Structure Refinement of the Partially Dehydrated Natural Chabazite
$Ca_{1.57}Na_{0.49}Al_{3.39}Si_{8.55}O_{24} \cdot 11.53H_2O$

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Structure analysis of a slightly partially-dehydrated natural chabazite was carried out using single crystal X-ray diffraction. The presences of the five water sites and four exchangeable-cation sites, found in the fully hydrated sample investigated by our recent study (Nakatsuka et al., 2007), were also confirmed in the present partially dehydrated sample. The final structure refinement converged to $R = 0.0280$ and $R_w = 0.0284$ for 926 reflections. The occupancy of the water site located at the center of the 8-ring window in the $[4^{12}6^28^6]$-cavity decreases significantly compared with that in the fully hydrated sample.

Key words: Zeolite, Chabazite, Dehydration, Crystal structure, Single crystal X-ray diffraction

1. INTRODUCTION

Chabazite, one of the most widespread natural zeolites, is a promising heat absorbent for the zeolite-water heat pump system because of its high heat-exchange abilities at low temperatures [1]. The heat-exchange abilities of zeolites are closely related to their thermodynamic hydration-dehydration process, and hence can depend on the strengths of the interactions between water molecules and their neighboring chemical species. Therefore, the investigation of dehydration behavior from water sites in chabazites is quite important for elucidating their properties as heat absorbents.

The structure of aluminosilicate framework in chabazite is built up of double 6-rings ($[4^66^2]$-rings), and consequently one $[4^{12}6^28^6]$-cavity per unit cell is formed (Fig. 1). Each cavity is connected to six neighboring $[4^{12}6^28^6]$-cavities by sharing the 8-ring windows and filled with water molecules and exchangeable cations. The occupancies of water sites and exchangeable-cation sites are usually less than unity and these are statistically distributed on each site. Such an occupation mode makes site assignments of water molecules and exchangeable cations difficult. Because of this, a
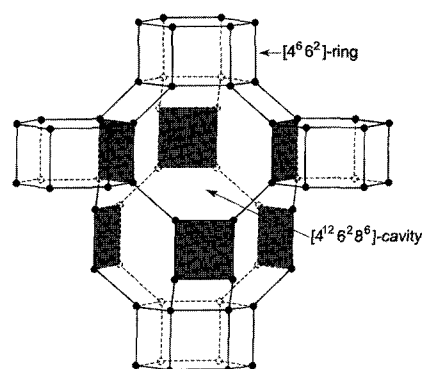

Fig. 1. Framework structure drawn by linking (Si, Al) positions denoted with circles (after Ref. [17]). Shaded quadrilaterals represent the 4-ring windows attaching the $[4^66^2]$-rings, four of which are shown in the figure.

consensus on the positions of water molecules and exchangeable cations in chabazites had not been obtained, although considerable efforts had been devoted to the determinations of their positions [2-16].

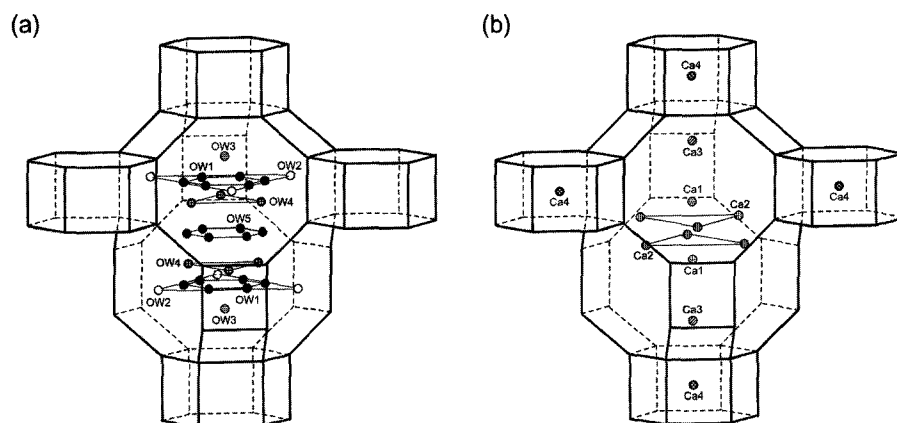(a)   (b)

Fig. 2. Arrangements of equivalent positions of (a) water sites and (b) exchangeable-cation sites.

