

Partially Dehydrated Fully Zn^{2+} -exchanged Zeolite Y (FAU, Si/Al = 1.70) and Its Structure

Sung Man Seo¹, Young Hun Kim², Seok Hee Lee^{3*}, and Woo Taik Lim^{1*}

¹Department of Applied Chemistry, Andong National University, Andong 760-749, Korea

²Department of Environmental Engineering, Andong National University, Andong 760-749, Korea

³Department of Science Education, Busan National University of Education, Busan 611-736, Korea

The crystal structure of partially dehydrated fully Zn^{2+} -exchanged zeolite Y was determined by X-ray diffraction techniques in the cubic space group $Fd\bar{3}m$ at 294(1) K and refined to the final error indices $R_1/wR_2 = 0.035/0.119$ for $[\text{Zn}_{35.5}(\text{H}_2\text{O})_{13}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]$ -FAU. About 35.5 Zn^{2+} ions per unit cell are found at six distinct positions; sites I, I', a second I', II', II, and a second II. In sodalite cavities, the 11 water molecules coordinate to $\text{Zn}(\text{I}'\text{b})$ and/or $\text{Zn}(\text{II}')$ ions; each of two H_2O bonds to a $\text{Zn}(\text{IIb})$ in supercages. Two different Zn^{2+} positions near 6-oxygen ring are due to their Si-Al ordering in tetrahedral site by Si/Al ratio leading to the different kinds of 6-rings.

Key words: Zinc, Zeolite Y, Structure, Ion exchange, Dehydrated

Introduction

The effects of distribution and coordination geometry of cations in the zeolites have received a great deal of attention over the last decades for their catalytic properties. Especially, zinc (Zn) has been used in industries as hydrocarbon catalyst (Chu, 1978; Rhee et al., 1983; Gairbekov et al., 1989) for the separation of hydrogen sulfide from fossil fuels (Brooks, 1990), isomerization of basic alkane (Brownscombe, 1991), hydrosulfurization of alcohols (Ziolek, 1992), decomposition of nitromethane (Blower et al., 1993), and conversion of butane into aromatics (Kumar et al., 1996).

The extensive hydrolysis of hydrated cation and over-exchange were observed in two structural studies of Zn^{2+} -exchanged zeolites X from an aqueous solution (Bae et al., 1999; Lee et al., 2000). A single crystal of dehydrated Zn^{2+} -exchanged zeolite X was prepared by flow method using 0.05 M $\text{Zn}(\text{NO}_3)_2$ for 48 h at 353 K, followed by vacuum dehydration at 673 K and 1×10^{-5} Torr (Bae et al., 1999). In the structure of $[\text{Zn}_{46}(\text{HAlO}_4)_8\text{H}_8][\text{Si}_{100}\text{Al}_{92}\text{O}_{384}]$ -FAU (Si/Al = 1.09), over-exchange, framework dealumination, charge valance of framework,

and loss of long-range Si/Al ordering were seen; 56 Zn^{2+} ions were found per unit cell and eight nonframework aluminate ions were found at the center of sodalite cavities. Lee and Kim also studied a dehydrated Zn^{2+} -exchanged zeolite X, $[\text{Zn}_{46}(\text{ZnO})_8][\text{Si}_{100}\text{Al}_{92}\text{O}_{384}]$ -FAU (Si/Al = 1.09), by single-crystal X-ray diffraction (Lee et al., 2000). The over-exchange of $\text{Zn}(\text{OH})_2$ had occurred in sodalite cavity; 54 Zn^{2+} ions were found per unit cell, eight more than needed to balance the negative charge of the zeolite framework.

The single-crystal structure of fully dehydrated Zn^{2+} -exchanged zeolite Y (FAU, Si/Al = 1.70), dehydrated at 673 K and 1×10^{-6} Torr, were determined by single-crystal synchrotron X-ray diffraction techniques by Seo et al. (Seo et al., 2011). In the structure of $[\text{Zn}_{35.5}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]$ -FAU, about 35.5 Zn^{2+} ions per unit cell were found at an unusually large number of crystallographic distinct positions, six.

This study was done to determine the structure of partially dehydrated fully Zn^{2+} -exchanged zeolite Y and to investigate the distribution and coordination geometry of cations and water molecules in the framework.

Materials and Methods

Large clear colorless octahedral single crystals of sodium zeolite Y, $[\text{Na}_{71}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]$ -FAU (Si/Al = 1.70), with a diameter up to 0.20 mm were prepared by

Received : 2013. 2. 28 Accepted : 2013. 4. 10

*Corresponding author : Phone: +82548205454

Fax: +82548225452

E-mail: wtlim@andong.ac.kr (W.T.L.),

Phone: +82515007243

Email: seok@bnue.ac.kr (S.H.L.)

