<sup>1+</sup>, Si<sup>0</sup>, Al<sup>3+</sup>, and Al<sup>0</sup> functions (Si/Al  $\cong$  1.70). All scattering factors were modified to account for anomalous dispersion.<sup>25,26</sup>

**Table 4.** Selected interatomic distances (Å) and angles (deg)<sup>a</sup>

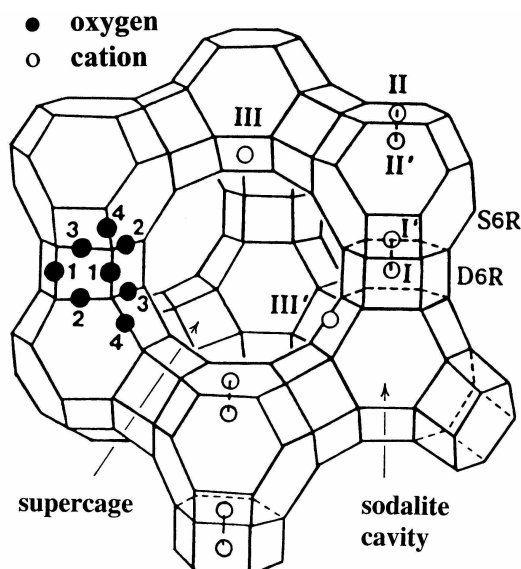
| Distances           |                   | Angles               |                       |
|---------------------|-------------------|----------------------|-----------------------|
| (Si,Al)-O(1)        | 1.6491(13)        | O(1)-(Si,Al)-O(2)    | 112.28(10)            |
| (Si,Al)-O(2)        | 1.6764(10)        | O(1)-(Si,Al)-O(3)    | 106.99(11)            |
| (Si,Al)-O(3)        | 1.7010(12)        | O(1)-(Si,Al)-O(4)    | 114.11(13)            |
| (Si,Al)-O(4)        | 1.6361(7)         | O(2)-(Si,Al)-O(3)    | 106.18(12)            |
| <b>Mean (Si,Al)</b> | <b>1.6657(12)</b> | O(2)-(Si,Al)-O(4)    | 104.32(14)            |
|                     |                   | O(3)-(Si,Al)-O(4)    | 112.77(13)            |
| Ca(I)-O(3)          | 2.4194(24)        |                      |                       |
| Ca(II')-O(2)        | 2.324(13)         | (Si,Al)-O(1)-(Si,Al) | 126.74(16)            |
| Ca(IIa)-O(2)        | 2.283(3)          | (Si,Al)-O(2)-(Si,Al) | 142.85(16)            |
| Ca(IIb)-O(2)        | 2.333(5)          | (Si,Al)-O(3)-(Si,Al) | 130.24(15)            |
|                     |                   | (Si,Al)-O(4)-(Si,Al) | 166.59(21)            |
|                     |                   | O(3)-Ca(I)-O(3)      | 87.00(8),<br>93.00(8) |
|                     |                   | O(2)-Ca(II')-O(2)    | 115.5(10)             |
|                     |                   | O(2)-Ca(IIa)-O(2)    | 118.94(17)            |
|                     |                   | O(2)-Ca(IIb)-O(2)    | 114.8(4)              |

<sup>a</sup>The numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

## Results and Discussion

This structure was determined twice using selected crystals from same batch. In the second determination, 984 reflections for  $F_o > 4\sigma(F_o)$  were refined to  $R_1 = 0.037$  and  $R_2 = 0.169$ ;  $a = 24.9080(10)$  Å. The work was repeated more carefully to increase the precision of the results, and only the first work is presented fully in this report. There are little differences between two crystals.

**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 supercage



**Figure 2.** Stylized drawing of the framework structure of zeolite Y. Near the center of 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. 27) would be obeyed. Extraframework cation positions are labeled with Roman numerals.

