Single-crystal Structure of Partially Dehydrated Partially Mg²⁺-exchanged Zeolite Y (FAU), |Mg₃₀.₅Na₁₄(H₂O)₂.₅|[Si₁₁₇Al₇₅O₃₈₄]-FAU

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The single-crystal structure of partially dehydrated partially Mg²⁺-exchanged zeolite Y, |Mg₃₀.₅Na₁₄(H₂O)₂.₅|[Si₁₁₇Al₇₅O₃₈₄]-FAU per unit cell, $a = 25.5060(1)$ Å, dehydrated at 723 K and 1×10^{-4} Pa, has been determined by single-crystal X-ray diffraction techniques in the cubic space group $Fd\overline{3}m$ at 100(1) K. The structure was refined using all intensities to the final error indices (using only the 561 reflections with $F_o > 4\sigma(F_o)$) $R_1 = 0.0377$ (Based on F) and $R_2 = 0.1032$ (Based on F^2). About 30.5 Mg²⁺ ions per unit cell are found at four different crystallographic sites. The 14 Mg²⁺ ions occupy at site I at the center of double 6-ring (Mg-O = 2.231(3) Å, O-Mg-O = 89.15(11)° and 90.85(11)°). Four Mg²⁺ ions are found at site I' in the sodalite cavity; the Mg²⁺ ions are recessed 1.22 Å into the sodalite cavity from their 3-oxygen plane (Mg-O = 2.20(3) Å and O-Mg-O = 92.3(14)°). Site II' positions (opposite single 6-rings in the sodalite cage) are occupied by 2.5 Mg²⁺ ions, each coordinated to an H₂O molecule (Mg-O = 2.187(20) Å and O-Mg-O = 114.2(16)°). The 10 Mg²⁺ ions are nearly three-quarters filled at site II in the supercage, being recessed 0.12 Å into the supercage (Mg-O = 2.123(4) Å and O-Mg-O = 119.70(19)°). About 14 Na⁺ ions per unit cell are found at one crystallographic site; the Na⁺ ions are located at site II in the supercage (Na-O = 2.234(7) Å and O-Mg-O = 110.5(4)°).

Key Words : Zeolite Y, Ion exchange, Dehydrated, Structure, Magnesium

Introduction

Zeolites are inorganic crystalline and nanoporous solids with well-defined structures. They have been widely studied and used as ion exchangers, adsorbents and catalysts in industrial processes, because of the properties originated from the unique crystal structure containing large pore size and void volume.[1] The thermal stability, sorption characteristics, and catalytic properties of a zeolite depend on the type and number of exchangeable cations and their distribution over the avabailable sites. A knowledge of the distribution of the cations in the zeolite structures is one of the key aspects to the understanding these properties and the improvments in industrial applications.[2] Mg²⁺- exchanged zeolite Y has been reported as a high catalyst for isomerization and cracking reactions.[3]

Various cation distributions in zeolites by X-ray diffraction methods have been widely studied and reported.[2] Despite, the great progress in these studies, the information on the distribution of Mg²⁺ ion in zeolite is still a lack. In addition, the information of Mg²⁺-exchanged zeolite Y is absent. This may be connected with distortions of the zeolite framework due to small size and high electric fied gradient at surface of Mg²⁺ ions.

The crystal structures of Mg²⁺-exchanged zeolites from aqueous solution have been reported by several researchers.[4,5] Anderson *et al*. determined the crystal structures of hydrated, |Mg₃₁Na₃₀(H₂O)₁₁₄|[Si₁₀₀Al₉₂O₃₈₄]-FAU (Mg₃₁Na₃₀(H₂O)₁₁₄-X) and fully dehydrated |Mg₃₁Na₃₀|[Si₁₀₀Al₉₂O₃₈₄]-FAU (Mg₃₁Na₃₀-X).[4] Mg²⁺ ions were located at three different crystallographic sites I', II', and III in the structure of Mg₃₁Na₃₀(H₂O)₁₁₄-

X and sites I, I', and II' in Mg₃₁Na₃₀-X. They observed large distortions of the zeolite framework on dehydration.