However, our recent study [17] succeeded in determining their reliable positions in a fully hydrated natural chabazite by single crystal X-ray diffraction, and revealed the presences of five partially occupied water sites and four partially occupied exchangeable-cation sites (Fig. 2). As a result, the crystallographic configurations of water molecules and exchangeable cations came to light, and information on hydrogen bonding, involved with water molecules, was also provided to some extent. However, the dehydration behavior from each water site remains to be solved.

In the present study, we perform structure analysis of a partially dehydrated chabazite using single crystal X-ray diffraction. To gain some insights into the dehydration behavior from the water sites, we compare the refined structure of the present sample with that of the fully hydrated sample reported by our recent study [17], with attention to the occupancies of the water sites.

2. EXPERIMENTAL

Single crystal of a fully hydrated natural chabazite from Komuro, Oh-hito, Shizuoka Prefecture, Japan used in our recent study [17] was partially dehydrated in the present study. In our recent study, the composition of the fully hydrated sample was determined to be $Ca_{1.57}Na_{0.49}Al_{3.39}Si_{8.55}O_{24} \cdot 12.47H_2O$ using an atomic absorption spectrophotometer and TG analysis. For the preparation of dehydrated sample, the single crystal ground into a sphere of 0.14 mm in diameter was put into a silica-glass capillary. The capillary was attached to a vacuum line and put into a furnace, after which, temperature was elevated up to 150 °C at the rate of 0.5 °C/min while evacuating. After the crystal was dehydrated by heating at this temperature for 1 hour under 5×10^{-5} Torr, the capillary was sealed and slowly cooled to room temperature.

X-ray diffraction intensity measurements were carried out at room temperature using a four circle diffractometer (Rigaku AFC-7R) with the graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å), and the operating conditions were 50 kV and 200 mA. The unit-cell parameters were determined by the least-squares method from a set of 26 reflections within the range of 40° ≤ 2θ ≤ 51°. Intensity data of reflections within 2° ≤ 2θ ≤ 80° with −16 ≤ h, l ≤ 16 and

$0 \le k \le 16$ were collected by continuous ω–2θ scan mode and corrected for Lorentz-polarization factors and spherical absorption effects (μr = 0.057 for Mo Kα). A total of 10485 reflections were measured and averaged in Laue symmetry $\bar{3}m$ to give 1911 independent reflections, of which 926 observed independent reflections with $|F_o| \ge 3\sigma(|F_o|)$ were used in the structure refinements. Internal residual of the equivalent reflections (R_{int}) was 0.0304.

3. STRUCTURE ANALYSIS

The structure refinements were carried out by minimizing the residual factor $\Sigma w(|F_o| - |F_c|)^2$ using a full matrix least-squares program RADY [18], where $w = 1/\sigma^2(|F_o|)$. In the structure refinements, scattering factors of Al^{3+} and Si^{4+} [19] were used for cations in the aluminosilicate framework and those of O^{2-} [20] were used for oxygen atoms in the framework and water molecules. Scattering factors for Ca^{2+} and Na^+ were also taken from Ref. [19], but the averaged scattering factors based on the Ca^{2+}/Na^+ ratio determined by the chemical analysis, $0.762 f(Ca^{2+}) + 0.238 f(Na^+)$, were used for the exchangeable cations. The correction terms for anomalous dispersion of each element were taken from Ref. [19] as well. The positions of water molecules and exchangeable cations were determined from difference Fourier syntheses, but positions of hydrogen atoms in water molecules were not determined. In the structure refinements, the occupancies of Si^{4+} and Al^{3+}, belonging to the aluminosilicate framework, were fixed at the values obtained from the chemical analysis. For all the atomic sites included in the refinements, an anisotropic thermal motion model was applied to the displacement parameters. A correction for isotropic extinction effects (Type II) [21, 22] was performed during the refinements.