(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 (in  $Fd\bar{3}m$ ) 192, respectively. Further description is available.<sup>28-30</sup>

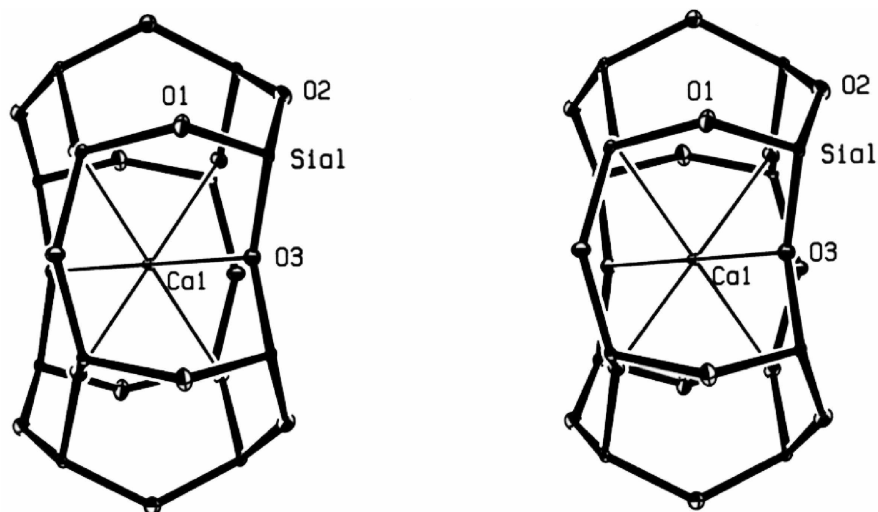
**Framework and  $\text{Ca}^{2+}$  ions.** In this structure, about 35.5  $\text{Ca}^{2+}$  ions have been found at four equi-points. The 14.5  $\text{Ca}^{2+}$  ions per unit cell fill site I at the center of the D6Rs (see Figure 3). One  $\text{Ca}^{2+}$  ion lies at  $\text{Ca}(\text{II}')$  (site II') and the 10  $\text{Ca}^{2+}$  ions are found at site II. The remaining 10  $\text{Ca}^{2+}$  ions occupy another site II positions (see Table 3 and Figure 4). The total number of  $\text{Ca}^{2+}$  ions found per unit cell, 37.9(26), does not differ significantly 35.5 within FSDs, the number required to balance the negative charge of the zeolite framework.

Of the 35.5  $\text{Ca}^{2+}$  ions within the unit cell, the 14.5  $\text{Ca}^{2+}$  lie at site I, at the center of the D6R (see Figure 3). Each  $\text{Ca}^{2+}$  ion at  $\text{Ca}(\text{I})$  coordinates to the six O(3) oxygen atoms of the D6R at a distance of 2.4194(24) Å, which is just a little longer than the sum of the conventional ionic radii of  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$ , 0.99 +

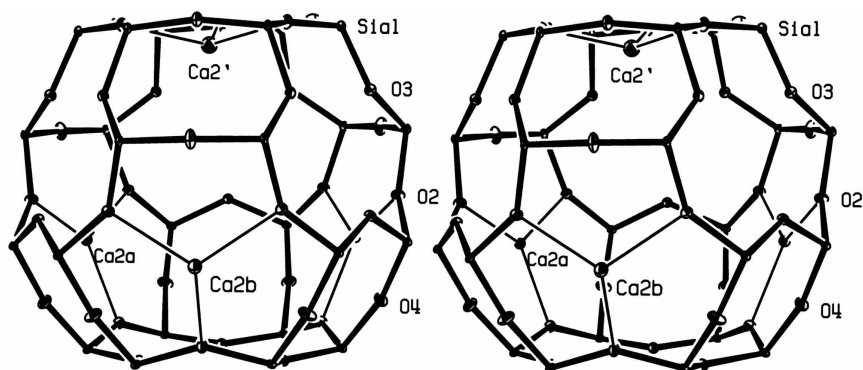
1.32 = 2.31 Å,<sup>31</sup> indicating a reasonably good fit. In the fully dehydrated fully  $\text{Ca}^{2+}$ -exchanged zeolites X<sup>3,4</sup> and Y, site I is nearly fully occupied with 16.3(5), 16.2(1), and 15.19(14)  $\text{Ca}^{2+}$  ions, respectively, indicating that sites I are preferred over III and III' for  $\text{Ca}^{2+}$  ions in zeolites X and Y (see Table 5).

