부분적으로 코발트 이온으로 치환한 제올라이트 A를 진공 탈수한 후 칼륨 증기로 반응시킨 3개의 결정구조

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Three Crystal Structures of Dehydrated Partially Co²⁺-Exchanged Zeolite A Treated with Potassium Vapor

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요 약

부분적으로 Co^{2+} 이온으로 치환된 제올라이트 A를 진공 탈수한 후 300°C에서 12시간, 6시간, 2시간 동안 각각 0.6 torr의 K 증기로 반응시킨 3개의 구조 ($a = 12.181(1)$ Å, $a = 12.184(1)$ Å, $a = 12.215(1)$ Å)를 21°C에서 입방공간군 $Pm\bar{3}m$를 사용하여 단결정 X-선 회절법으로 해석하고 정밀화 한다. K 증기로 반응시킨 3개의 구조는 Full-matrix 최소자승법 정밀화 계산에서 $I > 3\sigma(I)$ 인 70, 82, 80 개의 독립반사를 각각 사용하여 최종오차인자를 R (weight) = 0.090, 0.091, 0.090 까지 각각 정밀화 한다. 3개의 구조에서 4개의 Co^{2+} 이온과 4개의 Na^+ 이온 모두 K 증기에 의해서 환원되어 Co^{2+} 이온과 Na^+ 이온은 제올라이트 내에 더 이상 생성되지 않는다. K 종류는 5개의 다른 결정학적 자리에 위치하는데 3개의 K^+ 이온은 8-링의 평면에 완전히 채워져 위치하고 약 11.5개의 K^+ 이온은 3회 회전축상의 6-링에 위치하고 약 4개는 큰 동공, 4개는 소다라이트 동공, 0.5개는 큰 공동의 4-링과 마주보는 위치에 위치하고 3개의 K^0 원자는 3회 회전축상의 큰 동공 깊숙이 위치한다. 이들 구조는 제올라이트 A의 소다라이트 동공에서 사면체 K_4 (혹은 삼각형 K_3) 클러스터를 이루고 있으며 K_4 혹은 K_3 클러스터는 6-링의 3개의 산소와 삼면체로 결합한다. 이들 클러스터의 부분적으로 환원된 이온은 제올라이트 골조 산소와 우선적으로 결합한다. 이들 구조에서 제올라이트 골조의 음전하를 상쇄시키는데 필요한 12개의 K^+ 이온보다 많은 단위세포당 14.5개의 K 종류가 존재하는데 이들 결과로 K^0 원자가 흡착되었음을 알 수 있다. 큰 동공 깊숙이 위치한 3개의 K^0 원자는 4개의 큰 동공에 위치한 K^+ 이온 중 3개와 결합하여 K_7^{4+} 클러스터를 형성하며 K_7^{4+} 클러스터는 골조산소와 우선적으로 결합한다.

Abstract

Three crystal structures of dehydrated partially Co²⁺-exchanged zeolite A treated with 0.6 Torr of K at 300°C (for 12 hrs, 6 hrs, and 2 hrs) vapor have been determined by single-crystal X-ray diffraction techniques in the cubic space group $Pm\bar{3}m$ at 21(1) °C ($a = 12.181(1)$ Å, $a = 12.184(1)$ Å, and $a = 12.215(1)$ Å respectively). Their structures were refined to the final error indices, R (weight) of 0.090 with 70 reflections, 0.091 with 82 reflections, and 0.090 with 80 reflections, respectively, for which $I > 3\sigma(I)$. In each structure, all four Co²⁺ and four Na⁺ ions to be reduced by K atoms. The cobalt and sodium atoms produced are no longer found in the zeolite. K species are found at five different crystallographic sites: three K⁺ ions lie at the planes of 8-rings, filling that position, ca. 11.5 K⁺ ions lie on threefold axes, ca. 4.0 in the large cavity and ca. 4.0 in the sodalite cavity, and ca. 0.5 K⁺ ion is found near a 4-ring. ca. three K⁰ atoms are found deep into

the large cavity on threefold axes. In these structures, crystallographic results show that cationic tetrahedral K_4 (and/or triangular K_3) clusters have formed in the sodalites of zeolite A. The K_4 and/or K_3 clusters coordinate trigonally to three oxygens of a six-oxygen ring. The partially reduced ions of these clusters interact primarily with oxygen atoms of the zeolite structure rather than with each other. ca. 14.5 K species are found per unit cell, more than the twelve K^+ ions needed to balance the anionic charge of zeolite framework, indicating that sorption of K^0 has occurred. The three K^0 atoms in the large cavity are closely associated with three out of four K^+ ions in the large cavity to form K_7^{4+} clusters. The K_7^{4+} cluster not interacts primarily with framework oxygens.