The further detailed procedure of the structure analyses is described in our recent study [17]. In the difference Fourier syntheses, electron density peaks were observed at the same sites as those of the fully hydrated sample reported by our recent study [17]. The atomic assignments to these electron density peaks were based on the result of the fully hydrated sample [17], and the refined occupancies in the present sample provided the number of exchangeable cations of Ca + Na = 1.93 per unit cell. This value is in good agreement with that from the chemical analysis of the fully hydrated sample (Ca + Na = 2.06) [17]; consequently,

Table I. Crystallographic data, data-collection and refinement parameters

a (Å)	9.366(2)
α (°)	94.38(1)
V (Å³)	814.1(5)
Crystal system	rhombohedral
Space group	$R\bar{3}m$
Crystal size (mm, diameter)	0.14
Radiation used	Mo Kα
Diffractometer	Rigaku AFC-7R
Monochromator	graphite
Scan type	ω–2θ
2θ range (°)	2–80
No. of meas. refls.	10485
No. of obs. indep. refls. with $|F_o| \ge 3\sigma(|F_o|)$ after averaging equiv. refls.	926
R_{int}	0.0304
R	0.0280
R_w	0.0284
Weighting scheme	$1/\sigma^2(|F_o|)$

Table II. Refined positional parameters

atoms		x	y	z
Si/Al	[12i]	0.10475(5)	0.33344(4)	0.87647(5)
O1	[6f]	0.26091(17)	−0.26091	0
O2	[6g]	0.15342(15)	−0.15342	0.5
O3	[6h]	0.25363(17)	0.25363	0.89374(28)
O4	[6h]	0.02628(19)	0.02628	0.32569(24)
OW1	[12i]	0.814(6)	0.643(9)	0.558(8)
OW2	[3e]	0.5	0.5	0
OW3	[2c]	0.2571(9)	0.2571	0.2571
OW4	[6h]	0.299(3)	0.299	0.544(3)
OW5	[6g]	0.3694(12)	−0.3694	0.5
Ca1	[2c]	0.4105(5)	0.4105	0.4105
Ca2	[6h]	0.5835(3)	0.5835	0.2253(7)
Ca3	[2c]	0.2064(10)	0.2064	0.2064
Ca4	[1a]	0	0	0

Note: The notations in brackets represent the Wyckoff positions.

Table III. Refined anisotropic displacement parameters and equivalent isotropic displacement parameters (Å^2)

atoms	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
Si/Al	0.01259(16)	0.01031(18)	0.01874(21)	0.00109(12)	0.00131(14)	−0.00055(12)	1.102(4)
O1	0.0354(7)	0.0354	0.0468(13)	−0.0053(9)	−0.0114(6)	−0.0114	3.247(14)
O2	0.0387(7)	0.0387	0.0159(8)	0.0081(9)	0.0021(5)	0.0021	2.437(10)
O3	0.0242(6)	0.0242	0.0716(17)	0.0091(8)	0.0032(7)	0.0032	3.137(15)
O4	0.0367(7)	0.0367	0.0403(12)	0.0149(9)	0.0058(7)	0.0058	2.920(13)
OW1	0.41(7)	1.03(17)	0.72(11)	−0.59(11)	0.17(7)	−0.35(10)	60.5(2.4)
OW2	0.117(17)	0.117(13)	0.117	−0.040(9)	−0.040	0.019(13)	9.59(20)
OW3	0.065(5)	0.065	0.065	−0.015(4)	−0.015	−0.015	5.40(3)
OW4	0.593(62)	0.593	0.094(19)	−0.370(69)	0.074(16)	0.074	35.0(6)
OW5	0.33(3)	0.33	0.77(8)	0.30(3)	−0.13(5)	−0.13	38.2(8)
Ca1	0.102(3)	0.102	0.102	−0.015(3)	−0.015	−0.015	8.36(2)
Ca2	0.0355(18)	0.0355	0.0680(39)	−0.0133(18)	0.0072(13)	0.0072	3.70(4)
Ca3	0.043(4)	0.043	0.043	0.005(3)	0.005	0.005	3.38(3)
Ca4	0.52(23)	0.52	0.52	−0.17(12)	−0.17	−0.17	43.6(1.5)

