

Characterization of Li⁺-ion Exchanged Zeolite Y using Organic Solvents

Hu Sik Kim, Seok Hee Lee¹, Kyun Hye Park², Yong Hyun Park², Jun Woo Park²,
Ji Hyun Hwang², Jong Sam Park³, Sik Young Choi*, and Woo Taik Lim**

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

¹*Department of Science Education, Busan National University of Education, Busan 611-736, Korea*

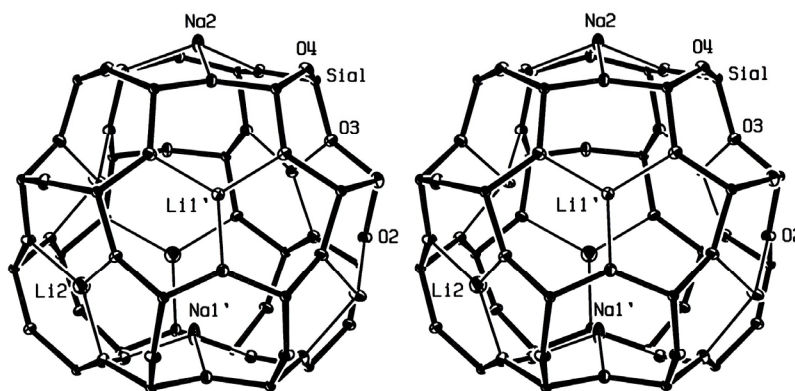
²*HanKuk Academy of Foreign Studies, Yongin 449-854, Korea*

³*Department of Radiologic Technology, Daegu Health College, Daegu 702-722, Korea*

(Received: May 20 2015, Revised: June 25 2015, Accepted: June 25 2015)

To investigate the tendency of Li⁺ exchange from polar organic solvents, Li⁺-ion exchange into zeolite Y (Si/Al = 1.56) was attempted by undried methanol (crystal 1) and formamide (crystal 2) solvent. Two single crystals of Na-Y were treated with 0.1 M LiNO₃ in each of the two solvents at 323 K, followed by vacuum dehydration at 723 K. Their structures were determined by single-crystal synchrotron X-ray diffraction techniques in the cubic space group Fd3m, at 100(1) K. In both structures, Li⁺ for Na⁺ ions filled preferentially sites I' and II. The remaining Na⁺ ions occupied sites I', II, and III' in both structures, in addition to above sites, and Na⁺ ions occupied site I in crystal 2. While the 68 % exchange of Li⁺ for Na⁺ was achieved from undried methanol, only 40 % exchange was observed from undried formamide, indicating that the undried methanol was more effective than undried formamide as solvent for Li⁺ exchange under the conditions employed.

Key words: Lithium, Zeolite Y, Ion exchange, Methanol, Formamide



A stereoview of representative sodalite units in crystals 1 and 2.

*Corresponding author : Phone: +82548205457, Fax: +82548225452, E-mail: sychoi@andong.ac.kr

**Co-corresponding author : Phone: +82548205454, Fax: +82548225452, E-mail: wtlm@andong.ac.kr

§Acknowledgement: The authors are grateful to the staff at beamline 2D SMC of the Pohang Light Source, Korea, for their assistance during data collection. This work was supported by a grant from 2012 Academic research Fund of Andong National University.

Introduction

Ion exchange into zeolite plays an important role in determining the characteristic properties of zeolite such as gas adsorption, separation, and catalysis (Herden *et al.*, 1982; Zhu *et al.*, 2007). Li⁺-exchanged zeolites are used as effective and selective adsorbents for N₂ adsorption in N₂/O₂ separation processes (Feuerstein and Lobo, 1998; Feuerstein *et al.*, 2000; Freude *et al.*, 2013). The adsorption capacity and selectivity for N₂ of Li⁺-exchanged zeolites are strongly correlated with the amount of charge-balancing Li⁺ ion and the distribution in zeolite (Feuerstein *et al.*, 1998). For improving of the adsorption properties as adsorbents for N₂ adsorption, it is necessary to achieve the largely Li⁺ containing zeolites and to have knowledge on the chemical environment of the cation in zeolites (Zhu *et al.*, 2007).

Generally, cation exchange is performed by direct exchange of cations within the zeolite with other cations from aqueous solution (Canfield *et al.*, 2010; Kim *et al.*, 2013a). However, the results of an aqueous ion exchange are not always simple. Sometimes, a number of difficulties problems such as incomplete exchange, partial exchange of H⁺, salt imbibition, and crystal damage are encountered (Bae and Seff, 1999; Bae and Seff, 2000; Ho *et al.*, 1995; Lee *et al.*, 2005; Ronay and Seff, 1985; Ronay and Seff, 1993; Seo *et al.*, 2012a; Seo *et al.*, 2012b).

In the case of Li⁺ ion exchange, the complete exchange was readily achieved for LSX (Si/Al = 1.0) from conventional aqueous solution at room temperature (Feuerstein and Lobo, 1998; Plevart *et al.*, 1997). However, often the problem of incomplete exchange was observed due to the strong hydration sphere and high chemical potential of Li⁺ ion when Si/Al ratio of zeolite was higher than 1.0 (Feuerstein and Lobo, 1998; Forano *et al.*, 1989; Kim *et al.*, 2012a; Kim *et al.*, 2012b; Shepelev *et al.*, 1990). In order to avoid this problem, Li⁺ exchange using NH₄⁺ form zeolite (Si/Al = 1.23, 1.25 and 2.36) was attempted by several scientists: perhaps the more loosely bond NH₄⁺ ions would be more easily exchanged by Li⁺ than Na⁺ ion (Feuerstein and Lobo, 1998; Forano *et al.*, 1989). However, both Na⁺ and H⁺ (after deamination) were found in the products (Forano *et al.*, 1989).