Seff *et al*. investigated the partially dehydrated fully Mg²⁺-exchanged zeoliteX using single-crystal X-ray diffraction techniques.[5] In their structure, Mg²⁺ ions were located at sites I, I', II', and II and water molecules at site II' in the sodalite cavity. They reported the loss of crystallinity in the single crystal of |Mg₄₆(H₂O)₄|[Si₁₀₀Al₉₂O₃₈₄]-FAU (Mg₄₆(H₂O)₄-X) at high dehydration temperature due to the large distortions of the framework occurring upon dehydration. When the exchangeable cations were relatively small and had large charges, the zeolite framework experienced high distortion and unstability.[6,7]

The structure stability of zeolite is related to the Si/Al ratio of framework in the same structural type. It is found that Mg²⁺-exchanged zeolite Y could be prepared without damage of crystal at high dehydration temperature due to its high structural stability.

In this work, we have focused on the investigation of the detail distribution and coordination geometry of Mg²⁺ ions in zeolite Y by single-crystal X-ray diffraction techniques, and compare its structure with that of Mg₄₆(H₂O)₄-X.[5]

Experimental Section

Ion Exchange. Large single crystal of zeolite Y (FAU), stoichiometry Na₇₅Si₁₁₇Al₇₅O₃₈₄, were synthesized in this laboratory.[8] One of synthesized |Na₇₅|[Si₁₁₇Al₇₅O₃₈₄]-FAU (Na₇₅-Y), a clear colorless octahedron about 0.20 mm in cross-section was lodged in its own Pyrex capillary. Mg²⁺ ion exchange was performed using dynamic ion-exchange

method in this capillary at 294 K from aqueous 0.05 M $MgCl_2 \cdot 6H_2O$ solution (Aldrich, 99.995%). The resulting clear colorless crystal was dehydrated at 723 K and a dynamic vacuum of 1×10^{-4} Pa 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 allowed to cool to ambient temperature to prevent the movement of water molecules from more distant parts of the vacuum system to each crystal. Still under vacuum in capillary, the crystal was allowed to cool to room temperature and was sealed in its capillary by torch. Microscopic examination showed that the colour of resulting single crystal was turned to dark yellow.

Single-crystal X-ray Diffraction Work. X-ray diffraction data for the crystal dehydrated at 723 K was collected at 100(1) K using an ADSC Quantum 210 detector at Beamline 6B MXI at The Pohang Light Source. The crystal evaluation and data collection were done using $\lambda = 0.9000$ wavelength of X-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 data file was prepared using the program HKL2000.[9] The reflections were successfully indexed by the automated indexing routine of the DENZO program.[9] The total reflections were harvested by collecting 72 sets of frames with 5° scans and an exposure time of 1 second per

Table 1. Summary of experimental and crystallographic data

	$Mg_{30.5}Na_{14}(H_2O)_{2.5}$-Y
Crystal cross-section (mm)	0.20
Ion exchange T (K)	294
Ion exchange for Ba^{2+} (day, mL)	2, 10
Dehydration T (K)	723
Crystal color	dark yellow
Data collection T (K)	100(1)
Space group, Z	$Fd\bar{3}m$, 1
X-ray source	Pohang Light Source (PLS), Beamline 6B MXI BL
Wavelength (Å)	0.90000
Unit cell constant, a (Å)	25.5060(1)
2θ range in data collection (deg)	60.65
No. of unique reflections, m	567
No. of reflections with $F_o > 4\sigma(F_o)$	561
No. of variables, s	53
Data/parameter ratio, m/s	10.6
Weighting parameters, a/b	0.032/159.9
Final error indices	
$\quad R_1/R_2$ ($F_o > 4\sigma(F_o))^a$	0.0377/0.1032
$\quad R_1/R_2$ (all intensities)^b	0.0379/0.1037
Goodness-of-fit^c	1.309

