Single-crystal Structure of Cd²⁺-exchanged Zeolite Y (FAU, Si/Al = 1.56), |Cd$_{27.5}$(Cd$_8$O$_4$)$_{2.5}$|[Si$_{117}$Al$_{75}$O$_{384}$]-FAU

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Zeolite framework contains channels and windows and interconnected voids which are occupied by the cations and water molecules. The cations are quite mobile and may usually be exchanged by other cations.[1,2] Ion exchange is the most important method for the modification of the physical and chemical properties of zeolites for use as catalysts, sorbents, and molecular sieves. The results of ion exchange into zeolites from aqueous solution are usually not simple. Often only a fraction of the original cations can be replaced, and attempts to overcome this may reveal a relatively sharp upper limit to exchange. When acetate salt of metal cations dissolves in water for exchange solution, metal hydroxide ions occurred. It can be exchanged for Na⁺ ions into zeolite framework, leading to over exchange.

The catalytic activity of Cd²⁺-exchanged zeolite Y for the formation of acetonitrile was studied for comparison with activated alumina (Al$_2$O$_3$) and also examined for the formation of acetonitrile from ethane and ammonia.[3,4] Its catalytic activity had much higher than that of Al$_2$O$_3$. It was found to be essentially inactive for the formation of acetonitrile from ethylamine.

When zeolite Y (Si/Al = 1.69) was ion exchanged in aqueous stream 0.05 M in Cd²⁺ (0.025 M Cd(NO$_3$)$_2$ and 0.025 M Cd(C$_2$H$_3$O$_2$)$_2$) for 5 days and dehydrated at 723 K and 2 × 10⁻⁶ Torr for 2 days, the resulting composition, |Cd$_{27.5}$(Cd$_8$O$_4$)$_2$|[Si$_{121}$Al$_{71}$O$_{384}$]-FAU, indicated that eight molecules of Cd(OH)$_2$ had been imbibed per unit cell.[5] With eight non-framework oxides, two Cd$_8$O$_4^{8+}$ clusters had formed per unit cell. It was stated that the ability of Cd²⁺ ions to hydrolyze at pH 7 facilitated this process, as did the ability of the sodalite unit to host and stabilize Cd$_4$(OH)$_4^{4+}$ clusters.

This study was done to investigate the behavior of Cd²⁺ in Cd²⁺-exchanged zeolite Y (Si/Al = 1.56) prepared at high ion-exchange temperature (353 K), with the expectation of forming more cadmium oxide cluster, Cd$_8$O$_4^{8+}$.

Synchrotron X-ray diffraction data were collected at 100 (1) K using an ADSC Quantum 210 detector at Beamline 6B MXI at the Pohang Light Source. Crystal evaluation and data collection were done using λ = 0.90000 Å radiation with a detector-to-crystal distance of 60 mm. Preliminary cell constants and an orientation matrix were determined from 72 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 HKL 2000.[6] The reflections

were successfully indexed by the automated indexing routine of the DENZO program.[6] The 87,989 reflections were harvested by collecting 144 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, and (negligible) corrections for crystal decay were also applied. The cubic space group $Fd\bar{3}m$ was determined by the program XPREP.[7] The summary of the experimental and crystallographic data is presented in Table 1.

Full-matrix least-squares refinement (SHELXL97)[8] 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 |Tl$_{75}$|[Si$_{117}$Al$_{75}$O$_{384}$]-FAU.[9] Initial refinement used anisotropic thermal parameters and

Table 1. Summary of experimental and crystallographic data

	|Cd$_{27.5}$(Cd$_8$O$_4$)$_{2.5}$|[Si$_{117}$Al$_{75}$O$_{384}$]-FAU
Crystal cross-section (mm)	0.30
Ion exchange T (K)	353
Ion exchange for Cd²⁺ (mL, days)	20, 3
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 (6B MXI BL)
Wavelength (Å)	0.90000
Unit cell constant, a (Å)	24.8600(1)
2θ range in data collection (deg)	70.32
Total reflections harvested	87,989
No. of unique reflections, *m*	852
No. of reflections with $F_o > 4\sigma(F_o)$	849
No. of variables, *s*	51
Data/parameter ratio, *m/s*	16.7
Weighting parameters, *a/b*	0.041/668.1
Initial error indices	
$R_1/wR_2 (F_o > 4\sigma(F_o))^a$	0.5416/0.8411
Final error indices	
$R_1/wR_2 (F_o > 4\sigma(F_o))^a$	0.0643/0.1747
R_1/wR_2 (all intensities)^b	0.0644/0.1750
Goodness-of-fit^c	1.36

$^a R_1 = \Sigma|F_o-|F_c||/\Sigma F_o$ and $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; R_1 and wR_2 are calculated using only the reflections for which $F_o > 4\sigma(F_o)$. $^b R_1$ and wR_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 is the number of unique reflections and s is the number of variables, respectively.