In our previous studies, Li⁺ ion exchange into zeolites X (Si/Al = 1.09) (Kim *et al.*, 2012b) and Y (Si/Al = 1.56) (Kim *et al.*, 2012a) was performed at 333 K to increase the extent of Li⁺ ion: perhaps the greater mobility of all cations at the higher ion-exchange temperature would be more easily exchanged by Li⁺ ion. However, despite the high temperature employed, the complete Li⁺ exchange did not occur in any zeolite composition: the degrees of Li⁺ ion are only 95 and 72 % for zeolite X (Kim *et al.*, 2012b)

and Y (Kim *et al.*, 2012a), respectively.

Recently, other method of ion exchange using organic solvents such as undried methanol (water concentration 0.02 M) and undried formamide (water concentration 0.06 M) was studied to prepare fully exchanged Li-X (Si/Al = 1.09) and Li-Y (Si/Al = 1.56) at 333 and 393 K, for methanol and formamide, respectively (Kim *et al.*, 2012a; Kim *et al.*, 2013a; Kim *et al.*, 2013b). The temperature was chosen at near their boiling points to maximize the extent of ion exchange.

Remarkably, in ion exchange using undried methanol solution (water concentration 0.02 M), complete and high level (up to 96 %) exchange of Li⁺ ion into zeolites X (Si/Al = 1.09) (Kim *et al.*, 2013a) and Y (Si/Al = 1.56) (Kim *et al.*, 2012a), respectively, were achieved. On the other hand, only 73 and 56 % exchange for zeolites X and Y were observed in Li⁺ exchange using undried formamide (water concentration 0.06 M) (Kim *et al.*, 2013b). These results show that undried methanol (water concentration 0.02 M) is particularly convenient and efficient as solvent for the ion exchange of Li⁺.

In order to better understand the adsorption properties, detailed information of Li⁺ ion in Li⁺-exchanged zeolites is desired. Accordingly, a large number of studies have been performed by various methods such as powder-neutron diffraction, single-crystal synchrotron X-ray diffraction, and solid-state MAS NMR spectroscopy (Feuerstein *et al.*, 2000; Forano *et al.*, 1989; Kim *et al.*, 2012a; Kim *et al.*, 2012b; Kim *et al.*, 2013a; Kim *et al.*, 2013b; Plevart *et al.*, 1997; Shepelev *et al.*, 1990; Wozniak *et al.*, 2008). According to the previous studies, Li⁺ ions preferentially occupy site I' and II, and the remaining Li⁺ ions were located at sites III or III' in the supercage (Feuerstein and Lobo, 1998; Feuerstein *et al.*, 2000; Forano *et al.*, 1989; Kim *et al.*, 2012a; Kim *et al.*, 2012b; Kim *et al.*, 2013a; Kim *et al.*, 2013b; Plevart *et al.*, 1997; Shepelev *et al.*, 1990; Wozniak *et al.*, 2008). Sometimes, remaining Li⁺ ions in supercage for charge balance of the zeolite framework were not found due to the high mobility and low occupancy of Li⁺ ion at certain sites (Feuerstein and Lobo, 1998; Forano *et al.*, 1989; Kim *et al.*, 2012a; Kim *et al.*, 2012b; Kim *et al.*, 2013b). In addition, large distortions of the zeolite framework were observed in dehydrated zeolites (Feuerstein and Lobo, 1998; Forano *et al.*, 1989; Kim *et al.*, 2012a; Kim *et al.*, 2012b; Kim *et al.*, 2013b; Shepelev *et al.*, 1990).

In present study, Li⁺-exchange into zeolite Y (Si/Al = 1.56) was performed from two different solvents, undried methanol and formamide, at an elevated temperature, 323 K, to study the Li⁺ ion exchange tendency on properties of solvents under same condition (ion exchange temperature and water concentration in solvent) and to investigate the

distribution of cations in zeolite framework. Methanol and formamide were selected as solvent for Li⁺ ion exchange because of different dielectric constant. Their structures were determined by single-crystal synchrotron X-ray diffraction techniques.

Materials and Methods

Ion exchange and dehydration Large single crystals of zeolite Y (FAU), stoichiometry Na₇₅Si₁₁₇Al₁₇₅O₃₈₄, were synthesized in this laboratory (Lim *et al.*, 2010). Each of two crystals, colorless octahedral about 0.30 mm in cross-section, was lodged in its own fine Pyrex capillary. Two ion-exchange solutions 0.1 M LiNO₃ (Aldrich, 99.99%, Ca 4.82 ppm, Na 1.91 ppm, Sc 0.48 ppm, Mg 0.42 ppm, Ba 0.41 ppm, Zr 0.31 ppm, Cu 0.21 ppm, Al 0.07 ppm, La 0.05 ppm, Sr 0.04 ppm) were prepared as follows.

Solutions 1 and 2 were prepared by dissolving LiNO₃ in undried methanol (Baker Analyzed HPLC Solvent, assay 100%) and in undried formamide (Aldrich, assay 99.5%), respectively. Although a previously unopened bottle of

solvents were used, the water content of solution could have increased significantly during its preparation by sorption of moisture from the LiNO₃(s) and from the atmosphere. The compositions of the solvents in two solutions are given in Table 1.

All two crystals were Li⁺-exchanged in their capillaries by dynamic method at 323 K. Each of the resulting clear colorless single crystal was slowly heated under dynamic vacuum to 723 K and dehydrated at 1×10^{-6} Torr 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. While still under vacuum, each crystal was allowed to cool to room temperature and was sealed in its capillary by torch.

Single-crystal X-ray Diffraction Synchrotron X-ray diffraction data for the two crystals were collected at

Table 1. Summary of experimental and crystallographic data.

