

# Synthesis and Single-crystal Structures of Fully Dehydrated and Highly Proton-exchanged Zeolites Y, $[\text{H}_{74}\text{Na}_1][\text{Si}_{117}\text{Al}_{75}\text{O}_{384}]\text{-FAU}$ and $[\text{H}_{73}\text{Na}_2][\text{Si}_{117}\text{Al}_{75}\text{O}_{384}]\text{-FAU}$

Sung Man Seo and Woo Taik Lim\*

Department of Applied Chemistry, Andong National University, Andong 760-749, Korea. \*E-mail: wtlim@andong.ac.kr  
Received August 18, 2009, Accepted September 11, 2009

**Key Words:** Proton, Zeolite Y, Ion exchange, Structure, Deamination

Zeolite Y has a wide range of industrial applications as an ion exchanger, a sorption agent, a molecular sieve, and a catalyst due primarily to its excellent structural stability, large and accessible pore volume, high activity, high resistance to nitrogen compounds, and high regenerability.<sup>1</sup> In particular, proton-exchanged zeolite Y (H-Y) is the most widely used zeolite in heterogeneously catalyzed reactions, including large-scale applications in the petrochemical industry. These Brønsted acids donate protons to molecules in the zeolite cages.<sup>2-3</sup> The market for H-Y currently exceeds  $2 \times 10^9$  US\$ per year.<sup>4</sup> H-Y is prepared by  $\text{NH}_4^+$  ion exchange and subsequent heating to temperatures at which  $\text{NH}_3$  is completely removed and some dehydroxylation (loss of some  $\text{H}^+$  ions and framework oxygen atoms as  $\text{H}_2\text{O}$ ) takes place. To understand the catalytic behavior of H-Y, it is required to know its 3-dimensional structure. However, it has been impossible to do it because of the difficulties to synthesis of large single crystals of zeolite Y and keep crystallinity of zeolite framework after full deamination of highly  $\text{NH}_4^+$  exchanged zeolites.

For the experiments, we synthesized colorless single crystals of sodium zeolite Y, stoichiometry  $\text{Na}_{75}\text{Si}_{117}\text{Al}_{75}\text{O}_{384}$ , with diameters up to 0.30 mm from a gel prepared using 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 (resistivity  $> 18.4 \text{ M}\Omega\text{-cm}$ ). Its composition was  $3.58\text{SiO}_2 : 2.08\text{NaAlO}_2 : 7.59\text{NaOH} : 455\text{H}_2\text{O} : 5.06\text{TEA} : 2.23\text{TCl}$ . Microscopic examination showed that the single crystals were transparent, colorless, and octahedral faujasite-type single crystals. The Si/Al ratio, 1.56, was determined by SEM-EDX and crystallographic method.<sup>5</sup>

To prepare  $\text{NH}_4^+$ -exchanged zeolite Y ( $\text{NH}_4^+\text{-Y}$ ), complete  $\text{K}^+$ -exchange was done first, to be followed by  $\text{NH}_4^+$ -exchange of  $\text{K}^+$ -exchanged zeolite Y (K-Y) because the complete  $\text{NH}_4^+$ -exchange of  $[\text{Na}_{75}][\text{Si}_{117}\text{Al}_{75}\text{O}_{384}]\text{-FAU}$  (Na-Y) is difficult to achieve. Crystals of hydrated K-Y were prepared by static ion-exchange of Na-Y with aqueous 0.05 M  $\text{KNO}_3$  (Aldrich, 99.999%, 10.2 ppm Na, 0.6 ppm B, 0.2 ppm Ca), pH = 5.9. This was done by mixing 20 mg of hydrated Na-Y with 15 mL of 0.05 M  $\text{KNO}_3$ , 6-fold excess. The mixture was then stirred on an orbital shaker for 2 h at 348 K. This was repeated 10 and 20 times with fresh  $\text{KNO}_3$  solution for crystals 1 and 2, respectively. The product was then filtered.