Table 2. Positional, thermal, and occupancy parameters[a]

Atom	Wyckoff position	Cation site	x	y	z	U_{11}[b] or U_{iso}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	Occupancy[c]		
												initial	varied	fixed[d]
						$\|Cd_{27.5}(Cd_8O_4)_{2.5}\|[Si_{117}Al_{75}O_{384}]$-FAU								
Si,Al	192(*i*)		-524(1)	1239(1)	368(1)	213(8)	148(8)	170(8)	-12(5)	12(5)	-7(6)	192		
O(1)	96(*h*)		-1017(2)	0	1017(2)	379(22)	213(30)	379(22)	-24(17)	-126(28)	-24(17)	96		
O(2)	96(*g*)		-12(2)	-12(2)	1458(2)	266(18)	266(18)	241(30)	-40(17)	-40(17)	79(24)	96		
O(3)	96(*g*)		-253(3)	732(2)	732(2)	407(39)	338(23)	338(23)	132(28)	111(23)	111(23)	96		
O(4)	96(*g*)		768(2)	768(2)	3195(3)	266(20)	266(20)	338(35)	9(19)	9(19)	87(25)	96		
Cd(I)	32(*e*)	I	0	0	0	143(13)	143(13)	143(13)	24(15)	24(15)	24(15)		3.2(1)	3
Cd(I'a)	32(*e*)	I'	645(1)	645(1)	645(1)	359(11)							15.7(5)	16
Cd(I'b)	32(*e*)	I'	767(1)	767(1)	767(1)	215(8)	215(8)	215(8)	3(10)	3(10)	3(10)		9.9(6)	10
Cd(IIa)	32(*e*)	II	2101(1)	2101(1)	2101(1)	232(7)	232(7)	232(7)	67(8)	67(8)	67(8)		13.4(2)	13
Cd(IIb)	32(*e*)	II	2297(3)	2297(3)	2297(3)	119(14)							4.1(2)	4
Cd(IIc)	32(*e*)	II	2430(6)	2430(6)	2430(6)	71(36)							1.7(3)	1.5
O(5)	32(*e*)	II'	1582(10)	1582(10)	1582(10)	462(101)	462(101)	462(101)	-18(117)	-18(117)	-18(117)		18.9(15)	10
												ΣCd^{2+} =	48.0(4)	47.5

[a]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. [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. [d]These integral values were used only in the presentation of this work, to facilitate readability.

Table 3. Selected interatomic distances (Å) and angles (deg)[a]

Distance		Angle	
(Si,Al)-O(1)	1.627(3)	O(1)-(Si,Al)-O(2)	111.38(24)
(Si,Al)-O(2)	1.677(3)	O(1)-(Si,Al)-O(3)	110.4(3)
(Si,Al)-O(3)	1.692(3)	O(1)-(Si,Al)-O(4)	113.6(3)
(Si,Al)-O(4)	1.6341(23)	O(2)-(Si,Al)-O(3)	104.0(3)
Mean (Si,Al)-O	1.657	O(2)-(Si,Al)-O(4)	107.2(3)
		O(3)-(Si,Al)-O(4)	109.8(3)
Cd(I)-O(3)	2.649(7)	(Si,Al)-O(1)-(Si,Al)	145.9(5)
Cd(I'a)-O(3)	2.253(7)	(Si,Al)-O(2)-(Si,Al)	138.7(4)
Cd(I'b)-O(3)	2.537(8)	(Si,Al)-O(3)-(Si,Al)	129.6(4)
Cd(I'b)-O(5)	2.096(15)	(Si,Al)-O(4)-(Si,Al)	147.6(4)
Cd(IIa)-O(2)	2.155(6)		
Cd(IIa)-O(5)	2.23(5)	O(3)-Cd(I)-O(3)	81.61(24),
			98.39(24)
Cd(IIb)-O(2)	2.219(7)	O(3)-Cd(I'a)-O(3)	100.4(3)
Cd(IIc)-O(2)	2.434(13)	O(3)-Cd(I'b)-O(3)	86.0(3)
		O(3)-Cd(I'b)-O(5)	102.6(8),
			168.1(12)
		O(5)-Cd(I'b)-O(5)	67.7(18)
		O(2)-Cd(IIa)-O(2)	118.57(8)
		O(2)-Cd(IIa)-O(5)	96.91(19)
		O(2)-Cd(IIb)-O(2)	113.3(4)
		O(2)-Cd(IIc)-O(2)	99.2(7)

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

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. Extra-framework cation positions are labeled with Roman numerals.

converged to the high error indices (given in Table 1). All shifts in the final cycles of refinement were less than 0.1% of their corresponding estimated standard deviations. The final error indices are given in Table 1. Structural parameters are given in Table 2, and selected interatomic distances and angles are given in Table 3.