About one  $\text{Ca}^{2+}$  ion at  $\text{Ca}(\text{II}')$  is located at site II' position, on a 3-fold axis inside the sodalite unit at the S6R (see Figure 4). This is 32-fold position, but it is occupied by only one  $\text{Ca}^{2+}$  ion. A  $\text{Ca}^{2+}$  ion coordinates trigonally at 2.324(13) Å to three O(2) framework oxygens and is recessed *ca.* 0.50 Å into the sodalite unit from their plane (see Figure 4 and Table 4). The O(2)- $\text{Ca}(\text{II}')$ -O(2) bond angle (115.5(10)°, near trigonal planar) indicates that  $\text{Ca}^{2+}$  fits this 6-ring well.

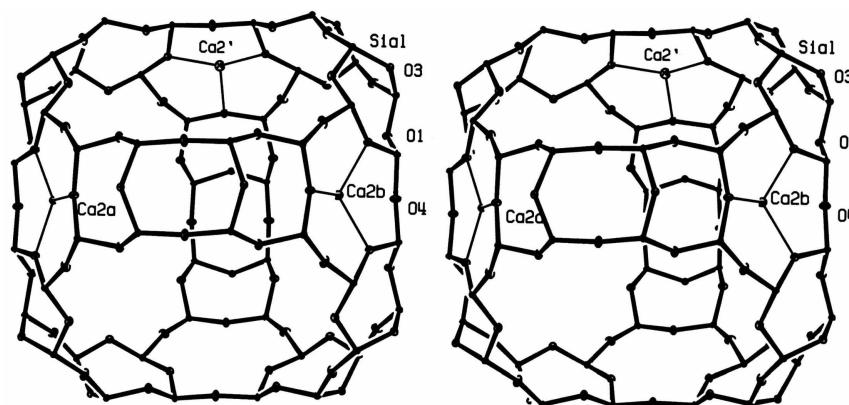
About 10  $\text{Ca}^{2+}$  ions at  $\text{Ca}(\text{IIa})$  are found at site II in the supercage (see Figures 4 and 5). Each is recessed *ca.* 0.24 Å into the supercage from the three O(2) oxygen plane of its S6R and coordinates to these three O(2)'s at 2.283(3) Å, indicative of a good fit considering their conventional ionic radii. The O(2)- $\text{Ca}(\text{IIa})$ -O(2) angle is 118.94(17)°. Finally, 10  $\text{Ca}^{2+}$  ions at  $\text{Ca}(\text{IIb})$  are found at another site II (see Figures 4 and 5). Each is much more recessed 0.30 Å into the supercage from the three O(2) oxygen plane of its S6R than  $\text{Ca}(\text{IIa})$ 's, 0.24 vs



**Figure 3.** Stereoview of a representative double 6-ring (D6R) in dehydrated  $[\text{Ca}_{35.5}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]$ -FAU. The zeolite Y framework is drawn with heavy bonds. The coordination of  $\text{Ca}^{2+}$  ions to oxygens of the zeolite framework are indicated by light bonds. Ellipsoids of 25% probability are shown.



**Figure 4.** A stereoview of a representative sodalite unit in dehydrated  $[\text{Ca}_{35.5}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]$ -FAU. See the caption to Figure 3 for other details.



**Figure 5.** A stereoview of a representative supercage in dehydrated  $\text{Ca}_{35.5}[\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]\text{-FAU}$ . See the caption to Figure 3 for other details.