1. Introduction

Zeolites can absorb alkali metal atoms to give cationic clusters. Zeolites with their well-defined, regular channels and cavities offer a great opportunity to encapsulate, isolate, stabilize and study these clusters. The smaller of these have been identified by ESR methods, but the larger are described only as "metallic".

Kasai and Rabo[1-4] exposed Na-Y zeolite powder to Na metal vapor and detected the tetrahedral alkali metal cluster Na_4^{3+} by electron spin resonance (ESR). Na_6^{5+} was found when Na-X was exposed to sodium metal vapor. Subsequently a series of ESR experiments were done by Edwards,[5-9] Jacobs,[10-12] and Kevan[13,14] on samples prepared by various synthetic methods. The new cationic alkali metal clusters Na_3^{2+}, Na_5^{4+}, K_3^{2+}, and K_4^{3+}, as well as Na, K, Rb, and Cs metal particles, were found in zeolite A, X, and Y. Barrer[15] and Smeulders[16,17] found by ESR that Na_4^{3+} clusters could form in synthetic socialites; this indicated that the Na_4^{3+} clusters in zeolites A, X, and Y might also be in sodalite cavities. However, the actual positions of all of these cationic clusters within zeolites remained entirely unknown, and little could be said about the bonding within the clusters.

Recently, linear Rb_4^{3+}, Cs_3^{2+}, and Cs_4^{3+} Clusters, and triangular Rb_3^{2+} clusters, were found crystallographically in the sodalite cavities of zeolite A.[18-25] Single crystals of K_n-A·3K (n = ca. 12) and K_{92}-X·50 K were synthesized by exposing Na-A and Na-X to potassium metal vapor, and their structures were determined by X-ray diffraction methods.[26] It was found that each sodalite cavity of zeolite A contained either a tetrahedral K_4^{n+} (n < 4) or (less likely) a triangular K_3^{m+} (m < 3) cluster, and that

two-dimensional potassium continua had formed in its large-cavity/8-ring-channel system. At high potassium loadings, all potassium clusters in the sodalite cavities of zeolite X were linked by potassiums at the centers of double six-oxygen rings (D6R's) to form rings or chains (one-dimensional continua: zig-zag strands). A three-dimensional potassium continuum, similar to that found in Cs_{92}-X·36Cs,[27] formed in K_{92}-X·50 K.[26]

More recently, Armstrong et al.[28] studies the crystal structure of dehydrated potassium LTA (K12-A) with a calibrated amount of potassium vapour at temperatures between 200 and 250°C. They reported the structure of K_5/K_{12}-A, K_{17}-A. Its structure was determined POLARIS diffractometer in the space group $Fm\overline{3}m$. Sun and Seff[29] found that K^{2+} could be produced by exposing K-A at 350°C to potassium, and its structure was determined by X-ray diffraction methods. They showed K_3^{2+} clusters form in the sodalite cavity. No excess potassium atoms are found in the large cavity. They found the one delocalized electron binds the potassium ions in K_3^{2+} more strongly than it can bind those in a K_4^{3+} cluster.

This work was done to determine the structure and placement of clusters within zeolite A. First, potassium metal vapor was ex- pected to react with Co_4Na_4-A to form K_{12}-A. It was hoped that additional potassium atoms would then be sorbed to form isolated clusters. Their existence could then be confirmed, and their placement and geometry determined, by single-crystal X-ray diffraction methods.

2. Experimental Section

Crystals of zeolite 4A were prepared by a modification of Charnell's method.[30] Ion exchange with an

aqueous solution of 0.1 M $Co(NO_3)_2$ was done by the static (batch) method.[31] This yielded a material whose approximate stoichiometry was $Na_4Co_4Al_{12}Si_{12}O_{48}$· xH_2O per unit cell, subsequently to be referred to as Co_4Na_4-A, exclusive of water molecules. One of the largest single crystals from this experiment, a light pink cube about 0.08 mm along on edge, was selected for X-ray diffraction study. It was placed in a finely drawn Pyrex capillary, attached to a vacuum system, and cautiously dehydrated by gradually increasing its temperature (ca. 25°C/h to 360°C) at a constant pressure of 2×10^{-6} Torr. Finally the system was maintained at this state for 48 h. The crystals at 300°C were brought into vapor contact (0.6 Torr) with K(g) at 300°C for 12, 6, and 2 hrs, respectively. After reaction, the crystals, now red-brown in color, were sealed off under vacuum.