$^aR_1 = \Sigma|F_o-|F_c||/\Sigma F_o$ and $R_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; R_1 and R_2 are calculated using only the 561 reflections for which $F_o > 4\sigma(F_o)$. $^bR_1$ and R_2 are calculated using all unique reflections measured. ^{c}Goodness-of-fit $= (\Sigma w(F_o^2-F_c^2)^2/(m-s))^{1/2}$, where m and s are the number of unique reflections and variables, respectively.
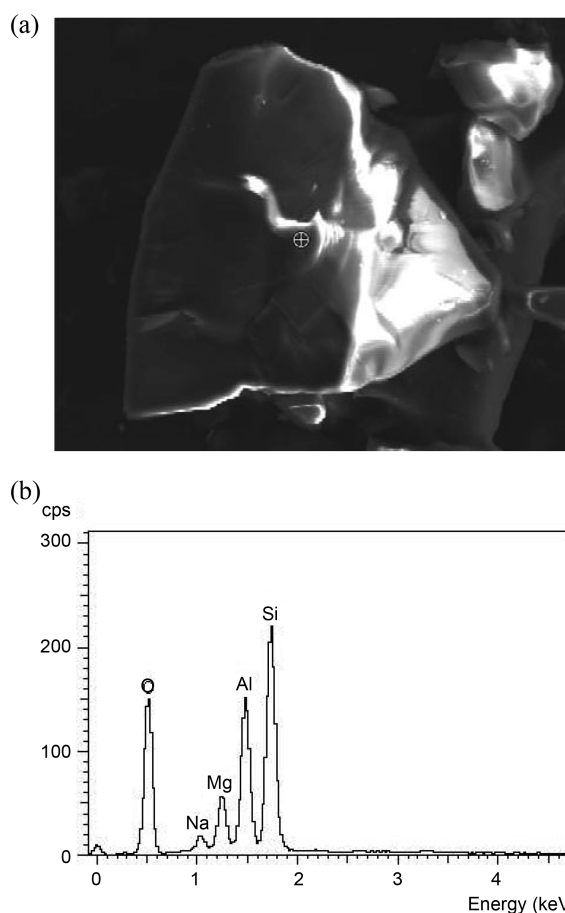

Figure 1. The SEM images of the intentionally broken single crystal (a) and EDX spectra of $Mg_{30.5}Na_{14}(H_2O)_{2.5}$-Y (b).

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.[10] A summary of the experimental and crystallographic data is presented in Table 1.

SEM-EDX Analysis. After X-ray diffraction data collection, the single crystal of Mg^{2+}-exchanged zeolite Y was removed from its capillary for SEM-EDX analysis. This single crystal was intentionally broken to expose fresh surface and was attached on the surface of carbon-arrach tape for analysis (Figure 1(a)). As shown in Figure 1(b), it was confirmed that Na^+ ions within zeolite Y was partially ion exchanged with Mg^{2+}. The SEM image and atomic concentration of the crystal were identified by JSEM-6300 scanning electron microsocope and Energy Dispersive X-ray spectrometer (EDX) both at 294 K and 1×10^{-5} Pa.

Structure Determination

Full-matrix least-squares refinement (SHELXL97)[11] was done on F_o^2 using all data for the crystal. Refinement was initiated with the atomic parameters of the framework atoms [(Si,Al), O(1), O(2), O(3) and O(4)] in dehydrated $|Mn_{37.5}|[Si_{17}Al_{75}O_{384}]$-FAU ($Mn_{37.5}$-Y).[12] The initial refine-

Table 2. Initial steps of structure refinement

Step	Occupancy[a] at Mg(I)	Mg(I')	Mg(II')	Mg(II)	Na(II)	O(5)	R_1	R_2
1[b]							0.2595	0.7168
2[c]	12.0(9)						0.1863	0.6117
3[c]	14.1(4)				23.5(7)		0.0735	0.1871
4[c]	14.3(3)			10.0(8)	14.2(7)		0.0452	0.1272
5[c]	14.3(3)	2.9(5)		10.3(7)	14.3(7)		0.0417	0.1112
6[c]	14.3(2)	2.9(5)	1.7(6)	10.4(8)	13.0(9)		0.0390	0.1069
7[c]	14.5(2)	3.4(5)	2.0(7)	10.3(8)	13.8(9)	3.0(9)	0.0378	0.1033
8[d]	14.5(2)	3.3(5)	2.0(7)	10.3(8)	13.9(9)	3.0(9)	0.0376	0.1031
9[e]	14.5(2)	3.3(5)	2.5(6)	10.1(9)	13.6(9)	2.5(6)	0.0377	0.1032

[a]The occupancy is given as the number of Mg^{2+} and Na^+ ions per unit cell. [b]Only the atoms of zeolite framework were included in the initial structure model. [c]Isotropic temperature factors were used for all Mg^{2+} and Na^+ positions. [d]Only Mg^{2+} ions at Mg(I) and Mg(I') were refined anisotropically. [e]The occupancies at Mg(II') and O(5) were constrained.