	Crystal 1	Crystal 2
Crystal cross-section (mm)	0.31	0.33
Solvent	CH ₃ OH	CHONH ₂
[H ₂ O] ^a	0.06	0.06
Ion exchange t(h),T (K)	24, 323	24, 323
Crystal color	colorless	colorless
Dehydration T (K)	723	723
Data collection T (K)	100(1)	100(1)
Space Group, Z	<i>Fd</i> $\bar{3}$ <i>m</i> , 1	<i>Fd</i> $\bar{3}$ <i>m</i> , 1
X-ray source	Pohang Light Source, Beamline 2D SMC	
Wavelength (Å)	0.63000	0.67000
Unit cell constant, <i>a</i> (Å)	24.6757(2)	24.7773(2)
2 θ range in data collection (deg)	72.17	65.60
No. of unique reflections, <i>m</i>	1911	1276
No. of reflections with $F_o > 4\sigma(F_o)$	1564	1193
No. of variables, <i>s</i>	55	56
Data/parameter ratio, <i>m/s</i>	34.7	22.8
Weighting parameters, <i>a/b</i>	0.095/80.5	0.063/123.0
Final error indices		
R_1/wR_2 ($F_o > 4\sigma(F_o)$) ^b	0.048/0.171	0.045/0.146
R_1/wR_2 (all intensities) ^c	0.057/0.203	0.047/0.152
Goodness-of-fit ^d	1.11	1.21

^aWater concentration (mol/L) in the exchange solution. ^b $R_1 = \sum |F_o - |F_c|| / \sum F_o$ and $R_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$; R_1 and R_2 are calculated using only the 1564 and 1193 reflections for which $F_o > 4\sigma(F_o)$. ^c R_1 and R_2 are calculated using all unique reflections measured. ^dGoodness-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.

Table 2. 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}	γ . U_{12}	^c Occupancy		
												initial	varied	fixed
[Li₅₁Na₂₄][Si₁₁₇Al₇₅O₃₈₄]-FAU, crystal 1														
Si,Al	192(i)		-509(1)	1240(1)	370(1)	97(2)	84(2)	84(2)	-12(1)	-2(1)	-2(1)	192		
O(1)	96(h)		-1015(1)	0	1015(1)	177(5)	177(7)	177(5)	-47(4)	-11(6)	-47(4)	96		
O(2)	96(g)		-2(1)	2(1)	1501(1)	157(4)	157(4)	135(6)	10(4)	10(4)	52(5)	96		
O(3)	96(g)		-232(1)	721(1)	721(1)	138(7)	133(4)	133(4)	10(5)	20(4)	20(4)	96		
O(4)	96(g)		-723(1)	777(1)	1723(1)	155(7)	146(4)	146(4)	-35(5)	20(4)	-20(4)	96		
Li(I')	32(e)	I'	445(2)	455(2)	455(2)	184(15)	184(15)	184(15)	36(20)	36(20)	36(20)		30.3(3)	30
Na(I')	32(e)	I'	672(8)	672(8)	672(8)	101(71)	101(71)	101(71)	30(58)	30(58)	30(58)		1.7(3)	2
Li(II)	32(e)	II	2224(4)	2224(4)	2224(2)	202(23)	202(23)	202(23)	3(31)	3(31)	3(31)		21.1(4)	21
Na(II)	32(e)	II	2400(15)	2400(15)	2400(15)	252(21)	252(21)	252(21)	130(21)	130(21)	130(21)		10.8(4)	11
Na(III')	192(i)	III'	440(13)	811(12)	4177(12)	1064(134)							15.9(12)	11
[Li₃₀Na₄₅][Si₁₁₇Al₇₅O₃₈₄]-FAU, crystal 2														
Si,Al	192(i)		-522(1)	1239(1)	365(1)	130(3)	114(3)	110(3)	-17(2)	-1(2)	-11(2)	192		
O(1)	96(h)		-1038(1)	0	1038(1)	201(6)	229(10)	201(6)	-47(5)	-5(8)	-47(5)	96		
O(2)	96(g)		-16(1)	-16(1)	1471(1)	193(6)	193(6)	204(10)	7(6)	7(6)	58(8)	96		
O(3)	96(g)		-263(1)	713(1)	713(1)	232(10)	182(6)	182(6)	15(7)	-5(6)	-5(6)	96		
O(4)	96(g)		-704(1)	767(1)	1733(1)	210(11)	217(7)	217(7)	-79(8)	22(6)	-22(6)	96		
Na(I)	16(c)	I	0	0	0	562(181)							1.6(3)	1.5
Li(I')	32(e)	I'	426(5)	426(5)	426(5)	187(34)	187(34)	187(34)	5(33)	5(33)	5(33)		21.7(4)	22
Na(I')	32(e)	I'	569(5)	569(5)	569(5)	339(46)	339(46)	339(46)	176(48)	176(48)	176(48)		6.5(4)	7
Li(II)	32(e)	II	2169(16)	2169(16)	2169(16)	369(110)							7.9(4)	8
Na(II)	32(e)	II	2355(1)	2355(1)	2355(1)	238(10)	238(10)	238(10)	89(9)	89(9)	89(9)		24.1(4)	24
Na(III')	192(i)	III'	1659(13)	1998(15)	4133(14)	850(134)							12.2(12)	12.5

^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.

100(1) K using an ADSC Quantum 210 detector at Beamline 2D SMC at The Pohang Light Source.

The ADSC Q210 ADX program (Arvai and Nielsen, 1983) was used for data collection (detector distance is 63 mm, omega scan: $\Delta\omega = 5^\circ$, exposure time 1 sec per frame) and HKL 3000sm was used for cell refinement, reduction, and absorption correction (Otwinowski and Minor, 1997). The space group $Fd\bar{3}m$, conventional for zeolite Y, was determined by the program XPREP (Brucker-AXS, 2001). A summary of the experimental and crystallographic data are presented in Table 1.