3. X-ray Data Collection

The cubic space group $Pm\bar{3}m$ (no systematic absences) was used throughout this work for reasons discussed previously.[32,33] Preliminary crystallographic experiments and subsequent data collection were performed with an automated four-circle Enraf-Nonius CAD-4 diffractometer, equipped with a graphite monochromator. $MoK\alpha$ radiation was used for all experiments ($K\alpha_1$, $\lambda = 0.70930$ Å; $K\alpha_2$, $\lambda = 0.71359$ Å). The cubic unit cell constant, as determined by a least-squares refinement of 25 intense reflections for which $19° < 2\theta < 24°$, are 12.181(1) Å, 12.184(1) Å, and 12.215(1) Å for crystal 1, 2, and 3, respectively. For each crystal, reflections from two intensity-equivalent regions of reciprocal space (hkl, $h \leq k \leq l$; hlk, $h \leq l \leq k$) were examined using the ω-2θ scan technique. The data were collected using variable scan speeds. Most reflections were observed at slow speeds from 0.23 and to 0.32 in w min^{-1}.

The intensities of three reflections in diverse regions of reciprocal space were recorded after every three hours to monitor crystal and X-ray source stability. Only small, random fluctuations of these check reflections were noted during the course of data collection. For each region of reciprocal space, the intensities of all lattice points for which

$2\theta \leq 70°$ were recorded. The intensities were corrected for Lorentz and polarization effects; the reduced intensities were merged, and the resultant estimated standard deviations were assigned to each averaged reflection by the computer programs PAINT and WEIGHT.[34] An absorption correction ($\mu R = 0.056$) was judged to be negligible and was not applied for all crystals.[35] Of the 858, 858, and 862, pairs of reflections for the crystal 1, 2, and 3 respectively, only 70, 82, and 80 pairs, respectively, for which $I > 3\sigma(I)$ were used in subsequent structure determinations. All structure calculation were done using MolEN programs supplied by system from Enraf-Nonius.

4. Structure Determination

Crystal 1. Treated with 0.6 Torr K(g) at 300°C for 12 hrs.

Least-squares refinement was initiated by using the Co(II) cation coordinates and framework positions ((Si, Al), O(1), O(2), and O(3)) of Co_4Na_4-A.[31] Anisotropic refinement quickly converged to $R_1 = (\Sigma|F_o - |F_c||)/\Sigma F_o = 0.33$ and $R_w = [\Sigma w(F_o - |F_c||)^2/\Sigma wF_o^2]^{1/2} = 0.38$.

The initial difference Fourier function revealed three large peaks at (0.117, 0.117, 0.117), (0.251, 0.251, 0.251), and (0.0, 0.471, 0.5) with heights of 4.5, 4.2, and 1.9 $eÅ^{-3}$, respectively. These three peaks were stable in least-squares refinement. Isotropic refinement including these as K(1), K(2), and K(3) positions, respectively, converged to $R_1 = 0.156$ and $R_2 = 0.170$, with occupancies given in the last column of Table 1. The thermal parameter at K(3) was large compared to that at other potassium positions in this structure (see Table 1), and a residual peak was seen at (0.0, 0.47, 0.5) in a second Fourier function. This position, and that at (0.0, 0.47, 0.47) found in sample K-A,[36] were examined by least-squares refinement. Each refined relatively well to lower isotropic thermal parameters without affecting the R indices.

A subsequent difference Fourier function revealed a large peak at (0.389, 0.391, 0.391) with a height of 2.9 $eÅ^{-3}$. Inclusion of this peak as K(4) (see Table 1) lowed the error indices to $R_1 = 0.115$ and

Table 1. [a]Positional, thermal, and occupancy parameters

Crystal 1. Dehydrated Co_4Na_4-A treated with 0.6 Torr K vapor at 300°C for 12 hrs

Atom	Wyc. Pos.	x	y	z	[b]β_{11} B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	[c]Occupancy varied	fixed
(Si,Al)	24(k)	0	1780(10)	3760(10)	110(10)	40(10)	30(10)	0	0	−30(30)		24.0[d]
O(1)	12(h)	0	2400(60)	5000	240(70)	200(100)	120(70)	0	0	0		12.0
O(2)	12(i)	0	3060(40)	3060(40)	50(50)	250(60)	250(60)	0	0	400(200)		12.0
O(3)	24(m)	1150(20)	1150(20)	3540(30)	10(10)	10(10)	150(50)	−90(60)	−40(50)	−40(50)		24.0
K(1)	8(g)	1160(20)	1160(20)	1160(20)	140(20)	140(20)	140(20)	90(60)	90(60)	90(60)	4.65(23)	4.0
K(2)	8(g)	2550(30)	2550(30)	2550(30)	80(20)	80(20)	80(20)	150(60)	150(60)	150(60)	3.77(22)	
K(3)	12(i)	0	4740(70)	4740(70)	12(3)[e]						3.18(20)	3.0
K(4)	8(j)	3930(60)	3930(60)	3930(60)	300(100)	300(100)	300(100)	100(300)	100(300)	100(300)	3.43(26)	
K(5)	96(g)	2520(100)	2520(100)	5000	15(fixed)						0.43(43)	

Crystal 2. Dehydrated Co_4Na_4-A treated with 0.6 Torr K vapor at 300°C for 6 hrs