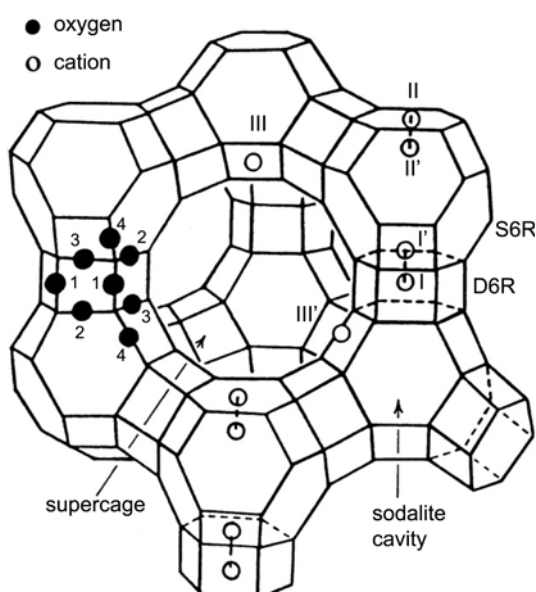The framework structure of zeolite Y (FAU) is charac-terized by the double 6-ring (D6R, hexagonal prism), the sodalite cavity (a cubooctahedron), and the supercage (see Fig. 1). Each unit cell has 8 supercages, 8 sodalite cavities, 16 D6Rs (32 S6Rs), 16 12-rings, and 32 single 6-rings (S6Rs). The exchangeable cations, which balance the negative charge of the zeolite Y framework, usually occupy some or all of the sites shown with Roman numerals in Figure 1. The maximum occupancies at the cation sites I, I', II, II', and III in zeolite Y are 16, 32, 32, 32, and 48, respectively. Site III'
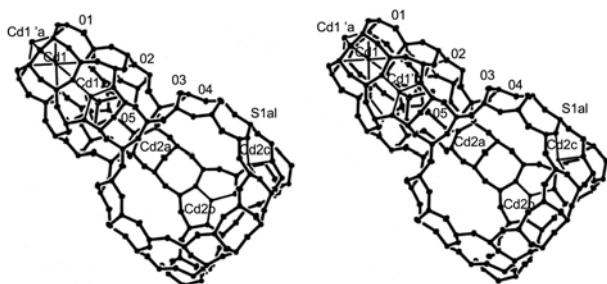
Figure 2. Stereoview of representative a double 6-ring (D6Rs), a sodalite cavity, and a supercage in fully dehydrated |Cd$_{27.5}$(Cd$_8$O$_4$)$_{2.5}$|[Si$_{117}$Al$_{75}$O$_{384}$]-FAU. The zeolite Y framework is drawn with heavy bonds. The coordination of the exchangeable cations to oxygens of the zeolite framework is indicated by light bonds. Ellipsoids of 25% probability are shown.

in zeolite Y studied using space group $Fd\overline{3}m$ is a 192-fold position. Further description is available.[9]

47.5 Cd^{2+} ions have been found at six equipoints within the unit cell in this structure: site I, two different sites I', and three dissimilar sites II.

The three Cd^{2+} ions per unit cell at Cd(I) nearly fill site I at the center of the D6Rs (see Fig. 2). Each coordinates octahedrally to six framework oxygens at O(3), 2.649(7) Å.

The 26 Cd^{2+} ions per unit cell occupy at two sites I'. Each Cd^{2+} ion at Cd(I'a) and Cd(I'b) coordinates to three O(3) framework oxygens at 2.253(7) and 2.537(8) Å, respectively. The latter distance is quite longer than the sum of the conventional ionic radii, 2.29 Å,[11] because Cd(I'b) coordinates further to three O(5) oxide ions.