ment used anisotropic thermal parameters for the framework atoms converged to the error indices (defined in Table 1, footnote *b*) $R_1 = 0.2595$ and $R_2 = 0.7168$, respectively. See Table 2 for the steps of structure determination and refinement Fourier electron-density functions. The final cycles of refinement were done with anisotropic temperature factors at Mg(I) and Mg(I'), and with the final refined weighting-scheme parameters (see Table 1). The final error indices R_1 and R_2 are given in Table 1. The largest peaks on the final difference-Fourier function 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. 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 $P = [Max(F_o^2, 0) + 2F_c^2]/3$, with $a = 0.032$ and $b =$

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

Distances		Angles	
(Si,Al)-O(1)	1.6436(16)	O(1)-(Si,Al)-O(2)	112.81(12)
(Si,Al)-O(2)	1.6700(14)	O(1)-(Si,Al)-O(3)	106.00(13)
(Si,Al)-O(3)	1.7110(16)	O(1)-(Si,Al)-O(4)	112.43(15)
(Si,Al)-O(4)	1.6265(9)	O(2)-(Si,Al)-O(3)	106.58(13)
Mean (Si,Al)	1.6625(16)	O(2)-(Si,Al)-O(4)	106.16(16)
		O(3)-(Si,Al)-O(4)	112.83(15)
Mg(I)-O(3)	2.231(3)		
Mg(I')-O(3)	2.20(3)	(Si,Al)-O(1)-(Si,Al)	127.40(20)
Mg(II')-O(2)	2.187(20)	(Si,Al)-O(2)-(Si,Al)	134.51(20)
Mg(II)-O(2)	2.123(4)	(Si,Al)-O(3)-(Si,Al)	121.80(17)
Na(II)-O(2)	2.234(7)	(Si,Al)-O(4)-(Si,Al)	160.97(25)
Mg(II')-O(5)	2.49(15)		
		O(3)-Mg(I)-O(3)	89.15(11), 90.85(11)
		O(3)-Mg(I')-O(3)	92.3(14)
		O(2)-Mg(II')-O(2)	114.2(16)
		O(2)-Mg(II)-O(2)	119.70(19)
		O(2)-Na(II)-O(2)	110.5(4)

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

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
Si, Al	192(*i*)		-533(1)	1219(1)	356(1)	153(6)	102(6)	137(6)	-23(3)	-14(3)	1(3)	192		
O(1)	96(*h*)		-1086(1)	0	1086(1)	243(11)	252(18)	243(11)	-97(10)	56(14)	-97(10)	96		
O(2)	96(*g*)		-26(1)	-26(1)	1467(1)	247(11)	247(11)	161(16)	47(10)	47(10)	90(14)	96		
O(3)	96(*g*)		-313(1)	605(1)	605(1)	179(17)	177(11)	177(11)	31(13)	15(9)	15(9)	96		
O(4)	96(*g*)		834(1)	834(1)	3141(1)	201(11)	201(11)	387(21)	59(11)	59(11)	86(14)	96		
Mg(I)	16(*c*)	I	0	0	0	133(14)	133(14)	133(14)	2(9)	2(9)	2(9)		14.5(2)	14
Mg(I')	32(*e*)	I'	586(11)	586(11)	586(11)	594(165)	594(165)	594(165)	42(121)	42(121)	42(121)		3.3(5)	4
Mg(II')	32(*e*)	II'	2047(19)	2047(19)	2047(19)	263(155)							2.5(6)	2.5
Mg(II)	32(*e*)	II	2201(8)	2201(8)	2201(8)	226(46)							10.1(9)	10
Na(II)	32(*e*)	II	2339(4)	2339(4)	2339(4)	145(31)							13.6(9)	14
O(5)	32(*e*)	II'	1461(32)	1461(32)	1461(32)	994(537)							2.5(6)	2.5
											ΣMg^{2+} (30.4(22)) + ΣNa^+ (13.6(9)) = 44(31)			

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

159.9 as refined parameters (see Table 1). Atomic scattering factors for Mg^{2+}, O^-, and $(Si,Al)^{1.82+}$ were used.[13,14] The function describing $(Si,Al)^{1.82+}$ is a weighted mean of the Si^{4+}, Si^0, Al^{3+}, and Al^0 functions assuming half formal charges. All scattering factors were modified to account for anomalous dispersion.[15,16]

Result and Discussion

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 (see Figure 2). 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 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 $Fd\overline{3}m$) 192, respectively. Further description is available.[18-20]

Distrubution of Mg²⁺ Ions. In the structure of $|Mg_{30.5}\text{-}Na_{14}(H_2O)_{2.5}|[Si_{117}Al_{75}O_{384}]\text{-FAU}$ ($Mg_{30.5}Na_{14}(H_2O)_{2.5}$-Y), Mg^{2+} ions are found at four different crystallographic sites and Na^+ ions at one site (see Table 3). The 14 Mg^{2+} ions per unit cell are filled at site I. The 4 and 2.5 Mg^{2+} ions per unit cell occupy sites I' and II', respectively. Two different site-II positions are occupied by 10 Mg^{2+} and 14 Na^+ ions, respectively.