Atom	Wyc. Pos.	x	y	z	[b]β_{11} B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	[c]Occupancy varied	fixed
(Si,Al)	24(k)	0	1790(10)	3750(10)	110(10)	40(10)	20(9)	0	0	−30(30)		24.0[d]
O(1)	12(h)	0	2400(50)	5000	280(70)	190(90)	50(40)	0	0	0		12.0
O(2)	12(i)	0	3060(30)	3060(30)	70(50)	170(40)	170(40)	0	0	400(200)		12.0
O(3)	24(m)	1170(10)	1170(10)	3540(20)	40(10)	40(10)	170(40)	−90(60)	−40(50)	−40(50)		24.0
K(1)	8(g)	1150(30)	1150(30)	1150(30)	170(30)	170(30)	170(30)	90(60)	90(60)	90(60)	4.44(22)	4.0
K(2)	8(g)	2570(20)	2570(20)	2570(20)	90(10)	90(10)	90(10)	150(60)	150(60)	150(60)	3.92(20)	
K(3)	12(i)	0	4710(70)	4710(70)	13(2)						3.56(22)	3.0
K(4)	8(j)	3900(50)	3900(50)	3900(50)	310(60)	310(60)	310(60)	100(300)	100(300)	100(300)	3.04(25)	
K(5)	96(g)	2440(40)	2440(40)	5000	15(fixed)						0.49(33)	

Crystal 3. Dehydrated Co_4Na_4-A treated with 0.6 Torr K vapor at 300 °C for 2 hrs

Atom	Wyc. Pos.	x	y	z	[b]β_{11} B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	[c]Occupancy varied	fixed
(Si,Al)	24(k)	0	1800(10)	3740(10)	80(10)	32(9)	20(10)	0	0	−20(30)		24.0[d]
O(1)	12(h)	0	2320(40)	5000	170(60)	100(70)	50(40)	0	0	0		12.0
O(2)	12(i)	0	3150(40)	3150(40)	210(70)	240(50)	240(50)	0	0	500(100)		12.0
O(3)	24(m)	1130(10)	1130(10)	3550(30)	10(10)	10(10)	150(40)	−90(60)	−70(50)	−70(50)		24.0
K(1)	8(g)	1210(20)	1210(20)	1210(20)	170(20)	170(20)	170(20)	100(60)	100(60)	100(60)	4.32(22)	4.0
K(2)	8(g)	2540(30)	2540(30)	2540(30)	70(20)	70(20)	70(20)	130(60)	130(60)	130(60)	3.96(24)	
K(3)	12(i)	0	4730(50)	4730(50)	8(3)						3.56(22)	3.0
K(4)	8(j)	3860(40)	3860(40)	3860(40)	290(60)	290(60)	290(60)	−0(200)	−0(200)	−0(200)	3.32(25)	
K(5)	96(g)	2410(50)	2410(50)	5000	15(fixed)						0.46(40)	

[a]Positional and anisotropic thermal parameters are given × 10^4. Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. [b]The anisotropic temperature factor = $exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [c]Occupancy factors are given as the number of atoms or ions per unit cell. Occupancies with e.s.d's were in least-squares. [d]Occupancy for (Si) = 12 and occupancy for (Al) = 12. [e]Isotropic thermal parameter in units of $Å^2$.

R_2 = 0.090. The number of K^0 atoms at K(4) refined to per unit cell.

Successive difference Fourier synthesis reveled a peak of height 1.5 $eÅ^{-3}$ at (0.255, 0.255, 0.5). This peak refined with an unusually large thermal parameter. Therefore, the isotropic thermal parameter of

K(5) was fixed at the more reasonable value given in Table 1. allowing all occupancies of K), i = 1-5 to vary except that at K(3), which was not permitted to exceed 3.0 (its maximum occupancy by symmetry), led to R_1 = 0.098 and R_2 = 0.087.

Therefore, the occupancy numbers of K(i), i = 1,

2, and 3 except for K(4) and K(5), were reset and fixed eithin their 2.0 esd's as in the last column of Table 1. The final error indices converged to R_1 = 0.109 and R_2 = 0.090. The final difference function was featureless except for a peak eÅ^{-3} in height at the origin.

Crystal 2. Treated with 0.6 Torr K(g) at 300°C for 6 hrs.

Full-matrix least-squares refinement was initiated with fixed positional and thermal parameters for the framework atoms [Si(Al), O(1), O(2), O(3)] of the previous structure. This model converged to R_1 = 0.32 and R_2 = 0.37.

A difference Fourier function disclosed five strong peak at (0.250, 0.250, 0.250), (0.115, 0.115, 0.115), and (0.0, 0.483, 0.483). Anisotropic refinement of these as K(2), K(1), and K(3), respectively, converged to R_1 = 0.164 and R_2 = 0.156, with occupancies given in the last column of Table 1.