To prepare  $\text{NH}_4^+\text{-Y}$  from K-Y, these crystals were treated with 15 mL of 0.1 M  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  (Aldrich, 99.999%  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ ,

4.4 ppm Na, 0.7 ppm Li, 0.2 ppm Zn, 0.1 ppm Mg), a 15-fold excess, pH = 6.9. The mixture was then stirred on an orbital shaker for 2 h at 348 K and 353 K for crystals 1 and 2, respectively. This was repeated 15 times with fresh  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  solution. The product was oven-dried at 323 K for 1 day (see Table 1).

Fully dehydrated and highly proton-exchanged zeolites Y ( $[\text{H}_{74}\text{Na}_1][\text{Si}_{117}\text{Al}_{75}\text{O}_{384}]\text{-FAU}$  (crystal 1) and  $[\text{H}_{73}\text{Na}_2][\text{Si}_{117}\text{Al}_{75}\text{O}_{384}]\text{-FAU}$  (crystal 2)) were prepared by deamination of  $\text{NH}_4\text{-Y}$  under dynamic vacuum to 473 and 573 K, respectively, and both at  $1 \times 10^{-6}$  Torr for 48 hours.

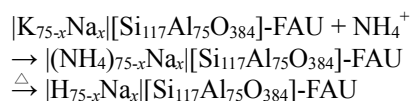
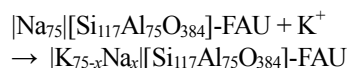
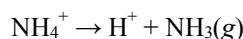
Because the zeolite framework is not involved, the deamination reaction is straightforward (see below).

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

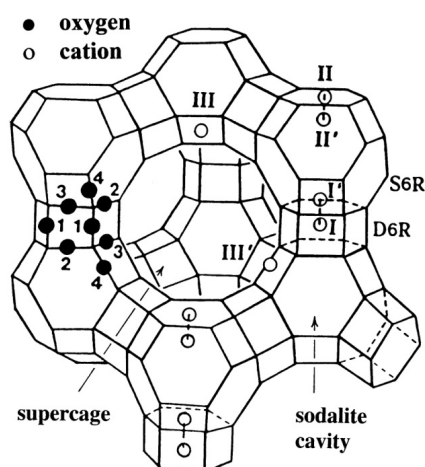
	Crystal 1	Crystal 2
Crystal cross-section (mm)	0.28	0.28
Ion exchange T (K)	348	353
Ion exchange for $\text{K}^+$ (day, mL)	10, 150	20, 300
Ion exchange for $\text{NH}_4^+$ (day, mL)	15, 225	15, 225
Dehydration T (K)	473	573
Crystal color	pale yellow	pale yellow
Data collection T (K)	294(1)	294(1)
Space group	$Fd\bar{3}m$	$Fd\bar{3}m$
X-ray source	Pohang Light Source, Beamline 4A MXW	
Wavelength (Å)	0.76999	0.76999
Unit cell constant, $a$ (Å)	24.8610(29)	24.7960(29)
$2\theta$ range in data collection (deg)	60.55	60.70
Total reflections harvested	89,784	126,418
No. of unique reflections, $m$	908	756
No. of reflections with $F_o > 4\sigma(F_o)$	784	461
No. of variables, $s$	39	38
Data/parameter ratio, $m/s$	23.3	19.9
Weighting parameters, $a/b$	0.075/81.1	0.090/143.4
Initial error indices		
$R_1/wR_2 (F_o > 4\sigma(F_o))^a$	0.050/0.161	0.064/0.236
Final error indices		
$R_1/wR_2 (F_o > 4\sigma(F_o))^a$	0.048/0.158	0.059/0.229
$R_1/wR_2$ (all intensities) <sup>b</sup>	0.054/0.176	0.094/0.366
Goodness-of-fit <sup>c</sup>	1.19	1.08

<sup>a</sup> $R_1 = \sum |F_o - F_c| / \sum F_o$  and  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ;  $R_1$  and  $wR_2$  are calculated using only the 784 and 461 reflections for which  $F_o > 4\sigma(F_o)$ .

<sup>b</sup> $R_1$  and  $wR_2$  are calculated using all unique reflections measured. <sup>c</sup>Goodness-of-fit =  $(\sum w(F_o^2 - F_c^2)^2 / (m-s))^{1/2}$ , where  $m$  and  $s$  are the number of unique reflections and variables, respectively.