The 14 Mg^{2+} ions at Mg(I) lie at site I in the center of a D6Rs (see Figure 3(a)). Each Mg^{2+} ion at Mg(I) is coordinated by the six O(3) oxygen atoms of its D6R at distance of 2.231 Å, which is longer than the sum of the conventional ionic radii of Mg^{2+} and O^{2-}, 0.66 + 1.32 (respectively) = 1.98
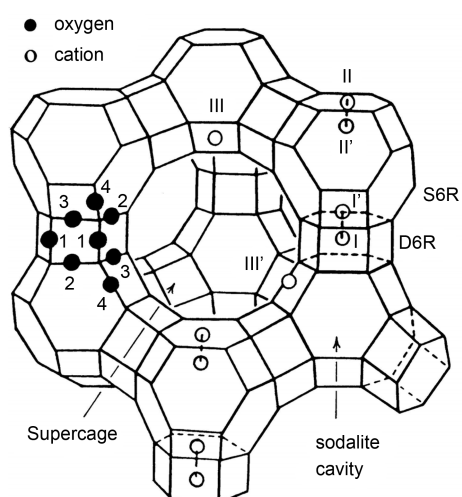

Figure 2. Stylized drawing of the framework structure of zeolite Y. Near the center of the each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1 to 4. There is no evidence in this work of any ordering of the silicon and aluminum atoms among the tetrahedral positions, although it is expected that Lowenstein's rule (ref. 17) would be obeyed. Extraframework cation positions are labeled with Roman numerals.
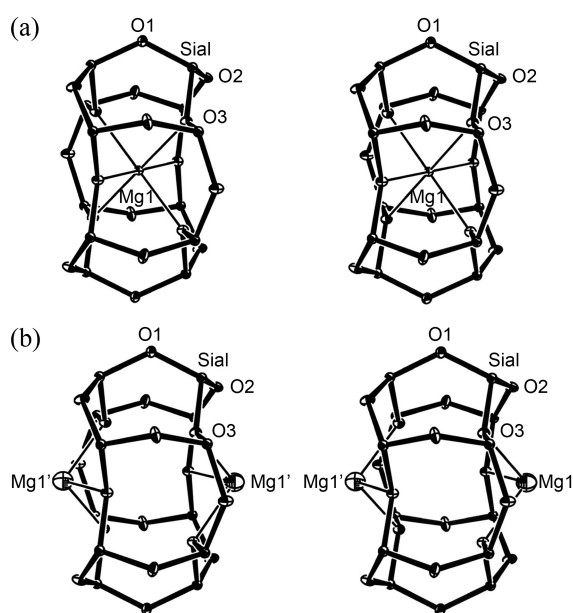

Figure 3. Stereoviews of D6Rs in partially dehydrated $Mg_{30.5}Na_{14}(H_2O)_{2.5}$-Y: (a) 14 of 16 D6Rs, Mg(I) located and (b) 2 of 16 D6Rs, Mg(I') located. The zeolite Y framework is drawn with heavy bonds. The coordination of Mg^{2+} ions to oxygens of the zeolite framework are indicated by light bonds. Ellipsoids of 25% probability are shown.

Å.[21] For comparison, Mg^{2+} ion at site I with framework oxygens, O(3), in the structure of $Mg_{46}(H_2O)_4$-X,[5] is similarly longer than the sum of the corresponding ionic radii, indicating a reasonably good fit. The O(3)-Mg(I)-O(3) bond angles are 89.15(11) and 90.85(11)°, nearly octahedral (see Table 4). Generally, hexagonal prism is not especially favorable to cation of small size as Li^+.[6,7] Contrary to Li^+, Mg^{2+} ion allows it to fit comfortably in site I despite its small ionic radious. This is due to the higher charge of Mg^{2+} than Li^+ ion.