Table IV. Refined occupancy parameters of the fully hydrated sample and the present sample

atoms	occupancy	
	fully hydrated sample [17]	the present sample
Si/Al	0.713 / 0.283	0.713 / 0.283
O1	1.0	1.0
O2	1.0	1.0
O3	1.0	1.0
O4	1.0	1.0
OW1	0.345(16)	0.278(20) [0.19(7)][b]
OW2	0.759(15)	0.588(23) [0.23(3)][b]
OW3	0.555(27)	0.545(26) [0.02(7)][b]
OW4	0.418(32)	0.438(41) [−0.05(13)][b]
OW5	0.406[a]	0.453(26) [−0.12(14)][b]
Ca1	0.385[a]	0.316[a]
	(Ca: 0.293, Na: 0.092)	(Ca: 0.241, Na: 0.075)
Ca2	0.146(4)	0.172(4)
	(Ca: 0.111, Na: 0.035)	(Ca: 0.131, Na: 0.041)
Ca3	0.173(15)	0.158(10)
	(Ca: 0.132, Na: 0.041)	(Ca: 0.120, Na: 0.038)
Ca4	0.068(11)	0.082(25)
	(Ca: 0.052, Na: 0.016)	(Ca: 0.062, Na: 0.020)

[a] Constraints for occupancy parameters:
$P(OW5) = \{12.47 - 12P(OW1) - 3P(OW2) - 2P(OW3) - 6P(OW4)\}/6$
$P(Ca1) = \{2.06 - 6P(Ca2) - 2P(Ca3) - P(Ca4)\}/2$
[b] The values in brackets represent the dehydration ratios calculated from $1 - P(OW)_d/P(OW)_h$.
where $P(i)$ is the occupancy of the atom i; the subscript letters "h" and "d" represent the fully hydrated and the present partially dehydrated samples, respectively.

Table V. Selected interatomic distances (Å) less than 3.20 Å

(Si,Al)–O1	1.6286(13)	OW1···OW2	2.35(7)
(Si,Al)–O2	1.6425(7)	OW1···OW3	2.08(7)
(Si,Al)–O3	1.6347(17)	OW1···OW4	2.50(8)
(Si,Al)–O4	1.6368(19)	OW1···OW4	1.53(7)
Ca1–OW1	2.17(6)×6	OW1···OW5	2.97(8)
Ca1–OW3	2.290(9)	OW1···OW5	2.59(7)
Ca1–OW4	1.99(3)×3	OW2···O3	3.1823(17) × 2
Ca1–OW5	2.238(12) × 6	OW2···OW1	2.35(7) × 4
Ca2–O2	2.757(4) × 2	OW3···O4	3.078(9) × 3
Ca2–O3	2.462(5)	OW3···OW1	2.08(7) × 6
Ca2–OW1	2.41(8) × 2	OW3···OW4	2.68(3) × 3
Ca2–OW2	2.254(6)	OW4···OW1	1.53(7) × 2
Ca2–OW4	2.49(2)	OW4···OW1	2.50(8) × 2
Ca2–OW4	2.81(3) × 2	OW4···OW3	2.68(3)
Ca2–OW5	1.659(11) × 2	OW4···OW5	2.03(3) × 2
Ca3–O3	3.055(10) × 3	OW4···OW5	3.18(3) × 2
Ca3–O4	2.661(10) × 3	OW5···O2	2.968(12)
Ca3–OW1	2.55(8) × 6	OW5···OW1	2.97(8) × 2
Ca3–OW3	0.758(12)	OW5···OW1	2.59(7) × 2
Ca4–O4	3.031(2) × 6	OW5···OW4	3.18(3) × 2
OW1···O3	3.18(6)	OW5···OW4	2.03(3) × 2
OW1···OW1	2.35(15)	OW5···OW5	3.11(2) × 2
OW1···OW1	3.10(11) × 2	OW5···OW5	1.795(16) × 2
OW1···OW1	1.17(17)		

we confirmed the presences of four partially occupied exchangeable-cation sites (Ca1–Ca4) and five partially occupied water sites (OW1–OW5), found in the fully hydrated sample [17]. Finally, the occupancies of the exchangeable-cation sites were constrained on the basis of the composition from the chemical analysis. The final refinement converged to $R = 0.0280$ and $R_w = 0.0284$ for 926 reflections.

The crystallographic data, data-collection and refinement parameters are given in Table I. The refined structural parameters are given in Tables II, III and IV. The selected interatomic distances are listed in Table V.