**Table 5.** Distribution of  $\text{Ca}^{2+}$  ions over sites

| Crystals   | Sites |      |     |      |      | Total Cation No. |
|--|-------|------|-----|------|------|------------------|
|  | I     | I'   | II' | II   |      |                  |
|  |       |      |     | IIa  | IIb  |                  |
| $\text{Ca}_{46}\text{-X}^{a,h}$  | -     | 20.1 | -   | 10.5 | -    | 47.1             |
| $\text{Ca}_{46}\text{-X}^{h,i}$  | 14.6  | 2.6  | -   | 29.0 | 2.7  | 48.9             |
| $\text{Ca}_{46}\text{-X}^{c,j}$  | 16.3  | -    | -   | 31.3 | -    | 47.6             |
| $\text{Ca}_{46}\text{-X}^{d,l}$  | 16.2  | -    | -   | 29.4 | -    | 45.6             |
| $\text{Ca}_{46}\text{-X}\cdot 30\text{C}_2\text{H}_4^{e,k}$            | 16.7  | -    | -   | 28.6 | -    | 45.3             |
| $\text{Ca}_{46}\text{-X}\cdot 30\text{C}_2\text{H}_2^{e,k}$            | 16.4  | -    | -   | 29.2 | -    | 45.6             |
| $\text{Ca}_{46}\text{-X}\cdot ca.149\text{H}_2\text{S}^{d,l}$          | 15.5  | -    | -   | 28.1 | -    | 43.6             |
| $\text{Ca}_{46}\text{-X}\cdot 28\text{C}_6\text{H}_6^{b,m}$            | 15.7  | -    | -   | 7.3  | 21.9 | 44.9             |
| $\text{Ca}_{46}\text{-X}\cdot ca.135\text{NH}_3^{d,n}$                 | 16.0  | -    | -   | 30.7 | -    | 46.7             |
| $\text{Ca}_{46}\text{-X}\cdot 30\text{C}_3\text{H}_6^{f,o}$            | 17.2  | -    | -   | 30.7 | -    | 47.9             |
| $\text{Ca}_{46}\text{-X}\cdot 8\text{C}_6\text{H}_{12}^{h,p}$          | 16.7  | -    | -   | 21.0 | 8.4  | 46.1             |
| $\text{Ca}_{46}\text{-X}\cdot 16\text{C}_3\text{H}_7\text{NI}_2^{g,q}$ | 16.0  | -    | -   | 14.1 | 17.2 | 47.3             |
| $\text{Ca}_{35.5}\text{-Y}^{h,r}$                                      | 15.19 | -    | 1.3 | 10.9 | 10.5 | 37.9             |

<sup>a</sup>Hydrated. <sup>b</sup>Dehydrated at 400 °C. <sup>c</sup>Dehydrated at 360 °C. <sup>d</sup>Dehydrated at 370 °C. <sup>e</sup>Dehydrated at 380 °C. <sup>f</sup>Dehydrated at 460 °C. <sup>g</sup>Dehydrated at 480 °C. <sup>h</sup>Reference 2. <sup>i</sup>Reference 3. <sup>j</sup>Reference 4. <sup>k</sup>Reference 5. <sup>l</sup>Reference 6. <sup>m</sup>Reference 7. <sup>n</sup>Reference 8. <sup>o</sup>Reference 9. <sup>p</sup>Reference 10. <sup>q</sup>Reference 11. <sup>r</sup>This work.

0.54 for Ca(IIa) and Ca(IIb), respectively. Ca(IIb) coordinates near trigonally to the three O(2) oxygens of its S6R at 2.333(5) Å which is almost same as the sum of the ionic radii of  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$ , 2.31 Å<sup>31</sup> (see Figures 4 and 5). The O(2)-Ca(IIb)-O(2) angle is 114.8(4)°. These Ca(IIa) and Ca(IIb) ions are partially occupied the 32-fold equipoint.