The final difference Fourier function showed a strong peak (0.393, 0.393, 0.393) at the center of the large cavity. It could be refined as ca. 3.56 potassiums per unit cell with a fixed isotropic thermal parameter. However, its inclusion lowered R_1 and R_2 only slightly to 0.118 and 0.091, respectively. This position was not included in the final structure. The final structural parameters and selected interatomic distances and angles are presented in Tables 1 and 2, respectively.

Crystal 3. Treated with 0.6 Torr K(g) at 300°C for 2 hrs.

Full-matrix least-squares refinement was initiated with fixed positional and thermal parameters for the framework atoms [Si(Al), O(1), O(2)] and five potassium positions at previous two structures. The final refinement converged nicely to R_1 = 113 and R_2 = 0.090. The final difference function was featureless. The largest maximum/minimum in the final difference function is 1.0 eÅ^{-3}/ 0.9 eÅ^{-3}. The final structural parameters and selected interatomic distances and angles are presented in Tables 1 and 2, respectively. The chemical composition indicated crystallographically is K-A per unit cell.

The full-matrix least-squares program used mini-

Table 2. Selected interatomic distances (Å) and Angles (deg) for dehydrated Co$_4$Na$_4$-A treated with K vapor

	Crystal 1	Crystal 2	Crystal 3
(Si,Al)-O(1)	1.69(4)	1.69(3)	1.66(2)
(Si,Al)-O(2)	1.78(5)	1.77(2)	1.79(3)
(Si,Al)-O(3)	1.62(1)	1.63(1)	1.62(1)
K(1)-O(3)	2.90(4)	1.83(6)	2.97(8)
K(2)-O(3)	2.70(3)	2.68(2)	2.95(6)
K(3)-O(1)	2.87(8)	2.83(6)	2.97(5)
K(3)-O(2)	2.89(7)	2.84(7)	2.74(6)
K(5)-O(3)	3.0(9)	2.8(3)	2.8(4)
K(5)-O(1)	3.1(2)	2.97(3)	2.95(6)
K(1)-K(1)	3.99(2)	3.95(2)	4.17(2)
K(3)-K(4)	4.99(2)	4.95(2)	4.95(2)
K(4)-K(4)	3.69(5)	3.78(4)	3.93(4)
K(3)-K(5)	4.1(9)	4.1(4)	4.1(5)
K(4)-K(5)	4.8(4)	5.0(2)	5.1(3)
K(2)-K(4)	2.91(5)	2.82(4)	2.79(4)
K(2)-K(4)'	4.90(3)	4.88(2)	4.95(2)
O(1)-(Si,Al)-O(2)	92.0(3)	92.0(2)	92.0(2)
O(1)-(Si,Al)-O(3)	111.0(2)	110(1)	109.0(1)
O(2)-(Si,Al)-O(3)	110(1)	109.0(8)	113.9(8)
O(3)-(Si,Al)-O(3)	120.0(1)	122.0(1)	116.0(1)
Si,Al)-O(1)-(Si,Al)	127.0(1)	127.0(4)	136.1(3)
(Si,Al)-O(2)-(Si,Al)	147.0(1)	147.0(2)	138.0(2)
(Si,Al)-O(3)-(Si,Al)	142.0(1)	141.0(1)	147.0(1)
O(3)-K(1)-O(3)	90.0(4)	88.8(7)	93.7(3)
O(3)-K(1)-O(3)	99.5(7)	99.1(6)	100.0(1)
O(3)-K(1)-O(3)	74(9)	78(9)	85(11)
O(3)-K(1)-O(3)	84.0(35)	98(1)	77(11)

Numbers in parentheses are estimated standard deviations in the least significant digit given for the corresponding value.

mized $\Sigma w(F_o - |F_c|)^2$; the weight of an observation was the reciprocal square of $\sigma(F)$, its standard deviation. Atomic scattering factors[37,38] for K^0 (valence), K^+, O^-, Co^{2+}, Na^+, and (Si,Al)$^{1.75+}$ were used. The function describing (Si,Al)$^{1.75+}$ is the mean of the Si^0, Si^{4+}, Al^0, and Al^{3+} functions. All scattering factors were modified to account for anomalous dispersion.[39] The final structural parameters and selected interatomic distances and angles are presented in Tables 1 and 2, respectively.

5. Discussion

Treating dehydrated Co$_4$Na$_4$-A with 0.6 Torr of K vapor at 300°C causes all four Co^{2+} and four Na$^+$

ions to be reduced by K atoms. The cobalt and sodium atoms produced are no longer found in the zeolite and that extra potassium atoms are sorbed into the zeolite structure. The chemical composition indicated crystallographically per cubic unit cell is K_n-A, where n is 14 or 15, or an intermediate value. K^+ ions are found at five crystallographic sites (Table 1).

