Ag$^+$ 이온으로 완전히 치환되고 탈수된 두개의 제올라이트 X의 결정구조

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(1996. 3. 22 접수)

Two Crystal Structures of the Vacuum-Dehydrated Fully Ag$^+$-Exchanged Zeolite X

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(Received March 22, 1996)

요 약. Ag$^+$ 이온으로 치환되고 탈수된 두 개의 제올라이트 X의 구조(a=24.922(1) Å, a=24.901(1) Å)를 21 ℃에서 입방공간군 $Fd3$을 사용하여 단결정 X-선 회절법으로 해석하고 구조를 정밀화하였다. 결정은 AgNO$_3$의 수용액을 사용하여 3일간 흐름법으로 이온 교환하였다. 첫 번째 결정은 300 ℃에서 2×10^{-6} torr 하에서 2일간 진공 탈수하였다. 두 번째 결정은 350 ℃에서 진공 탈수하였다. 첫 번째 구조는 Full-matrix 최소자승법 정밀화 계산에서 $I>3\sigma(I)$인 227개의 독립 반사를 사용하여 최종 오차 인자를 R_1=0.095, R_2=0.092까지 정밀화 계산하였고, 두 번째 구조는 334 개의 독립 반사를 사용하여 R_1=0.096, R_2=0.087까지 정밀화시켰다. 첫 번째 결정에서 Ag는 서로 다른 5개의 결정학적 자리에 위치하였다. 16개의 Ag$^+$ 이온은 D6R의 중심에 있는 자리 I를 채우면서 위치하고, 32개의 Ag원자는 D6R의 맞은편에 있는 소다라이트 공동에 있는 자리 I'에 위치하였고, 17개의 Ag$^+$ 이온은 큰 공동에 있는 6-산소 링에서 소다라이트 공동 내의 32-중축을 가진 II'에 위치하고, 15개의 Ag$^+$ 이온은 큰 공동에 32-중축을 가진 II에 위치하고, 나머지 12개의 Ag$^-$ 이온은 2중축을 약간 벗어난 큰 공동에 있는 III'에 위치하였다. 두 번째 결정에서 모든 Ag종은 첫 번째 결정과 유사한 자리에 있었다. 자리 I에 16개, 자리 I'에 28개, 자리 II에 16개, 자리 II'에 16개, 자리 III에 6개 또 다른 III'에 6개 모두 88개의 Ag종이 위치하였고 4개의 Ag원자는 탈수중에 골조 밖으로 이동하였다. 이들 결정에서 Ag원자는 소다라이트 공동의 중심에서 사면체의 Ag$_4$ 클라스터를 형성하였다. 이 클라스터는 2개의 Ag$^+$ 이온과 배위하여 안정화된다. 클라스터에서 Ag-Ag 거리는 약 3.05 Å이고 은금속에서 Ag-Ag 거리인 2.89 Å보다 약간 길었다. 소다라이트 공동에 위치한 자리 II에서 적어도 2개의 6-링에 위치한 Ag$^+$ 이온은 클라스터에 반드시 배위하며, 뒤틀린 팔면채 온 클라스터인(Ag$_6$)$^{2+}$로 존재한다.

ABSTRACT. Two crystal structures of the vacuum dehydrated Ag$^+$-exchanged zeolite X have been determined by single-crystal X-ray diffraction techniques in the cubic space group $Fd3$ at 21(1) ℃ (a= 24.922(1) Å and a=24.901(1) Å, respectively). Each crystal was ion exchanged in flowing streams of aqueous AgNO$_3$ for three days. The first crystal was dehydrated at 300 ℃ and 2×10^{-6} torr for two days. The second crystal was similarly dehydrated at 350 ℃. Their structures were refined to the final error indices, R_1=0.095 and R_2=0.092 with 227 reflections, and R_1=0.096 and R_2=0.087 with 334 reflections, respectively, for which $I>3\sigma(I)$. In the first crystal, Ag species are found at five different crystallographic