Lim et al. (Lim et al., 2007). To prepare Zn²⁺-exchanged zeolite Y (Zn-Y), 0.1 g of hydrated Na-Y was mixed with 10 mL of 0.05 M Zn(NO₃)₂ (Aldrich, 99.999%) in 15-mL conical tube and then the mixture was stirred for 4 h at 294 K (Seo et al., 2011). The ion-exchange procedure was repeated 5 times with the fresh Zn(NO₃)₂ solution. The product was dried at 323 K for 1 day. One of these, a hydrated Zn²⁺-exchanged zeolite Y crystal, was lodged in a fine Pyrex capillary and dehydrated at 673 K and 1×10^{-6} Torr for 1 h.

Synchrotron X-ray diffraction data was collected for the crystal 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 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 a scan interval of 5° with an exposure time of 1 s per frame. The basic scale file was prepared using the HKL2000 program (Otwinowski et al., 1997). The reflections were successfully indexed by the automated indexing

routine of the DENZO program (Otwinowski et al., 1997). The diffraction data were harvested by collecting 72 sets of frames with 5° scans with an exposure time of 1 s per frame. These highly redundant data sets were corrected for Lorentz and polarization effects, and a very small correction for crystal decay was applied. The space group $Fd\bar{3}m$, standard for zeolite Y, was determined by the XPREP program (Bruker-AXS, 2001). A summary of the experimental and crystallographic data is presented in Table 1.

Full-matrix least-squares refinement using SHELXL97 (Sheldrick, 1997) was done on F^2 using all data for crystal. The refinement was initiated with the atomic parameters of the framework atoms [(Si,Al), O(1), O(2), O(3), and O(4)] in fully dehydrated [Zn_{35.5}[Si₁₂₁Al₇₁O₃₈₄]-FAU (Seo et al., 2011). The initial refinement used anisotropic thermal parameters and converged to the high error indices $R_1/wR_2 = 0.37/0.81$. 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

Table 1. Summary of experimental and crystallographic data

	[Zn _{35.5} (H ₂ O) ₁₃][Si ₁₂₁ Al ₇₁ O ₃₈₄]-FAU
Crystal cross-section (mm)	0.20
Ion exchange T (K)	294
Ion exchange for Zn ²⁺ (mL)	50
Crystal color after dehydration	colorless
Data collection T (K)	294(1)
Space group, Z	$Fd\bar{3}m$, 1
X-ray source	Pohang Light Source (PLS) (Beamline 4A MXW)
Wavelength (Å)	0.77000
Unit cell constant, a (Å)	24.7670(3)
2θ range in data collection (deg)	60.52
Total reflections harvested	63,485
No. of unique reflections, m	899
No. of reflections with $F_o > 4\sigma(F_o)$	843
No. of variables, s	64
Data/parameters, m/s	14.1
Weighting parameters, a/b	0.040/114.1
Final error indices	
R_1/wR_2 ($F_o > 4\sigma(F_o)$) ^a	0.0350/0.1186
R_1/wR_2 (all intensities) ^b	0.0366/0.1240
Goodness-of-fit ^c	1.343

^a $R_1 = \sum |F_o - |F_c|| / \sum F_o$ 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 reflections for which $F_o > 4\sigma(F_o)$. ^b R_1 and wR_2 are calculated using all unique reflections measured. ^cGoodness-of-fit = $(\sum w(F_o^2 - F_c^2)^2 / (m-s))^{1/2}$, 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	^b U_{11} or U_{60}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	^c Occupancy		
												initial	varied	fixed ^d
Zn _{35.5} (H ₂ O) ₁₃ [[Si ₁₂₁ Al ₇₁ O ₃₈₄]-FAU														
Si,Al	192(i)		-520(1)	1238(1)	365(1)	182(4)	134(4)	139(4)	-24(2)	6(2)	-14(2)	192		
O(1)	96(h)		-1026(1)	0	1026(1)	398(11)	311(16)	398(11)	-107(9)	-83(14)	-106(9)	96		
O(2)	96(g)		-10(1)	-10(1)	1477(1)	336(10)	336(10)	211(13)	41(9)	41(9)	169(13)	96		
O(3)	96(g)		-256(1)	706(1)	706(1)	471(19)	319(10)	319(10)	128(13)	133(11)	133(11)	96		
O(4)	96(g)		780(1)	780(1)	3193(1)	260(9)	260(9)	296(15)	-5(8)	-5(8)	112(11)	96		
Zn(I)	16(e)	I	0	0	0	485(28)	485(28)	485(28)	54(22)	54(22)	54(22)		3.1(1)	3
Zn(I'a)	32(e)	I'	416(8)	416(8)	416(8)	406(65)	406(65)	406(65)	261(60)	261(60)	261(60)		4.5(4)	5
Zn(I'b)	32(e)	I'	592(2)	592(2)	592(2)	287(11)	287(11)	287(11)	-1(12)	-1(12)	-1(12)		10.7(4)	11
Zn(II')	32(e)	II'	2008(3)	2008(3)	2008(3)	131(29)	131(29)	131(29)	20(26)	20(26)	20(26)		7.3(12)	7.5
Zn(IIa)	32(e)	II	2176(99)	2176(99)	2176(99)	578(1191)	578(1191)	578(1191)	445(1180)	445(1180)	445(1180)		1.7(17)	2
Zn(IIb)	32(e)	II	2359(6)	2359(6)	2359(6)	408(24)	408(24)	408(24)	65(40)	65(40)	65(40)		7.2(11)	7
O(5)	96(g)		1383(13)	1670(10)	1670(10)	890(132)							15.0(11)	11
O(6)	32(e)		2886(54)	2886(54)	2886(54)	1699(1176)							2.4(10)	2
$\Sigma \text{Zn}^{2+} = 34.5(11)$												35.5		