Four potassium ions at K(1) are found on three-fold axes in every sodalite unit in $K_{14.5}$-A, half filling an eight-fold position. To avoid a short contact, ca. 2.92 Å for K(1)-K(1), these potassiums must be tetrahedrally arranged in the sodalite cavity (Figs. 3 and 4). Six K(1)-K(1) contacts are then each ca. 4.04 Å (Table 2).

Four potassium ions at K(2) are found on three-fold axes, like those at K(1), but in the large cavity. It is impossible to place two K^+ ions at K(1) and K(2) on the opposite sides of the same 6-ring because K(1)-K(2) would be too short, ca. 2.71 Å. Each 6-ring can therefore contain only one K^+ ion, and this requires that the ions at K(2) be arranged tetrahedrally about each sodalite cavity.

Three potassiums at K(3) are located in the planes of 8-rings; this had been seen in previously reported structure involving K^+ ions in zeolite A. Each K(3) cation is ca. 2.89(6) Å from four O(1) oxygens and ca. 2.82(7) Å from four O(2)'s (Table 2). These distances are substantially longer than the sum of the ionic radii of O^2 and K^+, 2.65 Å.[40] If the K(3)'s were located at the centers of the 8-rings, the K^+-O atomic distances would have been Å to all four O(1)'s, and Å to all O(2)'s, each far greater than the K(2)-O(3) distance of Å (which is near to the sum of the ionic radii of K^+ and O^{2-}, 1.33 + 1.32 = 2.65 Å).[40] Accordingly, it is reasonable that the K(3)'s are not found at the centers of the 8-rings.

The K^+ ion at K(5) lies opposite a 4-ring. This K^+ ion is rather far from the framework oxygens (ca. 3.01 Å from O(1) and ca. 2.87 Å from O(3), perhaps because of repulsive interactions with the K^+ ions on the sodalite unit site of in the adjacent 6-ring) (Table 3). This distance may be virtual, a bit too long; this particular 4-ring may be distorted from the mean 4-ring geometry due to the presence

Table 3. Deviations of atoms (Å) from the (111) plane at O(3) for dehydrated Co_4Na_4-A treated with K vapor

	Crystal 1	Crystal 2	Crystal 3
O(2)	0.20(3)	0.16(2)	0.34(3)
K(1)	−1.67(2)	−1.72(2)	−1.54(2)
K(2)	1.26(2)	1.28(2)	1.28(2)
K(4)	4.17(4)	4.09(3)	4.07(3)

A negative deviation indicates that the atom lies on the same side of the plane as the origin.

of its K^+ ion. This 4-ring position for alkali cations has been reported in Na-A and K-A, but always with very low occupancy, one or 0.5 per unit cell.[36,41] Sun and Seff exposed zeolite A to K metal vapor and the occupancy at opposite 4-rings found four per unit cell. In this model, K^+ ions at K(2) and K(5) are placed to maximize the distances among them and to avoid a short K(2)-K(5) contact, ca. 3.33 Å. However this placement distributes the ions at K(2) and K(5) more evenly among their equipoints of partial occupancy, but contains four of these short K(2)-K(5) contacts (Fig. 2). They concluded that the three excess electrons per unit cell (for K_{15}-A), are insufficient to provide the bonding which these short distances would indicate.

Generally, the K(5) position is least favored for cations in zeolite A. In the structures, the occupancy at K(5) (opposite 4-rings), ca. 0.5 per unit cell, is usual. This position could be refined as 0.5 potassiums per unit cell with a fixed isotropic thermal parameter. However, its inclusion lowered R_1 and R_2 only slightly and this was difficult to refine.