sites: sixteen Ag^+ ions fill the site I, the center of the double 6-ring, thirty-two Ag^0 atoms fill the I' site in the sodalite cavities opposite double six-rings, seventeen Ag^+ ions lie at the 32-fold site II' inside the sodalite cavity at the single six-oxygen ring in the supercage, fifteen Ag^+ ions lie at the 32-fold site II, in the supercage, and the remaining twelve Ag^+ ions lie at site III' in the supercage at a little off two-fold axes. In the second crystal, all Ag species are located similarly as crystal 1; 16 at site I, 28 at site I', 16 at site II, 16 at site II', 6 at site III and 6 at site III'. Total 88 silver species were found per unit cell. The remaining four Ag atoms were migrated out of the zeolite framework to form small silver crystallites on the surface of the zeolite single crystal. In the first structure, the numbers of Ag atoms per unit cell are approximately 32.0 and these may form tetrahedral Ag_4 clusters at the centers of the sodalite cavities. The probable four-atom cluster is stabilized by coordination to two Ag^+ ions. The Ag-Ag distance in the cluster, ca. 3.05 Å, is a little longer than 2.89 Å, Ag-Ag distance in silver metal. At least two six-ring Ag^+ ions on sodalite cavity (site II') must necessarily approach this cluster and this cluster may be viewed as a distorted octahedral silver cluster, $(Ag_6)^{2+}$.

INTRODUCTION

Metal ions in zeolites can be readily reduced. For example, Ni^{2+} ions in zeolite Y can be reduced to Ni^+ by sodium vapor, and to the metallic state by hydrogen.[1] Cu^{2+} ions in CuNa-Y were reduced to Cu^+ after treatment with carbon monoxide at elevated temperatures. On the other hand, the reduction of Cu^{2+} ions by hydrogen gas gave Cu^0.[2] The dipositive cations of the relatively volatile elements Hg, Cd, and Zn can be removed as atoms from zeolite X by heating in hydrogen.[3]

Silver ions in zeolites can be reduced by heating, by reaction with reducing agents, or by sorption of metal vapors. Tsutsumi and Takahashi[4] reported that Ag^+ ions in zeolite Y could be reduced to bulk clusters of Ag^0 after treatment with alcohols and alkylbenzene. Ag^+ ions in Ag-X and Ag-Y were also reduced after treatment with carbon monoxide at 350 ℃.[5] Matsumoto et al.[6] found that Ag^+-exchanged zeolite A is thermally unstable and loses its crystal structure at a lower temperature than Na_{12}-A does.[7] According to them, the more Ag^+ ions exchanged to zeolite A, the less its thermal stability. Beyer[8] also found that about 70% of the Ag^+ ions in zeolite A were reducible by hydrogen after dehydrated at 150 ℃, and that about 92% of the Ag^+ ions were reducible at 330 ℃. Beyer, Jacobs, and Uytterhoeven[9] reported that polynuclear cations of mean or approximate composition Ag^{3+} form upon partial reduction of dehydrated fully Ag^+-exchanged zeolite Y.

Ag^+ ions in zeolite A[10,11] are autoreduced upon dehydration to form uncharged silver cluster, Ag_6, each within a cube of eight Ag^+ ions, each near the plane of a six-oxygen ring. The number of silver clusters has been found to depend upon the dehydration and temperature. These clusters, of $(Ag_6)^0$ stabilized by coordination to eight Ag^+ ions, may be also viewed as $(Ag_{14})^{8+}$.

Schoonheydt and Leeman[12] studied the formation of the Ag_6^{x+} cluster upon H_2 reduction of zeolite AgM-A ($M = Na^+$, K^+, Cs^+, and Ca^{2+}) over the temperature range 258~298 K. They found that the diffusion of the cation with the highest activation energy determines the rate of formation of Ag_6^+ clusters. Its activation energy, determined from the temperature dependence of the initial rate of the Ag_6^+ cluster formation, was established to be in the range of 47~63 KJ/mol, for samples with 3, 4, and 6 Ag^+ ions per unit cell.

This work was initiated to investigate the cation distribution in the crystal structure of dehydrated fully Ag^+-exchanged zeolite X. The Ag^+ ions in zeolite X are autoreduced upon dehydration.[13,14] Therefore, it was also expected to determine the structure of new silver clusters within the cavities of zeolite X by single crystal X-ray diffraction techniques.

EXPERIMENTAL SECTION

Large single crystals of sodium zeolite X, stoichiometry $Na_{92}Al_{92}Si_{100}O_{384}$, were prepared in St.

Petersburg, Russia.[15] Each of two single crystals, a colorless octahedron ca. 0.22 mm (crystal 1) and ca. 0.25 mm (crystal 2) in cross-section was lodged in a fine Pyrex capillary.