It is very unusual for  $\text{Ca}^{2+}$  ions to have various distributions on sites II and II' in the supercage even though there is no organic compound sorption complex in zeolite framework (see Tables 5 and 6). When the fully dehydrated structures of  $[\text{Ca}_{35.5}[\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]\text{-FAU}]$  and organic compound sorption complexes of  $[\text{Ca}_{46}[\text{Si}_{100}\text{Al}_{92}\text{O}_{384}]\text{-FAU}]$ <sup>7,10,11</sup> are compared, it can be seen that there are many similarities in fractional coordinates of  $\text{Ca}^{2+}$  near of S6Rs, deviation of  $\text{Ca}^{2+}$  from the S6R plane at O(2), bonding distances, and bonding angles between  $\text{Ca}^{2+}$  and O(2) except for  $\text{Ca}^{2+}$  ion at site II' (see Table 6). In the single-crystal structures of  $\text{Ca}_{46}\text{-X}\cdot 28\text{C}_6\text{H}_6$ ,<sup>7</sup>  $\text{Ca}_{46}\text{-X}\cdot 8\text{C}_6\text{H}_{12}$ ,<sup>10</sup> and  $\text{Ca}_{46}\text{-X}\cdot 16\text{C}_3\text{H}_7\text{NI}_2$ ,<sup>11</sup> the coordination of benzene,

mesitylene, and methylamine caused  $\text{Ca}^{2+}$  ion to move 0.24, 0.26, and 0.15 Å, respectively, along its 3-fold axis more deeply into the supercage from the three O(2) plane, compared to its position in dehydrated  $[\text{Ca}_{46}[\text{Si}_{100}\text{Al}_{92}\text{O}_{384}]\text{-FAU}]$ .<sup>3,4</sup>

There is no indication that the structure contains the template cation, bis(2-hydroxyethyl)dimethylammonium, used in its synthesis. If it was present in the starting crystal, it was washed away by the intensive  $\text{Ca}^{2+}$ -exchange process.

**Comparison of  $[\text{Ca}_{35.5}[\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]\text{-FAU}]$  with  $[\text{Ca}_{46}[\text{Si}_{100}\text{Al}_{92}\text{O}_{384}]\text{-FAU}]$ .** Self *et al.*<sup>4</sup> investigated a dehydrated zeolite X with unit-cell composition  $\text{Ca}_{46}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$  (Si/Al = 1.09) by single-crystal X-ray diffraction. In their structure,  $\text{Ca}^{2+}$  ions were found at two different crystallographic sites with the fractional occupancies 16.2(1) and 29.4(2) at sites I and II, respectively. When the fully dehydrated structures of  $[\text{Ca}_{35.5}[\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]\text{-FAU}]$  and  $[\text{Ca}_{46}[\text{Si}_{100}\text{Al}_{92}\text{O}_{384}]\text{-FAU}]$  are compared, it can be seen that many more equipoints are occupied in  $[\text{Ca}_{35.5}[\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]\text{-FAU}]$  (see Table 3). This is attributed

**Table 6.** Comparison of the structural features of organic compound sorption complexes of [Ca<sub>46</sub>][Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>]-FAU and [Ca<sub>35.5</sub>][Si<sub>121</sub>Al<sub>7</sub>O<sub>384</sub>]-FAU

|   | Ca <sub>46</sub> -X-28C <sub>6</sub> H <sub>6</sub> <sup>a</sup> | Ca <sub>46</sub> -X-8C <sub>8</sub> H <sub>12</sub> <sup>b</sup> | Ca <sub>46</sub> -X-16CH <sub>3</sub> NH <sub>2</sub> <sup>c</sup> | Ca <sub>35.5</sub> -Y <sup>d</sup> |
|---|--|--|--|------------------------------------|
| number of Ca <sup>2+</sup> ions at site I                                 | 16   | 16   | 16   | 14.5                               |
| number of Ca <sup>2+</sup> ions near of S6Rs                              | -, 8, 22   | -, 22, 8   | -, 14, 16  | 1, 10, 10                          |
| fract. coord. of Ca <sup>2+</sup> near of S6Rs                            | -, 0.2224, 0.2295  | -, 0.2231, 0.2305  | -, 0.2206, 0.2274  | 0.2052, 0.2222, 0.2292             |
| deviation of Ca <sup>2+</sup> from the S6R plane at O(2) (Å) <sup>e</sup> | -, 0.24, 0.55  | -, 0.26, 0.58  | -, 0.15, 0.45  | -0.50, 0.24, 0.54                  |
| Ca <sup>2+</sup> -O(2) (Å)  | -, 2.266(11), 2.318(7)   | -, 2.272(9), 2.332(13)   | -, 2.296(7), 2.334(7)  | 2.324(13), 2.283(3), 2.333(5)      |
| O(2)-Ca-O(2) (deg)  | -, 118.9(7), 114.6(3)  | -, 118.7(4), 114.0(5)  | -, 119.6(3), 116.4(3)  | 115.5(10), 118.94(17), 114.8(4)    |

<sup>a</sup>Reference 7. <sup>b</sup>Reference 10. <sup>c</sup>Reference 11. <sup>d</sup>This work. <sup>e</sup>A positive and negative deviation indicate that the ion lies in the supercage and sodalite cavity, respectively.