The Cd(I'b)-O(5) distance, 2.096(15) Å, is just a little shorter than the sum of the conventional ionic radii, 2.29 Å.[11] To give reasonable coordination about these Cd^{2+} and O^{2-} ions, it may be concluded that the ions at Cd(I'b) and O(5) form neutral Cd$_4$O$_4$ clusters with symmetry $\overline{4}3m$ (T_d) (see Fig. 3). Each Cd^{2+} ions at Cd(I'b) is octahedrally coordinated in a trigonally distorted manner by three framework oxygens at O(3) and three O(5) oxygens. Cd(I'b)-O(5) distance is shorter than Cd(I'b)-O(3) distance because each O(5) coordinates to three Cd^{2+} ions while each O(3) bonds to one Cd^{2+}, one Al^{3+}, and one Si^{4+} ion. So, nonframework oxygen ion at O(5) has a greater net negative charge than framework oxygen ion at O(3).

The 13 Cd^{2+} ions per unit cell at Cd(IIa) are found at site II opposite S6Rs in the supercage (see Fig. 2). Cd(IIa) is 2.155-(6) Å from three O(2) framework oxygens and 2.23(5) Å from nonframework O(5) oxygen. The Cd(IIa)-O(5) distance should be shorter than the Cd(IIa)-O(2) distance as discussed as above, both distances are, however, nearly same because ten of 13 Cd^{2+} ions at Cd(IIa) are just participated to form cluster and remaining 3 Cd^{2+} ions are simply bonded to framework O(2) oxygens. The angles of Cd(I'b)-O(5)-Cd(IIa) and Cd(I'b)-O(5)-Cd(I'b) are 110.6(12)° and 108.4(12)° (see Table 3), respectively, so the coordination of four Cd^{2+} ions about each O(5) oxygen is mildly distorted tetrahedral. With these Cd^{2+} ions at Cd(IIa), it appears that Cd$_8$O$_4$$^{8+}$ clusters with symmetry $\overline{4}3m$ (T_d) have formed (see Fig. 3).
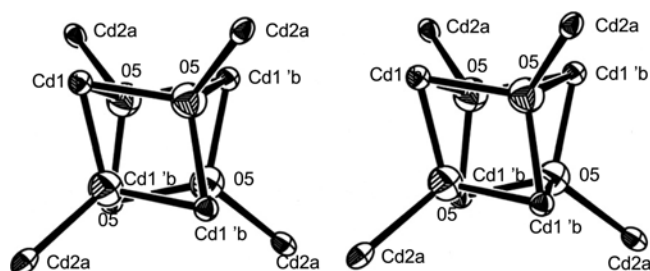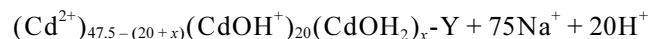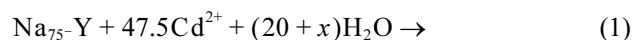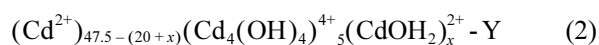

Figure 3. Stereoview of a Cd$_8$O$_4$$^{8+}$ cluster with symmetry $\overline{4}3m$ (T_d). Ellipsoids of 25% probability are shown.

The remaining 4 and 1.5 Cd^{2+} ions at site Cd(IIb) and Cd(IIc) are found at another two sites II (see Fig. 2 and Table 2). Cd(IIb) and Cd(IIc) coordinate near trigonally to the three O(2) framework oxygens at 2.219(7) and 2.434(13) Å, respectively. The Cd(IIb)-O(2) distance is a little shorter and the Cd(IIc)-O(2) distance is longer than the sum of the conventional ionic radii, 2.29 Å,[11] indicating a reasonably good fit.
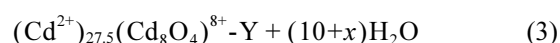
A number of divalent cations greater than the minimum required in zeolite Y with Si/Al = 1.56, 37.5 per unit cell, can better locally balance the anionic framework charge. During Cd^{2+} ion exchange at 353 K, zeolite Y (used in this work) had apparently imbibed 20 Cd(OH)$^+$ ions per unit cell. The ion-exchange reaction may be written as

$$\text{Na}_{75}\text{-Y} + 47.5\,\text{Cd}^{2+} + (20 + x)\text{H}_2\text{O} \rightarrow \qquad (1)$$

$$(\text{Cd}^{2+})_{47.5 - (20 + x)}(\text{CdOH}^+)_{20}(\text{CdOH}_2)_x\text{-Y} + 75\text{Na}^+ + 20\text{H}^+$$