Three potassiums at K(4) are located at the three-fold axes far into large cavity. This had not been seen in any previously reported structure involving K^+ ions in zeolite A. K(4) does not associate with a framework oxygen ion. This indicates that a reduced K^0 atom (an uncharged potassium cluster) and not a K^+ ion (or a cluster with a formal charge) exists at K(4). The distance between K(2) and K(4), ca. 2.84 Å, is too short to be an unmoderated K^+-K^+ contact, and too long to be a K^0-K^0 bond.[40] Each K(4) atom coordinates trigonally to three K^+ ions at K(2) to form a K_7^{4+} cluster. K_7^{4+} cluster is trigonal and shows at the center of the large cavity (Figs. 1
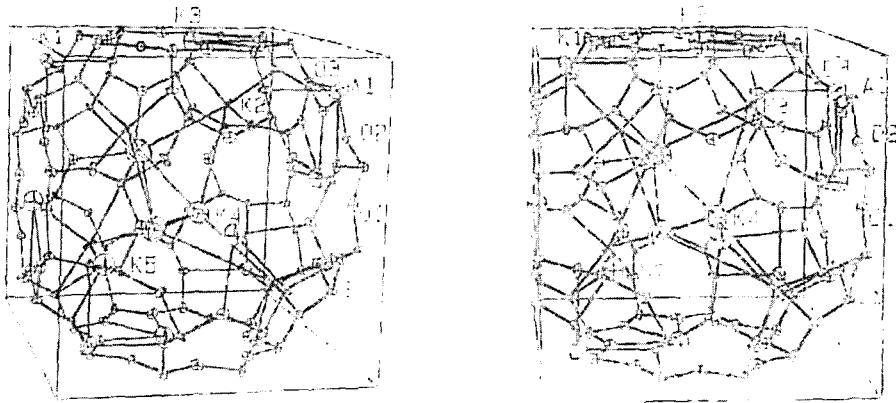
Fig. 1. A stereoview of a large cavity of dehydrated Co₄Na₄-A treated with K vapor. Four K⁺ ions at K(1), four K⁺ ions at K(2), three K⁺ ions at K(3), one K⁺ ions at K(5), three K species K(4), and one K_7^{4+} cluster are shown. Ellipsoids of 20% probability are shown.
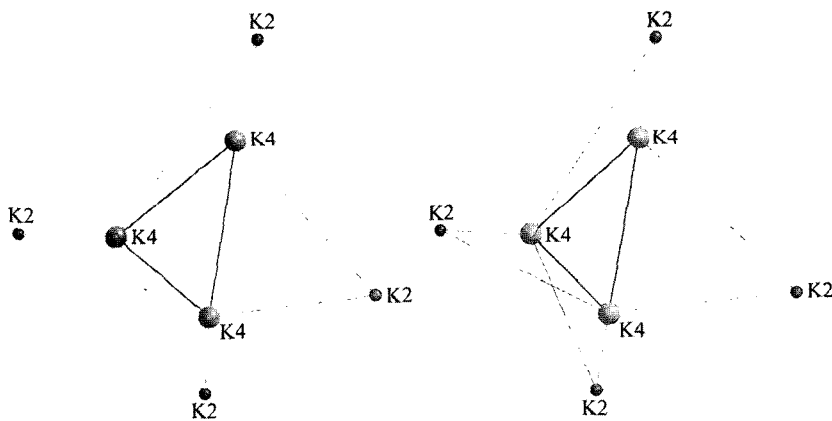

Fig. 2. The trigonal K molecule, stabilized by coordination to four K⁺ ions at K(2) is shown. Ellipsoids of 20% probability are shown.

and 2).

The potassium site (ca. 0.390, 0.390, 0.390) is known in dehydrated K_{12}-A[36,42] (ca. 0.356, 0.356, 0.356), and may be regarded as primarily ions in character. Importantly, no distinction can be drawn between potassium originally present in the zeolite and that absorbed from the vapour phase. Presumably in return for a framework coordination site, the incoming 'guest' potassium atoms give up their valence electrons which then interact with the framework cations. Similarly, the site is known in dehydrated Na_{92}-X reacted with Cs(g) at 450°C.[27] In this structure, the Cs position (0.375, 0.375, 0.375) is very far (7.25 Å) from its nearest frame-

work oxygens (O(4)), indicating that it is occupied not by ions but by atoms. In dehydrated $Ag_{4.6}Na_{7.4}$-A treated with hydrogen at 350°C.[43] The silver species at Ag(4) (0.264, 0.425, 0.425) and Ag(5) (0.365, 0.365, 0.365) are located deep inside the large cavity (Ag(4)-O(2) = 3.94(3) Å and Ag(5)-O(3) = 4.37(4) Å). In dehydrated $Ag_{5.6}K_{6.4}$-A treated with Cs(g) at 250°C,[44] about 4.5 Ag atoms at Ag(1), the products of the reduction of Ag⁺ by Cs⁰, are located (0.348, 0.5, 0.5) near the center of the large cavity (Ag(1)-O(1) = 5.42(2) Å. In present structure, the K(4) position (Fig. 1) is very far (4.95 Å) from its nearest framework oxygens (O(2)), indicating that it is occupied not by ions but by atoms.
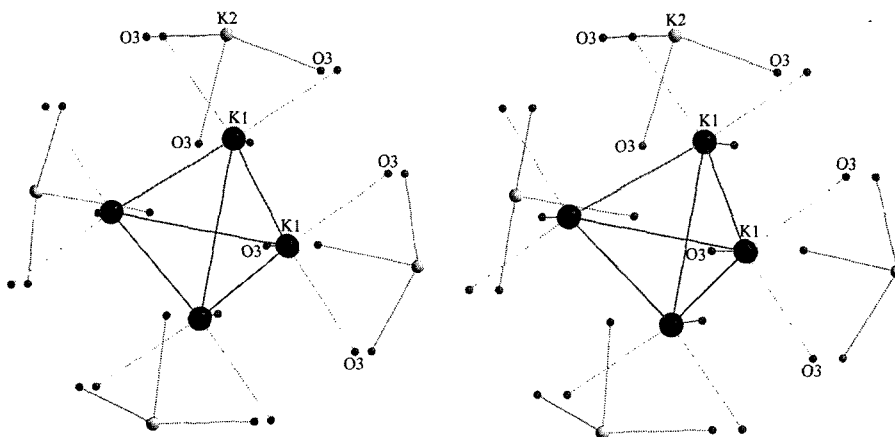
Fig. 3. A stereoview of sodalite cavities of dehydrated Co_4Na_4-A treated with K vapor. A tetrahedral (K_4) cluster are shown. Ellipsoids of 20% probability are shown.