**Table 7.** Comparison of the distances between Ca<sup>2+</sup> and its nearest framework oxygen atom in [Ca<sub>46</sub>][Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>]-FAU and [Ca<sub>35.5</sub>][Si<sub>121</sub>Al<sub>7</sub>O<sub>384</sub>]-FAU

|              | Ca <sub>46</sub> -X <sup>a</sup> | Ca <sub>46</sub> -X <sup>b</sup> | Ca <sub>35.5</sub> -Y <sup>c</sup> |
|--------------|----------------------------------|----------------------------------|------------------------------------|
| Ca(I)-O(3)   | 2.51(2)                          | 2.429(8)                         | 2.4194(24)                         |
| Ca(IIa)-O(2) | 2.24(2)                          | 2.276(5)                         | 2.283(3)                           |
| Ca(IIb)-O(2) | -                                | -                                | 2.333(5)                           |
| Ca(II')-O(2) | -                                | -                                | 2.324(13)                          |

<sup>a</sup>Reference 3. <sup>b</sup>Reference 4. <sup>c</sup>This work.

to the greater 6-ring diversity to be expected in zeolite Y. For [Ca<sub>35.5</sub>][Si<sub>121</sub>Al<sub>7</sub>O<sub>384</sub>]-FAU, 6-rings containing four Si and two Al atoms may predominate with the Al atoms in *meta* or in *para* positions. The 6-rings with three Al atoms are expected to be second in population and 6-rings with one and perhaps zero Al atoms may be present. Ca<sup>2+</sup> ions should occupy different positions in these rings, and this disorder has been absorbed into the anisotropic thermal parameters of the Ca<sup>2+</sup> ions in least-squares refinement. These thermal ellipsoids, therefore, do not accurately indicate thermal motion. For comparison, it may be expected that 83% of the 6-rings, a preponderance, are identical (except for the effects of the exchangeable cations) in [Ca<sub>46</sub>][Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>]-FAU,<sup>1</sup> with Al and Si alternating at the tetrahedral sites. Therefore the least-squares results should describe those 6-rings quite well. Nearly all of the remaining 17% should have four Si atoms and, at *meta* positions, two Al atoms.

The reduced aluminum content of zeolite Y as compared to zeolite X<sup>1</sup> should lead to a smaller negative charge density for the zeolite framework and, therefore, at each oxygen position. This in turn should lead to longer Ca-O distances (see Table 7).

### Summary

Fully Ca<sup>2+</sup>-exchanged zeolite Y (Si/Al = 1.70) was successfully prepared and its structure was determined by single-crystal X-ray diffraction method. About 35.5 Ca<sup>2+</sup> ions are distributed over the four sites. Surprisingly, Ca<sup>2+</sup> ions are distributed over the three kinds of sites near single 6-oxygen rings which could not be seen in the other structures of Ca<sup>2+</sup>-exchanged zeolite X.<sup>2-11</sup> See in particular Figures 4 and 5. [Ca<sub>35.5</sub>][Si<sub>121</sub>Al<sub>7</sub>O<sub>384</sub>]-FAU has 11 fewer Ca<sup>2+</sup> ions near of

single 6-oxygen rings than [Ca<sub>46</sub>][Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>]-FAU.<sup>3,4</sup>

**Supporting information available.** Tables of calculated and observed structure factors (14 pages). The supporting materials will be given upon your request to a corresponding author (Fax: +82-54-822-5452; E-mail: wlim@andong.ac.kr), and can also be accessed with the electronic version of this paper on ScienceDirect.

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