By comparison with the structures of fully dehydrated Cd^{2+}-exchanged zeolite Y (Si/Al = 1.69)[5], |Cd$_{27.5}$(Cd$_8$O$_4$)$_2$|[Si$_{121}$Al$_{71}$O$_{384}$]-FAU, it could be seen and confirmed that suggested five [Cd$_4$(OH)$_4$]$^{4+}$ groups per unit cell within sodalite units during Cd^{2+} exchange at 353 K.

$$(\text{Cd}^{2+})_{47.5 - (20 + x)}(\text{CdOH}^+)_{20}(\text{CdOH}_2)_x\text{-Y} \rightarrow$$

$$(\text{Cd}^{2+})_{47.5 - (20 + x)}(\text{Cd}_4(\text{OH})_4)^{4+}{}_5(\text{CdOH}_2)_x{}^{2+}\text{-Y} \qquad (2)$$

After dehydration at 723 K, 20 Cd(OH)$^+$ ions are decomposed to give 2.5[Cd$_8$O$_4$]$^{8+}$ clusters with complete dehydration. It appears that the following reaction occurred upon dehydration

$$(\text{Cd}^{2+})_{47.5 - (20 + x)}(\text{Cd}_4(\text{OH})_4)^{4+}{}_5(\text{CdOH}_2)_x{}^{2+}\text{-Y} \rightarrow$$

$$(\text{Cd}^{2+})_{27.5}(\text{Cd}_8\text{O}_4)^{8+}\text{-Y} + (10 + x)\text{H}_2\text{O} \qquad (3)$$

As the structure of crystal in this study, Cd^{2+}-exchanged zeolite Y (Si/Al = 1.69) prepared by nearly same experiments with our recipe, just different dehydration temperature, had seemingly imbibed eight Cd(OH)$_2$ molecules per unit cell. These decomposed upon vacuum dehydration at 623 K to give two Cd$_8$O$_4$$^{8+}$ clusters. When the fully dehydrated structures of |Cd$_{27.5}$(Cd$_8$O$_4$)$_{2.5}$|[Si$_{117}$Al$_{75}$O$_{384}$]-FAU (in this study) and |Cd$_{27.5}$(Cd$_8$O$_4$)$_2$|[Si$_{121}$Al$_{71}$O$_{384}$]-FAU[5] are

compared, it can be seen that two structures are nearly similar appearance of $[Cd_8O_4]^{8+}$ cluster. The distances of Cd-O formed distorted cube and another Cd-O formed cubane in $|Cd_{27.5}(Cd_8O_4)_{2.5}|[Si_{117}Al_{75}O_{384}]$-FAU (in this study) and $|Cd_{27.5}-(Cd_8O_4)_2|[Si_{121}Al_{71}O_{384}]$-FAU[5] are 2.096(15) and 2.23(5) Å and 2.12(8) and 2.324(9) Å, respectively, which are considerably different due to their Si-Al ordering in tetrahedral site by Si/Al ratio of zeolite Y leading to the diverse kinds of 6-rings (3Si3Al, 4Si2Al, and 5Si1Al).

Experimental Section

Large, clear, colorless, octahedral single crystals of sodium zeolite Y, $|Na_{75}|[Si_{117}Al_{75}O_{384}]$-FAU (Si/Al = 1.56), with diameters up to 0.32 mm were prepared by Lim *et al.*[9] One of these was lodged in its own Pyrex capillary. It was Cd^{2+}-exchanged by the flow method using aqueous exchange solution of $Cd(NO_3)_2$ (Aldrich, 99.999%, K 0.9 ppm, Na 0.8 ppm, Zn 0.3 ppm, Ag 0.1 ppm, Cr 0.1 ppm) and $Cd(C_2H_3O_2)_2$ (Aldrich, 99.99+%, Hg 4.2 ppm, Pb 3.0 ppm, Na 0.9 ppm, Tl 0.8 ppm, Ag 0.7 ppm, Zr 0.6 ppm, Zn 0.5 ppm, Mg 0.4 ppm, Ca 0.3 ppm, Fe 0.1 ppm, Mn 0.1 ppm, Co 0.1 ppm) in the molar ratio 1:1 with a total Cd^{2+} concentration of 0.05 M for 3 days at 353 K.[5] The pH of this solution was 6.0 at 294 K. The resulting clear colorless crystal was dehydrated at 723 K and a dynamic vacuum of 1×10^{-6} Torr for 2 days. After dehydration, microscopic examination showed that crystal had become dark yellow.

Supporting Information Available. Tables of calculated and observed structure factors (9 pages). The supporting materials are available *via* the Internet *http://www.kcsnet.or.kr/bkcs*.

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