Structure Determination Full-matrix least-squares refinements (SHELXL97) (Sheldrick, 1997) were done on F_o^2 using all data for two crystals. Each refinement was initiated with the atomic parameters of the framework atoms [(Si,Al), O(1), O(2), O(3), and O(4)] in dehydrated $[K_{71}][Si_{121}Al_{71}O_{384}]-FAU$ (Lim *et al.*, 2006). Each initial refinement used anisotropic thermal parameters and converged to the high error indices. The further steps of structure determination and refinement as new atomic

positions were found on successive difference Fourier electron density functions. The final cycles of refinement were done with anisotropic temperature factors for all positions except those that were not stable in anisotropic refinement: Na(III') in crystal 1, Na(I), Li(II), Na(III') in crystal 2. The final error indices R_1 and wR_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 and were not otherwise within bonding distance of any other position. All shifts in the final cycles of refinements were less than 0.1% of their corresponding estimated standard deviations (esds). The final structural parameters are presented in Table 2, and selected interatomic distances and angles are given in Table 3.

Fixed weights were used initially; the final weights were assigned using the formula $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$, with a and b as refined parameters (see Table 1). Atomic scattering factors for Li^+ , Na^+ , O^- , and $(Si,Al)^{1.82+}$ were used (Doyle and

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

	Crystal 1	Crystal 2
(Si,Al)-O(1)	1.6360(7)	1.6436(9)
(Si,Al)-O(2)	1.6741(8)	1.6699(10)
(Si,Al)-O(3)	1.6863(8)	1.6895(11)
(Si,Al)-O(4)	1.6383(7)	1.6427(8)
Mean (Si,Al)	1.6587	1.6614
Na(I)-O(3)	-	2.583(2)
Li(I')-O(3)	1.924(2)	1.981(3)
Na(I'')-O(3)	2.227(16)	2.121(8)
Li(II)-O(2)	2.022(3)	2.114(2)
Na(II)-O(2)	2.238(5)	2.262(3)
Na(III')-O(1)	2.56(3)	2.47(3)
Na(III'')-O(4)	2.49(3)	2.40(4)
O(1)-(Si,Al)-O(2)	113.15(7)	112.25(8)
O(1)-(Si,Al)-O(3)	109.62(8)	110.10(9)
O(1)-(Si,Al)-O(4)	110.00(8)	110.15(10)
O(2)-(Si,Al)-O(3)	105.46(8)	105.58(10)
O(2)-(Si,Al)-O(4)	107.11(8)	107.05(11)
O(3)-(Si,Al)-O(4)	111.43(8)	111.62(11)
(Si,Al)-O(1)-(Si,Al)	145.38(13)	140.65(13)
(Si,Al)-O(2)-(Si,Al)	131.82(11)	136.75(15)
(Si,Al)-O(3)-(Si,Al)	127.67(10)	130.10(14)
(Si,Al)-O(4)-(Si,Al)	141.53(12)	145.98(15)
O(3)-Na(I)-O(3)	-	82.9(1), 97.10(1)
O(3)-Li(I')-O(3)	118.7(1)	119.3(2)
O(3)-Na(I'')-O(3)	96.1(9)	107.5(6)
O(2)-Li(II)-O(2)	118.6(2)	120.0(1)
O(2)-Na(II)-O(2)	102.0(3)	108.1(1)
O(1)-Na(III')-O(4)	64.1(8)	67.2(9)

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

Turner, 1968; Ibers and Hamilton, 1974a). The function describing (Si,Al)^{1.82+} is a weighted mean of the Si⁴⁺, Si⁰, Al³⁺, and Al⁰ functions (Si/Al = 1.56). All scattering factors were modified to account for anomalous dispersion (Cromer, 1965; Ibers and Hamilton, 1974b). Other crystallographic details are given in Table 1.

Results and Discussion

The framework structure of zeolite Y (FAU) is characterized 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 6-rings), 16 12-rings, and 32 single 6-rings

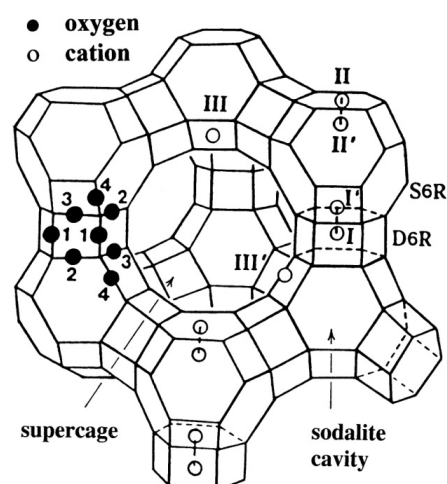


Fig. 1. Stylized drawing of the framework structures of zeolite Y. Near the center of each line segment is an oxygen atom. The nonequivalent oxygen atoms are indicated by the numbers 1 to 4. There is no evidence in this work of any ordering of the silicon and aluminum atoms among the tetrahedral positions, although it is expected that Loewenstein's rule (Loewenstein, 1954) would be obeyed. Extraframework cation positions are labeled with Roman numerals.

(S6Rs).

The exchangeable cations, which balance the negative charges of the zeolite Y framework, usually occupy some or all of the sites shown with Roman numerals in Fig. 1 (Loewenstein, 1954). The maximum occupancies at the cation sites I, I', II, II', III, and III' in zeolite Y 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 (Break, 1974; Van Bekkum *et al.*, 2001).

Crystal Structure of [Li₅₁Na₂₄][Si₁₁₇Al₇₅O₃₈₄]-FAU (Crystal 1). About 51 Li⁺ ions per unit cell are found at two different crystallographic sites. The 30 nearly fill site I' and 21 occupy site II (see Table 2). Residual 24 Na⁺ ions are found at three different crystallographic sites I', II, and III' with occupancies of 2, 11, and 11, respectively (see Table 2). The degree of Li⁺ ion exchange is taken to be 51/75, about 68%, in this structure.

The Li⁺ ions at site I' (opposite D6Rs in the sodalite cavity) are coordinated by the three O(3) oxygen atoms of the D6R at 1.924(2) Å, which is very close to the sum of the conventional ionic radii of Li⁺ and O²⁻, 1.91 Å (see Table 3) (Lide, 1996/1997a). It indicates that Li⁺ ion coordinate strongly to their three O(3) oxygens in the 6-rings (see Figs. 2(a) and (b)). Each Li⁺ ion lies relatively near inside the sodalite cavity 0.22 Å from its three O(3) plane (see Fig. 3 and Table 4). The O(3)-Li(I')-O(3) bond angle, 118.7(1)°, is near trigonal planar (see Table 3).