^aPositional 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. ^bThe anisotropic temperature factor is $\exp[-2\pi^2 a^2(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{23}kl + 2U_{13}hl + 2U_{12}hk)]$. ^cOccupancy factors are given as the number of atoms or ions per unit cell. ^dThese integral values were used only in the presentation of this work, to facilitate readability.

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

Distances		Angles	
(Si,Al)-O(1)	1.6312(12)	O(1)-(Si,Al)-O(2)	112.65(12)
(Si,Al)-O(2)	1.6773(12)	O(1)-(Si,Al)-O(3)	108.81(15)
(Si,Al)-O(3)	1.6956(15)	O(1)-(Si,Al)-O(4)	112.56(14)
(Si,Al)-O(4)	1.6322(10)	O(2)-(Si,Al)-O(3)	104.98(14)
Mean (Si,Al)	1.6591	O(2)-(Si,Al)-O(4)	106.74(13)
		O(3)-(Si,Al)-O(4)	110.85(15)
Zn(I)-O(3)	2.552(3)		
Zn(I'a)-O(3)	1.949(4)	(Si,Al)-O(1)-(Si,Al)	143.25(23)
Zn(I'b)-O(3)	2.138(5)	(Si,Al)-O(2)-(Si,Al)	135.28(19)
Zn(I'b)-O(5)	1.98(3)	(Si,Al)-O(3)-(Si,Al)	128.58(19)
Zn(II')-O(2)	2.195(5)	(Si,Al)-O(4)-(Si,Al)	148.50(20)
Zn(II')-O(5)	2.07(3)		
Zn(IIa)-O(2)	2.098(7)	O(3)-Zn(I)-O(3)	82.60(12), 97.40(12)
Zn(IIb)-O(2)	2.249(9)	O(3)-Zn(I'a)-O(3)	119.55(22)
Zn(IIb)-O(6)	2.26(23)	O(3)-Zn(I'b)-O(3)	104.0(3)
		O(3)-Zn(I'b)-O(5)	97.7(6), 144.4(10)
		O(5)-Zn(I'b)-O(5)	51.1(17)
		O(2)-Zn(II')-O(2)	110.9(3)
		O(2)-Zn(II')-O(5)	87.9(9), 116.89(5)
		O(2)-Zn(IIa)-O(2)	119.8(7)
		O(2)-Zn(IIb)-O(2)	107.1(6)
		O(2)-Zn(IIb)-O(6)	111.7(6)

^aThe numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

are given in Table 2, and selected interatomic distances and angles are given in Table 3.

Results and Discussion

The framework structure of zeolite Y (FAU) is characterized by the double 6-ring (D6R, hexagonal prism), sodalite cavity (a cubooctahedron), and supercage (see Fig. 1). Each unit cell has 8 supercage, 8 sodalite cavities, 16 D6Rs, 16 12-rings, and 32 S6Rs (single 6-rings). 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 Fig. 1. The maximum occupancies at the cation sites I, I', II', II, and III are 16, 32, 32, 32, and 48, respectively. Site III' in zeolite Y studied using space group $Fd\bar{3}m$ is a 192-fold position. Further description is available (Breck, 1974; Van Bakkum et al., 2001).