X-ray diffraction data for two single crystals 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 done using  $\lambda = 0.76999$  Å 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>6</sup> The reflections were successfully



**Figure 1.** Stylized drawing of the framework structure of zeolite Y. Near the center of the each line segment is an oxygen atom. The nonequivalent 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 Loewenstein's rule (ref. 10) would be obeyed. Extraframework cation positions are labeled with Roman numerals.

indexed by the automated indexing routine of the DENZO program.<sup>6</sup> The 89,784 and 126,418 reflections (see Table 1) were harvested for each crystal by collecting 72 sets of frames with 5° scans and 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.<sup>7</sup> A summary of the experimental and crystallographic data is presented in Table 1.

Full-matrix least-squares refinement using SHELXL97<sup>8</sup> was done 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  $[\text{Cs}_{45}\text{Na}_{30}][\text{Si}_{117}\text{Al}_{75}\text{O}_{384}]\text{-FAU}$ .<sup>9</sup> Each initial refinement used anisotropic thermal parameters and converged to the initial error indices given in Table 1.

A Fourier function revealed a peak 0.78 and 0.94  $\text{e}\text{\AA}^{-3}$  in height at Na(I'), (0.0508, 0.0508, 0.0508) and (0.0521, 0.0521, 0.0521) in crystals 1 and 2, respectively; their occupancies refined nicely to 1.2(3) and 2.2(5)  $\text{Na}^+$  ions per unit cell, respectively. Anisotropic refinement at all positions converged to  $R_1/wR_2 = 0.048/0.158$  and 0.059/0.229 for crystals 1 and 2, respectively.

An attempt was made to find the hydrogen atoms (formally  $\text{H}^+$ ). The four largest peaks on the penultimate Fourier function for crystal 1, at (0.0, 0.0, 0.0), (0.2201, 0.2201, 0.2201), (0.2560, 0.2560, 0.2560), and (0.1599, 0.1599, 0.1599) with heights of 0.45, 0.36, 0.33, and 0.32  $\text{e}\text{\AA}^{-3}$ , respectively, and for crystal 2 at (0.125, 0.125, 0.125), (0.0333, 0.0333, 0.0333), (0.2803, 0.2803, 0.2803), and (0.0903, 0.0903, 0.3352) with heights of 0.45, 0.30, 0.20, and 0.20  $\text{e}\text{\AA}^{-3}$ , respectively, were all too far from framework oxygen atoms to be  $\text{H}^+$  ions. Refinement including them one at a time at fixed positions in the final model also failed to lower  $R_1$  and  $wR_2$ . When allowed to vary, they did not refine properly.

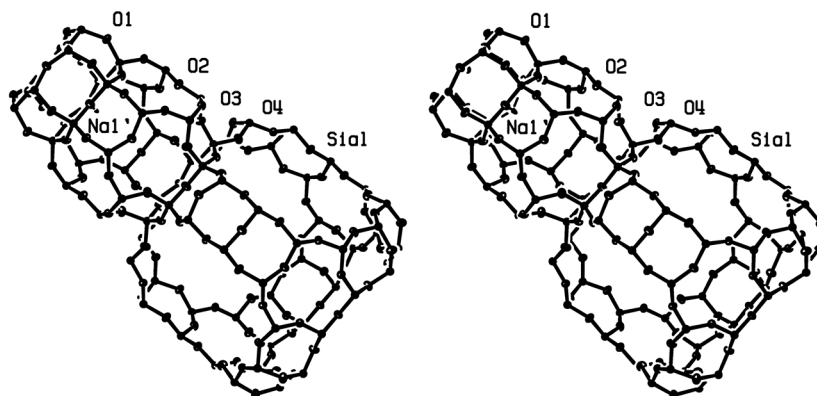
The framework structure of faujasite is characterized by the double 6-ring (D6R, hexagonal prism), sodalite cavity (a cuboctahedron), and supercage (see Figure 1). Each unit cell has 8 supercages, 8 sodalite cavities, 16 D6Rs, 16 12-rings, and 32 S6Rs (single 6-rings). The exchangeable cations, which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