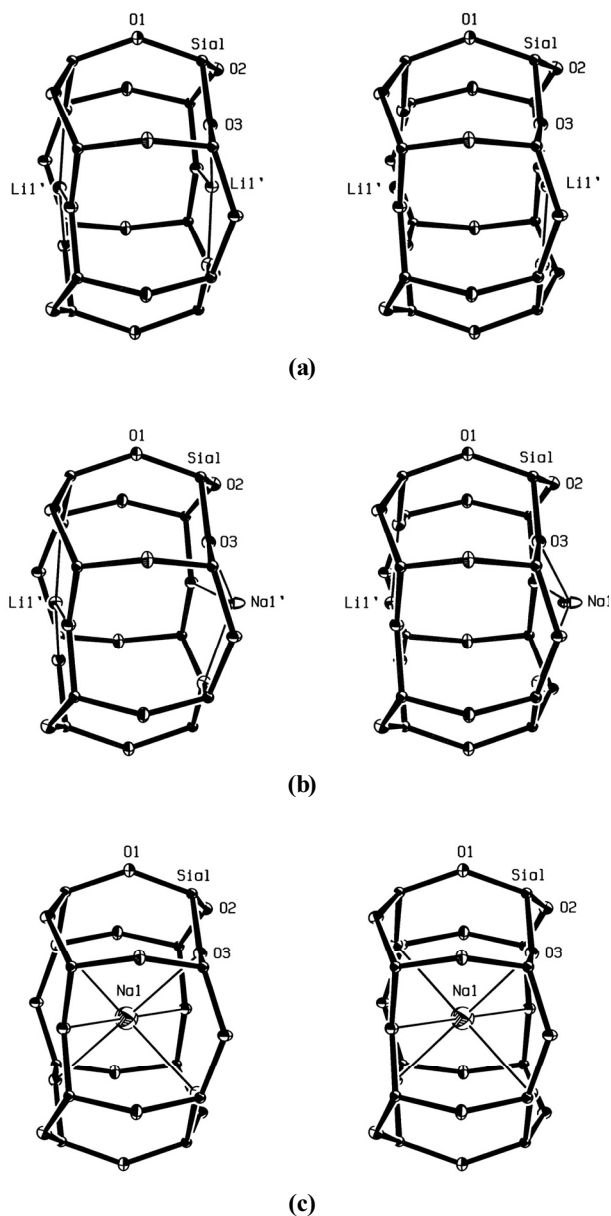


Fig. 2. Stereoviews representative D6Rs in crystals 1 and 2. Of the 16 D6Rs per unit cell in crystal 1, the arrangements of Li^+ and Na^+ ions are possible as shown in (a) and (b). For crystal 2, Li^+ and Na^+ ions are occupied as shown in (a), (b), and (c). The zeolite Y framework is drawn with heavy bonds. The coordination of Li^+ ions to oxygens of the zeolite framework is indicated by light bonds. Ellipsoids of 25% probability are shown.

Each Li^+ ion at Li(II) (opposite S6Rs in the supercage) extends inside the supercage, 0.24 Å, from the plane of their O(2) framework oxygen atoms (see Fig. 4 and Table 4). The O(2)-Li(II) distance is 2.022(3) Å, which are in close agreement with the sum of the ionic radii, 1.91 Å (see Table 3) (Lide, 1996/1997a).

Residual Na^+ ions at sites I' and II are shown Figs. 2 and 3, respectively. Each Na^+ ion at Na(I') and Na(II) extends inside the sodalite cavity and supercage 1.14 and

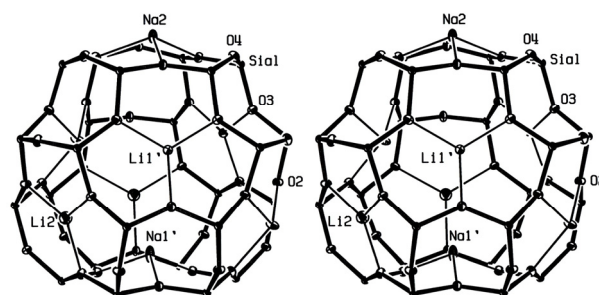


Fig. 3. A stereoview of representative sodalite units in crystals 1 and 2. See the caption to Fig. 2 for other details.

Table 4. Displacements of atoms (Å) from 6-ring planes.

positions	sites	crystal 1		crystal 2	
		at O(3) ^a	at O(2) ^b	at O(3) ^a	at O(2) ^b
Na(I)	I			-1.67	
Li(I')	I'	0.22		0.17	
Na(I')	I'	1.14		0.78	
Li(II)	II		0.24		0.02
Na(II)	II		0.97		0.80

^aA positive displacement indicates that the cation lies in a sodalite cavity; a negative deviation indicates that cation lies in a D6R. (Na(I) lies at the center of D6Rs). ^bA positive displacement indicates that the cation lies in a supercage.

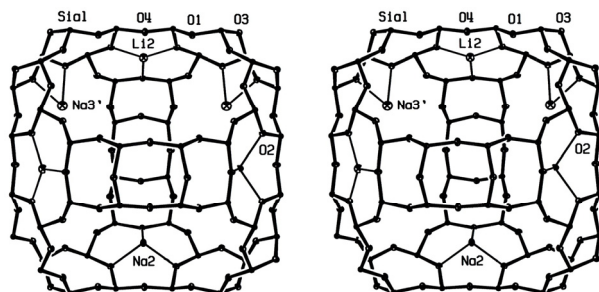


Fig. 4. A stereoview of representative supercages in crystals 1 and 2. See the caption to Fig. 2 for other details.