4. RESULTS AND DISCUSSION

4.1 Water content

The resulting occupancies of the present sample, vacuum-dehydrated at 150 °C, provide a composition of $Ca_{1.57}Na_{0.49}Al_{3.39}Si_{8.55}O_{24}\cdot 11.53H_2O$. This water content is much larger than that ($8.66H_2O$) at this temperature

observed by TG analysis performed for the fully hydrated sample under an atmospheric condition, although dehydration should occur more remarkably under a vacuum condition than under an atmospheric condition. This discrepancy indicates that the equilibrium water content at 150 °C under the vacuum condition could not be kept in the present dehydration treatment. However, the lattice volume of the present sample [814.1(5) Å^3] is significantly smaller than that of the fully hydrated sample [821.5(1) Å^3] [17], which indicates that the present sample was slightly but certainly partially-dehydrated. Investigating site occupancies of such slightly dehydrated sample is meaningful for understanding the behavior of water molecules at an early stage of dehydration. This will be discussed in the next section.

4.2 Occupancy parameters of water sites

Table IV shows the refined occupancy parameters of the present partially dehydrated sample, together with those of the fully hydrated sample [17]. Our recent study

[17] showed that the maximum allowance for occupancies of OW1 and OW5 sites is 0.5 because of the restrictions for the configurations of the occupied positions in both sites. The occupancies of both sites in the present sample are reasonably lower than 0.5, as well as those in the fully hydrated sample [17].

The occupancy of OW2 site in the present sample is significantly lower than that in the fully hydrated sample and its dehydration ratio is the highest (Table IV). On the other hand, the significant difference in the occupancies of the remaining water sites between both samples is not observed within the uncertainties of 3σ. Thus, OW2 site is expected to be one of the most preferential water sites for dehydration. In general, $O\cdots O$ distances related to hydrogen bonding are in the range of approximately 2.4~3.2 Å [23]. The separations between the water sites and the framework oxygen atoms within this range are OW1$\cdots$O1 [3.18(2) Å], OW2$\cdots$O3 [3.1967(12) Å], OW3$\cdots$O4 [3.055(9) Å] and OW5$\cdots$O2 [2.927(10) Å] for the fully hydrated sample [17], and OW1$\cdots$O3 [3.18(6) Å], OW2$\cdots$O3 [3.1823(17) Å], OW3$\cdots$O4 [3.078(9) Å] and OW5$\cdots$O2 [2.968(12) Å] for the present sample. Of these, OW2$\cdots$O3 distances are the longest in both samples and nearly equal to the upper limit of the acceptable $O\cdots O$ distances for hydrogen bonding. Thus, the hydrogen bonds formed between OW2 water molecules and the framework oxygen atoms (O3) will be extremely weak even if they are present. This weak interaction can be responsible for the preferential dehydration from OW2 site.

4.3 Displacement parameters

In general, displacement parameters of water sites and exchangeable-cation sites in zeolites are relatively large because they are loosely bonded to their neighboring chemical species. Such large displacement parameters are also observed in the present sample (Table III). In particular, those of OW1, OW4 and OW5 sites are remarkably large, and the same observation was also reported in the fully hydrated sample investigated by our recent study [17]. This can be due to remarkable positional disorders of OW1, OW4 and OW5 water molecules, in addition to the loose bonding with their neighboring chemical species. These positional disorders are closely related to the variety of actual configurations of Ca1, Ca2 and Ca3 cations partially occupying each site and their coordination environments, and its detailed explanation is provided in Ref. [17].

5. CONCLUSIONS

We have prepared the single crystal of partially dehydrated natural chabazite with a composition of $Ca_{1.57}Na_{0.49}Al_{3.39}Si_{8.55}O_{24}\cdot11.53H_2O$, and have determined its crystal structure using single crystal X-ray diffraction. From comparison of the refined occupancies of the present partially dehydrated sample with those of the fully hydrated sample [17], we conclude that OW2 site, located at the center of the 8-ring window in the $[4^{12}6^28^6]$-cavity, is promising as the most preferential water site for dehydration. Judging from the interatomic distances, this can be due to the extremely weak interactions between OW2 water molecules and their nearest framework oxygen atoms (O3). We also observed that OW1, OW4 and OW5 sites

have peculiarly large displacement parameters due to remarkable positional disorders of these water molecules, as in the fully hydrated sample [17].

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