**Table 2.** Positional, thermal, and occupancy parameters.<sup>a</sup>

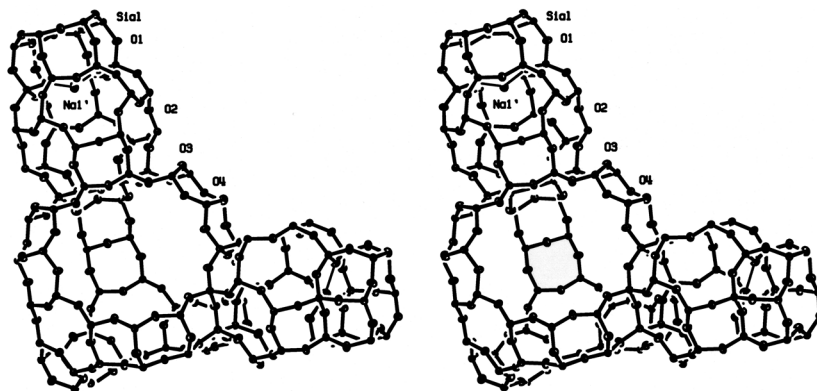
atom	Wyckoff position	Cation site	x	y	z	$bU_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	Occupancy		
												initial	varied	fixed
Crystal 1														
Si,Al	192( <i>i</i> )		-532(1)	1252(1)	363(1)	321(5)	280(5)	268(4)	-49(3)	9(3)	-40(3)	192		
O(1)	96( <i>h</i> )		-1061(1)	0	1061(1)	501(12)	511(19)	501(12)	-128(10)	-106(15)	-128(10)	96		
O(2)	96( <i>g</i> )		-31(1)	-31(1)	1436(1)	469(11)	469(11)	399(17)	-45(10)	-45(10)	165(14)	96		
O(3)	96( <i>g</i> )		-323(2)	721(1)	721(1)	654(23)	425(11)	425(11)	69(14)	37(11)	37(11)	96		
O(4)	96( <i>g</i> )		751(1)	751(1)	3211(1)	393(10)	393(10)	408(16)	-37(9)	-37(9)	128(12)	96		
Na(I')	32( <i>e</i> )	I'	509(20)	509(20)	509(20)	303(243)	303(243)	303(243)	223(206)	223(206)	223(206)		1.2(3)	1
Crystal 2														
Na(I')	32( <i>e</i> )	I'	527(13)	527(13)	527(13)	446(246)	446(246)	446(246)	-123(150)	-123(150)	-123(150)		2.2(5)	2

<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.



**Figure 2.** Stereoview of representative a double 6-ring (D6Rs), a sodalite cavity, and a supercage for crystal 1. Of the 8 sodalite cavities per unit cell, one  $\text{Na}^+$  ion is occupied. The zeolite Y framework is drawn with heavy bonds. The coordination of the exchangeable cations to oxygens of the zeolite framework are indicated by light bonds. Ellipsoids of 25% probability are shown.



**Figure 3.** Stereoview of representative two double 6-rings (D6Rs), two sodalite cavities, and a supercage for crystal 2. Of the 8 sodalite cavities per unit cell, two  $\text{Na}^+$  ions are occupied. See the caption to Fig. 2 for other details.

some or all of the sites shown with Roman numerals in Figure 1. The maximum occupancies at the cation sites I, I', II, II', and III, in faujasite are 16, 32, 32, 32, and 48, respectively. Site III' in faujasite studied using space group  $Fd\bar{3}m$  has a maximum occupancy of 96 at Wyckoff positions 96(g) and 96(h) and 192 at the general Wyckoff position 192(i). Further description is available.<sup>1</sup>