In the structure of |Zn_{35.5}(H₂O)₁₃[[Si₁₂₁Al₇₁O₃₈₄]-FAU, about 35.5 Zn²⁺ ions are found at six distinct positions. Three Zn²⁺ ions per unit cell at Zn(I) occupy site I (at the center of the D6Rs, see Fig. 2). Each coordinates to six O(3) framework oxygens of its D6R at 2.552(3) Å much longer than the sum of the corresponding conventional

Acknowledgement

We gratefully acknowledge the support of beamline 4A MXW at the Pohang Light Source, Korea, for their diffraction and computing facilities. The study was supported by the Education Research Institute, Busan National University of Education in 2013.

References

- Bae, D., S. Zhen, K. Seff. 1999. Structure of dehydrated Zn²⁺-exchanged zeolite X. Overexchange, framework dealumination and reorganization, stoichiometric retention of monomeric tetrahedral aluminate. *J. Phys. Chem. B.* 103: 5631-5636.
- Blower, C.J., T.D. Smith. 1993. The gas-phase decomposition of nitromethane over metal ion-exchanged sodium Y zeolite and sodium X zeolite. *Zeolites.* 13: 394-398.
- Brooks, C. 1990. Desulfurization over metal zeolites. *Sep. Sci. Technol.* 25: 1817-1828.
- Breck, D.W. 1974. Zeolite molecular sieves. John Wiley & Sons, New York. p. 93.
- Brownscombe, T.F. 1991. Basic alkaline earth metal-zeolite compositions. US Patent 5053372.
- Bruker-AXS (ver. 6.12), XPREP. 2001. Program for the automatic space group determination. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chu, P. 1978. Aromatization of ethane. US Patent 4120910.
- Gairbekov, T.M., M.I. Takaeva, A.K. Manovyan, I.L. Aleksandrova. 1989. Aromatization of gasoline on zinc-modified zeolite-containing catalysts. *Chem. Technol. Fuels Oils.* 25: 473-475.
- Kumar, N., L.E. Lindfors, R. Byggningsbacka. 1996. Synthesis and characterization of H-ZSM-22, Zn-H-ZSM-22 and Ga-H-ZSM-22 zeolite catalysts and their catalytic activity in the aromatization of n-butane. *Appl. Catal. A.* 139: 189-199.
- Lee, S.H., Y. Kim. 2000. Two crystal structures of dehydrated Zn²⁺-exchanged zeolite X: Zn₄₆Si₁₀₀Al₉₂O₃₈₄·8ZnO and Zn₁₃Tl₆₆Si₁₀₀Al₉₂O₃₈₄·2ZnO. *Bull. Korean Chem. Soc.* 21: 180-186.
- Lim, W.T., S.M. Seo, G.H. Kim, H.S. Lee, K. Seff. 2007. Six single-crystal structures showing the dehydration, deamination, dealumination, and decomposition of NH₄⁺-exchanged zeolite Y (FAU) with increasing evacuation temperature. Identification of a Lewis acid site. *J. Phys. Chem. C.* 111: 18294-18306.
- Loewenstein, W. 1954. The distribution of aluminum in the tetrahedral of silicates and aluminates. *Am. Mineral.* 39: 92-96.
- Otwinowski, Z., W. Minor. 1997. Processing of X-ray diffraction data collected in oscillation mode. *Methods Enzymol.* 276: 307-326.
- Peterson, B.K. 1999. A simulated annealing method for determining atomic distributions from NMR data: silicon and aluminum in faujasite. *J. Phys. Chem. B.* 103: 3145-3150.
- Rhee, K.H., F.R. Brown, D.H. Finseth, J.M. Stencel. 1983. Infrared studies on the acidity of metal impregnated ZSM-5. *Zeolites.* 3:344-347.
- Seo, S.M., H.S. Kim, M. Park, W.T. Lim. 2011. Synthesis and structural refinement of fully dehydrated fully Zn²⁺-exchanged zeolite Y (FAU), [Zn_{35.5}][Si₁₂₁Al₇₁O₃₈₄]-FAU. *J. Porous Mater.* 18:47-56.
- Sheldrick, G.M. 1997. SHELXL97, Program for the refinement of crystal structure. University of Gottingen, Germany.
- Van Bekkum, H., E.M. Flanigen, P.A. Jacobs, J.C. Jansen. 2001. Introduction to zeolite science and practice. Elsevier. p. 44.
- Ziółek, M., K. Nowińska, K. Leckowska. 1992. Reactions of alcohols with hydrogen sulfide over zeolites: Part V. The role of Brønsted acid sites in thiols formation-A comparative study of zeolites and heteropoly acids. *Zeolites.* 12: 710-715.