Four Mg^{2+} ions at Mg(I') are found at site I' position opposite D6Rs in the sodalite cavities (see Figures 1(b) and 2). This is 32-fold position, but it is occupied by only 4 Mg^{2+} ions. Each Mg^{2+} ion lies inside the sodalite cavity 1.22 Å from plane of the three O(3) frame work oxygen of the D6R to which it is bonded (see Table 5). The Mg(I')-O(3) distance is 2.20(3) Å, which is just a little longer than the sum of the corresponding ionic radii of Mg^{2+} and O^{2-}, 1.98 Å.[21] The

Table 5. Displacements of atoms (Å) from 6-ring planes

	Position	Site	Displacement
At O(3)[a]	Mg(I)	I	-1.31
	Mg(I')	I'	1.22
At O(2)[b]	Mg(II')	II'	-0.54
	Mg(II)	II	0.12
	Na(II)	II	0.71

[a]A positive deviation indicates that the cation lies in a sodalite cavity; a negative deviation indicates that the cation lies in a D6R. (Mg(I) lies at the center of D6Rs). [b]A positive displacement indicates that the cation lies in a supercage; a negative deviation indicates the cation lies in a sodalite cavity.
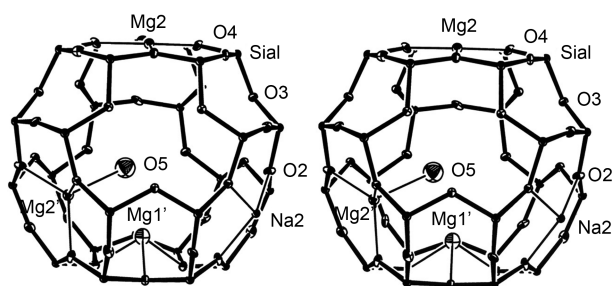
Figure 4. Stereoviews of a representative sodalite unit in partially dehydrated $Mg_{30.5}Na_{14}(H_2O)_{2.5}$-Y. One Mg^{2+} ion at Mg(I'), one Mg^{2+} ion at Mg(II'), one Mg^{2+} ion at Mg(II), and one Na^+ ion at Na(II) are shown. One Mg^{2+} ion at Mg(II') coordinates to one water molecule. See the caption to Fig. 3 for other details.

shortest approach distances between the sites I and I' is only 2.53 Å, which is avoided because of electrostatic repulsion. The O(3)-Mg(I')-O(3) bond angle is 92.3(14)°, far from trigonal planer due to the repulsin between Mg^{2+} ions at sites I' (see Table 4).

The 2.5 Mg^{2+} ions at Mg(II') are located at site II' positions opposite S6Rs in the sodalite cavity (see Figure 2). These Mg^{2+} ions at site (II') coordinate trigonally at 2.187(20) Å to three O(2) framework oxygen of the S6Rs to which each is bound and is recessed about 0.54 Å into the sodalite unit from their plane (see Figure 2 and Table 5). Each Mg^{2+} ion binds to one water molecule at O(5) at 2.49(15) Å. The O(2)-Mg(II')-O(2) bond angle is 114.2(16)°, much closer to trigonal plannar (see Table 4). The 10 Mg^{2+} and 14 Na^+ ions at Mg(II) and Na(II), respectively, are found at two different crystallographic site II positions in the supercage (see Figure 5). The Mg^{2+} and Na^+ ion are coordinated by three O(2) oxygens of the S6Rs at 2.123(4) and 2.234(15) Å, respectively, which are almost the similar as the sum of the ionic radii of Mg^{2+} and O^{2-}, 1.98 Å and Na^+ and O^{2-}, 0.97 + 1.32 (respectively) = 2.29 Å.[21] Each Mg(II) and Na(II) ion extends 0.12 and 0.71 Å, respectively, into supercage from its three O(2) plane (see Figure 5 and Table 5). Na^+ ions extend more than Mg^{2+} ions due to the large size of Na^+ ion.

In the structure of dehydrated Mg^{2+}-exchanged zeolites X[5] and Y, sites I and II preferentially were occupied by Mg^{2+}
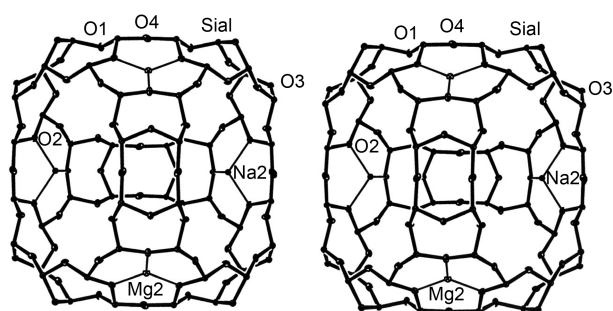

Figure 5. Stereoviews of a representative supercage in partially dehydrated $Mg_{30.5}Na_{14}(H_2O)_{2.5}$-Y. Two Mg^{2+} ions at Mg(II) and two Na^+ ions at Na(II) ions are shown. See the caption to Fig. 3 for other details.

ions, leaving sites I' and II' poor occupied. The sites I and II were not fully occupied. This may be due to the Si/Al ording in thetrahedral site.