0.97 Å from its three O(3) and O(2) plane, respectively (see Table 4). The Na(I')-O(3) and Na(II)-O(2) bond lengths are 2.227(16) and 2.238(5) Å, respectively, which are in close agreement with the sum of the ionic radii of Na^+ and O^{2-} , 2.29 Å (Weast, 1989/1990).

The remaining 11 Na^+ ions are located at site III' in the supercage on close to the side of the 12-rings near an O(1)-Al-O(4) sequence (see Fig. 4). These Na^+ ions bind only to two oxygen atoms, O(1) and O(4) at 2.56(3) and 2.49(3) Å, respectively (see Table 3). These distances are somewhat longer than the sum of the Na^+ and O^{2-} radii (Weast, 1989/1990). However, such long distances have been seen in fully dehydrated Na-X (Olson, 1995; Zhu and Seff, 1999). Local distortions may allow the actual

Table 5. Number of Li⁺ and Na⁺ ions per unit cell at their sites.

Crystal no.	Site I	Site I'		Site II		Site III'		Total Cations		% IE ^a
	Na ⁺	Li ⁺	Na ⁺	Li ⁺	Na ⁺	Na ⁺	Total Li ⁺	Total Na ⁺		
1		30	2	21	11	11	51	24	68	
2	1.5	22	7	8	24	12.5	30	45	40	

^aPercent ion exchange of Li⁺ ion.

distances to be less.

Crystal Structure of [Li₃₀Na₄₅][Si₁₁₇Al₇₅O₃₈₄]-FAU (Crystal 2). In this structure, 30 Li⁺ ions per unit cell occupy two crystallographic sites and 45 Na⁺ ions occupy four different sites (see Table 2). The degree of Li⁺ ion exchange in this crystal is taken to be 30/75, about 40%.

Unlike crystal 1, the 1.5 Na⁺ ions per unit cell at Na(I) occupy site I (at the centers of the D6Rs, see Fig. 2(c)). Each coordinates to six O(3) framework oxygens of its D6R at distance of 2.583(2) Å, which is somewhat longer than the sum of the corresponding conventional radii of Na⁺ and O²⁻, 2.29 Å (Weast, 1989/1990), indicating a reasonably good fit (see Table 3). Because 14.5 D6R's are empty and only one and a half contain a Na⁺ ion at site I, the O(3) position can be expected to have refined to describe the predominant geometry, that of the empty D6R's. The true Na(I)-O(3) distance is substantially less than 2.58 Å as the Na⁺ ions pull their coordinating oxygens closer. Accordingly, these longer distances have consistently been in the structures of partially Li⁺-exchanged zeolite Y (Kim *et al.*, 2013b). The O(3)-Na(I)-O(3) bond angles are 82.9(1)° and 97.10(1)°, nearly perfectly octahedral (see Table 3). No Li⁺ ions are found at site I because Li⁺ ion is too small to be located in site I.

The 22 Li⁺ and 7 Na⁺ ions at Li(I') and Na(I'), respectively, are found at site I' (see Figs. 2(a) and 2(b)). To avoid the very short distance between site I and the two occupied I' site where intercationic electrostatic repulsion should be severe, the two I' sites of a D6R should not be occupied if its site I is (Kim *et al.*, 2012a; Kim *et al.*, 2013b). Accordingly, there are only (16-1.5) × 2 = 29 site I' positions available for cations which are in agreeable with the number found at site I' (see Table 2). Each Li⁺ and Na⁺ ion extend inside the sodalite cavity, 0.17 and 0.78 Å, respectively, from the plane of three O(3) framework oxygens (see Table 4). The distances of Li(I') and Na(I') to the framework oxygens at O(3) are 1.981(3) and 2.114(2) Å, respectively, which are same as in crystal 1 (see Table 3).

About 8 Li⁺ and 24 Na⁺ ions per unit cell at Li(II) and Na(II), respectively, are located at site II position, complete the filling of the 6-rings. While Li(II) extends 0.02 Å into the supercage from its O(2) plane, Na(II) extends 0.80 Å, which is 0.78 Å much further than Li(II) (see

Fig. 4 and Table 4). Because, Li⁺ ion is smaller than Na⁺ ion, it must pull the oxygen atoms of the 6-rings that it occupies in toward the 6-ring centers. Correspondingly, the O(2)-Li(II)-O(2) and O(2)-Na(II)-O(2) angles are 120.0(1)° and 108.1(1)°, respectively (see Table 3).

As in crystal 1, the remaining Na⁺ ions are located at site III' in the supercages in the vicinity of 12-rings. Their placements may be seen in Fig. 4. The geometry about them is reasonable (see Tables 2 and 3), much like that described for crystal 1.

In both structures, Li⁺ ion are found at two different locations: the majority of the Li⁺ ions are located at site I' and remaining Li⁺ ions occupy site II (see Table 5). Similarly to our previous work (Kim *et al.*, 2012a; Kim *et al.*, 2012b; Kim *et al.*, 2013b), Li⁺ ion prefers to fill at site I' first and then site II. The number of Li⁺ ions at sites I' and II increases with increasing Li⁺ exchange level (see Table 5). Residual Na⁺ ions occupy the sites I', II, and III' in both structures, in addition to above sites, Na⁺ ions occupy site I with decreasing Li⁺ exchange level in crystal 2. Unlike previous works, all cations are found per unit cell to balance the negative charge of the zeolite framework in this work.

According to the previous reports (Plevart *et al.*, 1997; Kim *et al.*, 2012a; Kim *et al.*, 2012b; Kim *et al.*, 2013b; Shepelev *et al.*, 1990), the location of Li⁺ ion at the center of the 6-rings induces the large distortions of the zeolite framework occurring upon dehydration due to the presence strong interactions between Li⁺ ions and oxygen framework atoms as it is reflected in the T-O-T bond angles.