In the sodalite cavity opposite a D6R (see Figures 2 and 3), one and two  $\text{Na}^+$  ions per unit cell have been found at site I' for crystals 1 and 2, respectively (see Table 2). It is in the sodalite cavity opposite a D6R (see Figs. 2 and 3). Each  $\text{Na}^+$  ion is recessed *ca.* 0.59 and 0.65 Å into the sodalite cavity from its three O(3) oxygen plane where it coordinates at 2.199(23) and 2.198(18) Å to those three oxygens for crystals 1 and 2, respectively. This is just a little less than the sum of the ionic radii of  $\text{Na}^+$  and  $\text{O}^{2-}$ ,  $0.97 + 1.32 = 2.29$  Å.<sup>11</sup> The O(3)-Na(I')-O(3) angles are 113.1(18) and 111.7(12)° for crystals 1 and 2, respectively (see Table 3). The *ca.* 74 and 73 hydrogen atoms per unit cell for crystals 1 and 2, respectively, could not be located in these structures despite our best efforts.

**Supporting Information Available.** Tables of calculated and observed structure factors (19 pages). The supporting materials are available *via* the Internet <http://www.kcsnet.or.kr/bkcs>.

**Table 3.** Selected interatomic distances (Å) and angles (deg)<sup>a</sup>

	Crystal 1	Crystal 2
(Si,Al)-O(1)	1.6633(15)	1.6606(30)
(Si,Al)-O(2)	1.6488(12)	1.6472(26)
(Si,Al)-O(3)	1.6758(15)	1.6802(32)
(Si,Al)-O(4)	1.6296(11)	1.6194(25)
<b>Mean (Si,Al)</b>	<b>1.6544(15)</b>	<b>1.6519(33)</b>
Na(I')-O(3)	2.199(23)	2.198(18)
O(1)-(Si,Al)-O(2)	110.83(13)	111.22(27)
O(1)-(Si,Al)-O(3)	107.92(15)	108.16(29)
O(1)-(Si,Al)-O(4)	108.81(15)	109.24(30)
O(2)-(Si,Al)-O(3)	107.41(17)	107.01(34)
O(2)-(Si,Al)-O(4)	110.35(15)	109.87(31)
O(3)-(Si,Al)-O(4)	111.51(16)	111.32(32)
(Si,Al)-O(1)-(Si,Al)	138.17(24)	138.56(45)
(Si,Al)-O(2)-(Si,Al)	145.06(21)	144.21(44)
(Si,Al)-O(3)-(Si,Al)	137.87(23)	137.04(46)
(Si,Al)-O(4)-(Si,Al)	145.54(21)	146.11(44)
O(3)-Na(I')-O(3)	113.1(18)	111.7(12)

<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.

**Acknowledgments.** We gratefully acknowledge the support of beamline 4A MXW at the Pohang Light Source, Korea, for their diffraction and computing facilities. This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2009-0074190).

### References

1. Lim, W. T.; Seo, S. M.; Kim, G. H.; Lee, H. S.; Seff, K. *J. Phys. Chem. C* **2007**, *111*, 18294.
  2. Frising, T.; Leflaive, P. *Microporous Mesoporous Mater.* **2008**, *114*, 27.
  3. Kanellopoulos, J.; Gottert, C.; Schneider, D.; Knorr, B.; Prager, D.; Ernst, H.; Freude, D. *J. Catal.* **2008**, *255*, 68.
  4. Watkins, K. *Eng. News* **2001**, *79*, 40.
  5. Lim, W. T.; Seo, S. M.; Wang, L. Z.; Lu, G. Q.; Heo, N. H.; Seff, K. submitted in *Microporous Mesoporous Mater.* **2009**.
  6. Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.
  7. Bruker-AXS (ver. 6.12), XPREP, Program for the Automatic Space Group Determination, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
  8. Sheldrick, G. M. SHELXL97, Program for the Refinement of Crystal Structures, University of Gottingen, Germany, 1997.
  9. Seo, S. M.; Kim, G. H.; Lee, S. H.; Bae, J. S.; Lim, W. T. *Bull. Korean Chem. Soc.* **2009**, *30*(6), 1285.
  10. Loewenstein, W. *Am. Mineral.* **1954**, *39*, 92.
  11. *Handbook of Chemistry and Physics*, 70<sup>th</sup> ed.; The Chemical Rubber Co.: Cleveland, OH, 1989/1990; p F-187.
-