Comparison of Mg^{2+}-ecchanged Zeolites X and Y. Seff *et al.* investigated the structure of a partially dehydrated Mg^{2+}-exchanged zeolite X, $Mg_{46}(H_2O)_4$-X,[5] by single-crystal X-ray diffraction techniques. In their structure, Mg^{2+} ions were found at four different crystallographic sites with the fractional occupancies 13.8(2), 4.0(3), 3.8(3), and 26.2(4) at sites I, I', II', and II, respectively. The Mg^{2+} ions at site II' bind water molecule.

When the partially dehydrated structures of $Mg_{46}(H_2O)_4$-X[5] and $Mg_{30.5}Na_{14}(H_2O)_{2.5}$-Y are compared, it can be seen that there are many similarities in distribution of Mg^{2+} ions and water molecule, but the Na^+ ions are not found in the structure of $Mg_{46}(H_2O)_4$-X.[5]

Considering previous work by Seff *et al.*,[5] we made attempt to prepare to fully dehydrated fully Mg^{2+}-exchanged zeolite Y (Si/Al = 1.56) but complete ion exchange of Mg^{2+} ion in the conventional aqueous solution method at room temperature has not been achieved in this work. This is attributed to the difference of the content of aluminum, regulating the density and distributions of negative charge through the framework between zeolites X and Y. To explain incomplete exchange, the competitive attraction of Mg^{2+} to the water and the framework oxygen should be taken into account. Because of the lower Al content of zeolite Y as compared to zeolite X, the negative charges of the framework oxygens and electric fields are lessened. Consequently, the framework oxygen could not act as an effective ligand for cations of high ionic potential like Mg^{2+}. Probably, the Mg^{2+} prefers to keep water instead of replacing it with the framework oxygen, discouraging ion exchange process. In contrast, the Mg^{2+} replaces easily water in its coordination sphere with the framework oxygen of zeolite X, completing exchange process.

Seff *et al.* found the loss of crystallinity in the single crystal of $Mg_{46}(H_2O)_4$-X due to the distortions of the zeolite framework occurring upon dehydration by the strong interactions between Mg^{2+} ions and the oxygen framework atoms.[5] In this work, this can be seen in the angles at O(2) and O(3), 134.5(2)° and 121.8(2)°, respectively, which are much smaller than those seen in Na_{75}-Y,[22] 146.2(2)° and 141.1(2)°, respectively. Howerever, there is no any crystallographic evidence for the indication of the loss of crystallinity. It is strongly correlated with relatively higher structural stability of Mg^{2+}-exchanged zeolites Y than X at high temperature.

Nearly always, when ion exchange is done from solution, the solvent used is water. Unfortunately, the result of ion-exchange experiment from aqueous solution is usually not simple. Often ion exchange is incomplete as this result. The behavior of Mg^{2+} exchange into zeolite Y shown in this study is not fundamental, considering that water has been generally accepted as the most unique and convenient solvent for ion exchange, taking advantage of its physico-chemical nature. A careful thought based on this work

suggests that the study of exploring new solvent systems, to maximize the extent of ion exchange in zeolite Y is needed.

Summary

The structure of partially Mg^{2+}-exchanged zeolite Y was determind by single-crystal X-ray diffraction techniques. About 30.5 Mg^{2+} ions per unit cell are distributed at the four different crystallographic sites I, I', II' and II with the occupancies of 14, 4, 2.5, and 10 Mg^{2+} ions per unit cell, respectively. About 14 Na^+ ions occupy site II. Water molecules are found in this structure. Water molecules coordinate to 2.5 Mg^{2+} ions at site II' in the sodalite cavity. The lower aluminum content of zeolite Y relative to zeolite X should lead to smaller negative charge of the framework oxygens and resulting the extent of Mg^{2+} ion exchange are diminished.

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