In agreement with previous reports (Plevart *et al.*, 1997; Kim *et al.*, 2012a; Kim *et al.*, 2012b; Kim *et al.*, 2013b), the T-O-T angles at O(2) and O(3), 131.82(11)°/127.67(10)° and 136.75(15)°/130.10(10)° for crystals 1 and 2, respectively, are very narrow compared to those as seen in fully dehydrated Na-X (Olson, 1995; Zhu and Seff, 1999). This result indicates that zeolite framework is experienced some level of strain due to strongly interaction of Li⁺ ion. The T-O-T angles at O(2) and O(3) in crystal 1 are smaller than crystal 2, it can be attributed to the higher level of Li⁺ exchange. In addition, significant decrease the unit cell constant of the zeolite framework is also seen in crystal 1.

Table 5 shows the degree of Li^+ ion exchange into zeolite Y ($\text{Si}/\text{Al} = 1.56$) from undried methanol (crystal 1) and undried formamide (crystal 2) solvent at given ion-exchange temperature and content of water. While approximately 68 % exchange is achieved from undried methanol, only 40 % exchange is observed from undried formamide. This are attributed to the difference of the properties of the ion-exchange solution between methanol and formamide: the dielectric constants of methanol and formamide are 33.0 and 111.0 ϵ_r , respectively, at 293.2 K (Lide, 1996/1997b). As the dielectric constant of solvent increase, the degree of Li^+ ion exchange decreases.

According to the previous reports (Canfield *et al.*, 2007; Kim *et al.*, 2012a; Kim *et al.*, 2012b; Kim *et al.*, 2013b), the solvent with low dielectric constant increase the extent of cation exchange due to weak polarity because the cation is likely to give up solvent easily in its coordination sphere to replace it with the framework oxygen of zeolite during ion exchange process.

Considering the properties of methanol and formamide, the dielectric constant of methanol is lower than of formamide, thus, facilitating the ion exchange of Li^+ ions in undried methanol into zeolite Y. On the other hand, the formamide coordinate around the Li^+ ions very strongly, indicated by its large dielectric constant, making it difficult for the formamide molecules to dissociate and allow the Li^+ ion to move through the zeolite windows. This seems to hinder the exchange of Li^+ ion into zeolite Y, resulting in low exchange level. Consequently, these results show the undried methanol solvent for Li^+ exchange to be more effective than the undried formamide under same condition.

References

- Arvai, A.J., and C. Nielsen. 1983. ADSC Quantum- 210 ADX Program, Area Detector System Corporation; Poway, CA, USA
- Bae, D. and K. Self. 1999. Structures of cobalt(II)-exchanged zeolite X. *Micropor. Mesopor. Mater.* 33: 265-280.
- Bae, D. and K. Self. 2000. Extensive intrazeolitic hydrolysis of Zn(II): partials structures of partially and fully hydrated Zn(II)-exchanged zeolite X. *Micropor. Mesopor. Mater.* 40: 233-245.
- Break, D.W. 1974. *Zeolite Molecular Sieves*, Wiley & Sons, New York. p 93.
- Bruker-AXS (ver 6.12), XPREP. 2001. Program for the Automatic Space Group Determination, Bruker AXS Inc., Madison, Wisconsin, USA.
- Canfield, G.M., M. Bizimis, and S.E. Lattner. 2007. Sodalite ion exchange in polyethyleneoxide oligomer solvents. *J. Mater. Chem.* 17: 4530-4534.
- Canfield, G.M., M. Bizimis, and S.E. Lattner. 2010. Transition-Metal ion exchange using poly(ethylene glycol) oligomers as solvents. *Chem. Mater.* 22: 330- 337.
- Cromer, D.T. 1965. Anomalous dispersion corrections computed from self-consistent field relativistic dirac-slater wave functions. *Acta Crystallogr.* 18: 17-23.
- Doyle, P.A., and P.S. Turner. 1968. Relativistic hartree-fock X-ray and electron scattering factors. *Acta Crystallogr. Sect. A.* 24: 390-397.
- Feuerstein, M., and R.F. Lobo. 1998. Characterization of Li cations in zeolite LiX by solid-state NMR spectroscopy and neutron diffraction. *Chem. Mater.* 10: 2197-2204.
- Feuerstein, M., R.J. Accardi, and R.F. Lobo. 2000. Adsorption of nitrogen and oxygen in the zeolite LiA and LiX investigated by ^6Li and ^7Li MAS NMR spectroscopy. *J. Phy. Chem. B.* 104: 10282-10287.
- Forano, C., R.C.T. Slade, E. Krogh Andersen, I.G. Krogh Andersen, and E. Prince. 1989. Neutron diffraction determination of full structures of anhydrous Li-X and Li-Y zeolites. *J. Solid State Chem.* 82: 95-102.
- Freude, D., S. Beckert, F. Stallmach, R. Kurzhals, D. Taschner, H. Toufar, J. Karger, and J. Haase. 2013. Ion and water mobility in hydrated Li-LSX zeolite studied by ^1H , ^6Li and ^7Li NMR spectroscopy and diffusometry. *Micropor. Mesopor. Mater.* 172: 174-181.
- Herden, H., W.D. Einicke, R. Scholler, W.J. Mortier, L.R. Gellens, and J.B. Uytterhoeven. 1982. Location of Li-ions in synthetic zeolites X and Y. *Zeolite.* 2: 131-134.
- Ho, K.H., H.S. Lee, B.C. Leano, T. Sun, and K. Seff. 1995. Failure of ion exchange into zeolites A and X from four diverse nonaqueous solvents. *Zeolites.* 15: 377-381.
- Ibers, J.A., and W.C. Hamilton. 1974a. *International Tables for X-ray Crystallography*, Vol. IV (Kynoch Press, Birmingham, England), pp. 71-98.
- Ibers, J.A., and W.C. Hamilton. 1974b. *International Tables for X-ray Crystallography*, Vol. IV (Kynoch Press, Birmingham, England), pp. 148-150.
- Kim, H.S., D. Bae, W.T. Lim, and K. Seff. 2012a. Li^+ exchange into zeolite Na-Y (FAU) from aqueous methanol. Single-crystal structures of fully dehydrated Li, Na-Y. *J. Phy. Chem. C.* 116: 9009-9018.
- Kim, H.S., S.O. Ko, and W.T. Lim. 2012b. Single-crystal structures of Li^+ -exchanged zeolite X (FAU, $\text{Si}/\text{Al} = 1.09$) from aqueous solution depends on ion-exchange temperatures at 293 and 333 K. *Bull. Korean Chem. Soc.* 33: 3303-3310.
- Kim, H.S., S.Y. Choi, and W.T. Lim. 2013a. Complete Li^+ exchange into zeolite X (FAU, $\text{Si}/\text{Al} = 1.09$) from undried methanol solution. *J. Porous Mater.* 20: 1449-1456.
- Kim, H.S., J.S. Park, J.J. Kim, J.M. Suh, and W.T. Lim. 2013b. Li^+ -exchanged zeolites X and Y (FAU) from undried formamide solution. *Korean J. Soil Sci. Fert.* 46: 260-269.