Recently, also we found to the position (0.389, 0.389, 0.389) at the dehydrated Ag_4Ca_4-A treated K(g) at 300°C. Therefore, the position is also consistent with these structure and conclusion.

It is most interesting to observe the position of the K atoms at K(4). It lies at a position relatively loosely defined by the electrostatic field of the framework and the other K^+ cations. Its nearest neighbors, all part of the nearest 6-ring or arranged symmetrically about it, are three O(3)'s at ca. 4.75 Å, three O(2)'s at ca. 4.95 Å, the single K(2) at ca. 2.84 Å, six O(1)'s at ca. 5.27 Å, and one K(5)'s at ca. 2.64 Å. Its broad oblate thermal ellipsoid appears to be consistent with the maintenance of the distance between K(4) and its nearest neighbors at K(2) and K(5).

The four ions at K(2) do not have equivalent environments. Three of the four are close to three potassium atoms at K(4), whereas the remaining one interacts only with framework oxygens. If all of four potassium ions at K(2) interact with four potassium atoms at K(4), the two distances, K(2)-K(4) ca. 4.91 Å and the K(2)-K(4) ca. 2.84 Å, is much shorter. The chemical composition, therefore, is about $K_{14.5}$-A, which can be viewed as a mixture of K_{15}-A and K_{14}-A. The potassium arrangement in the large cavity of K_{14}-A would be the same as that in K_{15}-A, but some to most of the sodalite cavities would contain triangular K_3^{m+} clusters instead of tetrahedral K_4^{n+}.
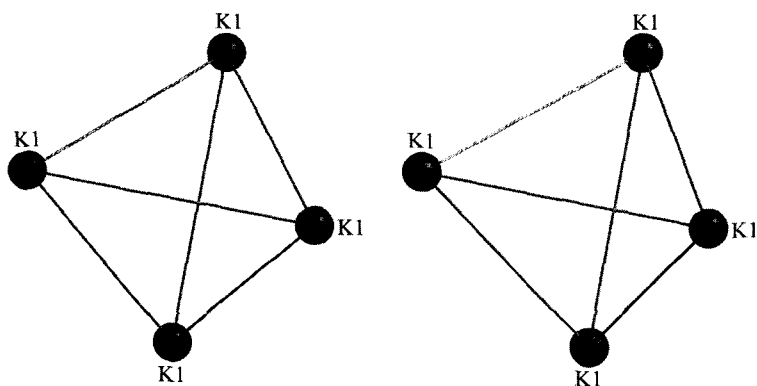

Fig. 4. The tetrahedral potassium cluster, K_4 is shown in sodalite cavity. Ellipsoids of 20% probability are shown.

K_{15}-A shows an ideal potassium distribution in the sodalite (Fig. 3) and large (Fig. 1) cavities of zeolite A. K_4^{n+} clusters, present in all sodalite units, have no very short K(1)-K(1) contacts. The very short K(2)-K(5) distance is avoidable by segregating the ions at K(2) from those at K(5), by placing them an opposite sides of the large cavity.

To summarize, $K_{14.5}$-A was prepared by exposing Co_4Na_4-A at 300°C to potassium vapor, and its structure was determined by X-ray diffraction methods. A crystal of K_n-A, n = 14 or 15, has been produced by replacing all of the sodium and cobalt ions in the parent samples by redox reaction with potassium metal, followed by the sorption of extra potassium atoms. The crystallographic results show that potassium ions have formed either a tetrahedral K_4^{n+} or possibly a triangular K_3^{m+} cluster in each sodalite cavity of zeolite A. The partially reduced ions of these clusters interact primarily with oxygen atoms (ions) of the zeolite structure. Four potassium ions per unit cell lie on the threefold axes in the large cavity, where each trigonally coordinates to three oxides of a 6-ring. Potassium ions, probably partially reduced, in the 8-ring windows and opposite 4-rings are loosely bonded together by ca. one or two electrons atoms form a triangular which is capped by an 6-ring potassium ion to form a K_7^{4+} cluster. The K_7^{4+} clusters not interact primarily with framework oxygens.

Acknowledgement

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