$AgNO_3$ (0.05 M) was allowed to flow past the crystal at about 1 cm/sec for 3 days. Since the exchange of Ag^- for Na^+ has been shown to be facile and complete after milder treatment, complete exchange was assured in this case.[16] One crystal was dehydrated at 300 °C and 2×10^{-6} torr for two days and the other was dehydrated at 350 °C and 2×10^{-6} torr for two days. After cooling to room temperature, each crystal, still under vacuum, was sealed in its capillary by torch. Microscopic examination showed that the crystal 1 had become dark gray and crystal 2 had become black after dehydration, respectively.

The cubic space group $Fd3$ was used throughout this work. The unit cell constants at 21(1) °C determined by least-squares refinements of 25 intense reflections for which $22°<2\theta<27°$ are $a = 24.922(1)$ Å for crystal 1 and $14°<2\theta<22°$ are $a = 24.901(1)$ Å for crystal 2, respectively. Of the 1184 reflections for both crystals 1 and 2, respectively, only the 227 and 334, reflections, respectively, for which $I>3\sigma(I)$ were used in subsequent structure determinations. An absorption correction ($\mu R = 0.38$, $\rho_{cal} = 2.316$ g/cm³ and F(000)=9944 for crystal 1, and $\mu R = 0.37$, $\rho_{cal} = 2.264$ g/cm³ and F(000)=9719 for crystal 2) was made empirically using a ψ scan for each crystal.[18] The calculated transmission coefficients ranged from 0.982 to 0.989 for crystal 1, and 0.984 to 0.987 for crystal 2, respectively. This correction had little effect on the final R indices. Other details are the same as previously reported.[19]

STRUCTURE DETERMINATION

The crystal structures were solved in the cubic space group $Fd3$. This is established for zeolite X, and is consistent with the systematic absences observed.

Dehydrated Ag₉₂-X at 300°C. Full-matrix least-squares refinement of dehydrated Ag_{92}-X was initiated with atomic parameters of the framework atoms [Si, Al, O(1), O(2), O(3) and O(4)] in

dehydrated K_{92}-X.[16] Initial isotropic refinement of the framework atoms converged to an unweighted R_1 index, $(\Sigma|F_o-F_c|)/\Sigma F_o)$ of 0.50 and a weighted R_2 index, $(\Sigma w(F_o-|F_c|)^2/\Sigma wF_o^2)^{1/2}$ of 0.56.

A difference Fourier function revealed two large peaks at (0.0, 0.0, 0.0) and (0.245, 0.245, 0.245) with heights of 10.0 and 7.68 eÅ⁻³, respectively. These two peaks were stable in least-squares refinement. Isotropic refinement including these Ag^+ ions at Ag(1) and Ag(4) positions converged to $R_1=0.37$ and $R_2=0.45$ with occupancies of 16.3(2) and 15.0(4), respectively (see Table 1).

A subsequent difference Fourier synthesis showed the positions of Ag^0 atoms at Ag(2), (0.082, 0.082, 0.082), with peak height 8.3 eÅ⁻³; Ag^+ ions at Ag(3), (0.184, 0.184, 0.184), with peak height 5.2 eÅ⁻³. These were stable in least-squares refinement, and anisotropic refinement of framework atoms and isotropic refinement of Ag(2) and Ag(3) converged to $R_1=0.129$ and $R_2=0.121$ with occupancies of 32.7(4) and 17.4(4), respectively.

From a successive difference Fourier, one peak was found at (0.42, 0.06, 0.05), height=4.75 eÅ⁻³, which was refined as Ag(5). Simultaneous positional and isotropic thermal parameter refinement with varied occupancy numbers converged to the error indices $R_1=0.119$ and $R_2=0.108$. The occupancy numbers of Ag(1), Ag(2), Ag(3), Ag(4) and Ag(5) per unit cell were refined to 16.3(2), 32.7(4), 17.4(4), 15.0(4), and 12.7(8), respectively. Anisotropic refinement of all except for Ag(5), which was refined isotropically converged to $R_1=0.093$ and $R_2=0.091$ (see Table 1). The occupancies of Ag(1), Ag(2), Ag(3), Ag(4), and Ag(5) were fixed at the values shown in Table 1 considering the cationic charge per unit cell (+92 per $Fd3$ unit cell).