- Lee, Y.M., G.H. Jeong, Y. Kim, and K. Seff. 2005. Single crystal structure of fully dehydrated, excessively Cd²⁺-exchanged zeolite Y, [Cd_{27.5}(Cd₈O₄)₂][Si₁₂₁Al₇₁O₃₈₄]-FAU, containing Cd₈O₄⁸⁺ clusters. *Micropor. Mesopor. Mater.* 88: 105-111.
- Lide, D.R. 1996/1997a. *Handbook of Chemistry and Physics*, 77th ed., CRC Press: Boca Raton, FL, p. 12-14.
- Lide, D.R. 1996/1997b. *Handbook of Chemistry and Physics*, 77th ed., CRC Press: Boca Raton, FL, p. 6-152.
- Lim, W.T., S.Y. Choi, J.H. Choi, Y.H. Kim, N.H. Heo, and K. Seff. 2006. Single-crystal structure of fully dehydrated fully K⁺-exchanged zeolite Y (FAU), K₇₁Si₁₂₁Al₇₁O₃₈₄. *Micropor. Mesopor. Mater.* 92: 234-242.
- Lim, W.T., S.M. Seo, L.Z. Wang, G.Q. Lu, N.H. Heo, and K. Seff. 2010. Single-crystal structures of highly NH₄⁺-exchanged, fully deaminated, and fully TI⁺-exchanged zeolite Y (FAU, Si/Al = 1.56), all fully dehydrated. *Micropor. Mesopor. Mater.* 129: 11-21.
- Loewenstein, W. 1954. The distribution of aluminum in the tetrahedral of silicates and aluminates. *Am. Mineral.* 39: 92-96.
- Olson, D.H. 1995. The crystal structure of dehydrated NaX. *Zeolites.* 15: 439-443.
- Otwinowski, Z., and W. Minor. 1997. Processing of X-ray diffraction data collected in oscillation mode. *Methods Enzymol.* 276: 307-326.
- Plevart, J., F. Di Renzo, F. Fajula, and G. Chiari. 1997. Structure of dehydrated zeolite Li-LSX by neutron diffraction: Evidence for a low-temperature orthorhombic faujasite. *J. Phys. Chem. B.* 101: 10340-10346.
- Ronay, C., and K. Seff. 1985. Crystal structure of lead (Pb₆)-A and lead hydroxide hydrate (Pb₉(OH)₈(H₂O)₃)-A. Zeolite A ion exchanged with lead(2+) at pH 4.3 and 6.0 and evacuated. *J. Phys. Chem.* 89: 1965-1970.
- Ronay, C., and K. Seff. 1993. Lead oxide hydroxide clusters in Pb₉O(OH)₄-A, zeolite A exchanged with Pb²⁺ at Ph 6.0. *Zeolites.* 13: 97-101.
- Seo, S.M., W.T. Lim, and K. Seff. 2012a. Crystallographic verification that Copper(II) coordinates to four of the oxygen atoms of zeolite 6-rings. Two single-crystal structures of fully dehydrated, largely Cu²⁺-exchanged zeolite Y (FAU, Si/Al = 1.56). *J. Phys. Chem. C.* 116: 963-974.
- Seo, S.M., W.T. Lim, and K. Seff. 2012b. Single-crystal structures of fully and partially dehydrated zeolite Y (FAU, Si/Al = 1.56) Ni²⁺ exchanged at a low pH, 4.9. *J. Phys. Chem. C.* 116: 13985-13996.
- Sheldrick, G.M. 1997. SHELXL97, Program for the Refinement of Crystal Structures. University of Gottingen, Germany.
- Shepelev, Y.F., A.A. Anderson, and Y.I. Smolin. 1990. Crystal structure of a partially lithium-exchanged X zeolite in hydrated (25°C) and dehydrated (275°C) states. *Zeolites.* 10: 61-63.
- Van Bekkum, H., E.M. Flanigen, P.A. Jacobs, and J.C. Jansen. 2001. *Introduction to Zeolites Science and Practice*. Elsevier. p 44.
- Weast, R.V. 1989/1990. *Handbook of Chemistry and Physics*, 70th ed., The chemical Rubber Co.: Cleveland, OH, p. F-187.
- Wozniak, A., B. Marler, K. Angermund, and H. Gies. 2008. Water and cation distribution in fully and partially hydrated Li-LSX zeolite. *Chem. Mater.* 20: 5968-5976.
- Zhu, J., N. Mosey, T. Woo, and Y. Huang. 2007. Study of the adsorption of toluene in zeolite LiNa-Y by Solid-State NMR spectroscopy. *J. Phys. Chem. C.* 111: 13427-13436.
- Zhu, L., and K. Seff. 1999. Reinvestigation of the crystal structure of dehydrated sodium zeolite X. *J. Phys. Chem. B.* 103: 9512-9518.