All shifts in the final cycles of least-squares refinement were less than 0.1% of their corresponding standard deviations. The final error indices converged to $R_1=0.094$ and $R_2=0.091$. (The structure was refined to the final error indices $R_1=0.146$ and $R_2=0.096$ with 351 reflections for which $I>1\sigma(I)$.) The final difference function was featureless except for a peak at (0.0, 0.0, 0.5) of height 1.60 eÅ⁻³. This peak was not within bonding distance of any other atom, and was not considered

Table 1. Positional,[a] thermal, and occupancy parameters
Crystal 1. Ag₉₂-X dehydrated at 300 ℃

Atom	Sites	Wyc. Pos.	x	y	z	β_{11}[b] B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy[c] varied	fixed
Si		96(g)	−516(6)	363(6)	1240(7)	6(3)	4(3)	8(3)	4(5)	−2(7)	−13(6)		96
Al		96(g)	−509(6)	1230(7)	370(6)	4(3)	1(2)	8(3)	−4(7)	−4(6)	−0(6)		96
O(1)		96(g)	−1020(10)	20(20)	980(10)	2(5)	18(7)	9(6)	10(10)	−20(10)	−30(10)		96
O(2)		96(g)	−20(10)	0(10)	1450(10)	21(7)	6(5)	10(6)	30(10)	−10(20)	−30(10)		96
O(3)		96(g)	−270(10)	670(10)	720(10)	40(10)	8(7)	2(6)	−0(20)	4(20)	−10(10)		96
O(4)		96(g)	−730(10)	780(10)	1710(10)	10(7)	11(7)	8(7)	−0(20)	−0(10)	−0(10)		96
Ag(1)	I	16(c)	0	0	0	8(1)	8(1)	8(1)	1(2)	1(2)	1(2)	16.3(2)	16
Ag(2)	I′	32(e)	821(2)	821(2)	821(2)	31(1)	31(1)	31(1)	−17(3)	−17(3)	−17(3)	32.7(4)	32
Ag(3)	II′	32(e)	1849(3)	1849(3)	1849(3)	9(1)	9(1)	9(1)	4(3)	4(3)	4(3)	17.4(4)	17
Ag(4)	II	32(e)	2337(6)	2337(6)	2337(6)	37(2)	37(2)	37(2)	58(5)	58(5)	58(5)	15.0(4)	15
Ag(5)	III′	96(g)	4290(3)	800(30)	−50(30)	13(2)[d]						12.7(8)	12

Crystal 2. Ag₉₂-X dehydrated at 350 ℃

Atom	Sites	Wyc. Pos.	x	y	z	β_{11}[b] B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy[c] varied	fixed
Si		96(g)	−528(4)	1240(4)	370(3)	8(2)	12(2)	2(1)	0(4)	−4(3)	1(3)		96
Al		96(g)	−503(3)	360(4)	1241(4)	2(1)	6(2)	10(2)	2(3)	−1(4)	8(3)		96
O(1)		96(g)	−1017(8)	10(10)	997(9)	7(4)	30(5)	19(5)	−2(9)	−22(7)	−34(8)		96
O(2)		96(g)	3(9)	−17(9)	1478(7)	18(4)	6(3)	12(3)	9(7)	3(8)	−28(7)		96
O(3)		96(g)	−272(7)	699(8)	677(8)	13(4)	7(4)	9(4)	4(8)	−5(8)	3(7)		96
O(4)		96(g)	−715(7)	791(8)	1716(7)	12(4)	17(4)	1(3)	−22(8)	−7(7)	−5(6)		96
Ag(1)	I	16(c)	0	0	0	10(1)	10(1)	10(1)	−1(1)	−1(1)	−1(1)	16.5(2)	16
Ag(2)	I′	32(e)	813(2)	813(2)	813(2)	27(1)	27(1)	27(1)	−11(2)	−11(1)	−11(2)	27.7(8)	32[e]
Ag(3)	II′	32(e)	1862(2)	1862(2)	1862(2)	13(1)	13(1)	13(1)	14(2)	14(2)	14(2)	16.8(4)	16
Ag(4)	II	32(e)	2320(3)	2320(3)	2320(3)	18(1)	18(1)	18(1)	24(2)	24(2)	24(2)	16.3(3)	16
Ag(5)	III′	96(g)	4150(30)	700(30)	120(30)	10(2)[d]						6.6(5)	6
Ag(6)	III	48(f)	3960(20)	1250	1250	13(2)						5.5(3)	6

[a]Positional and anisotropic thermal parameters are given × 10⁴. 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. [d]Isotropic thermal parameter in units of Å². [e]The occupancy number was not fixed at 32 in the least-square refinement but used this number in the discussion as a representative unit cell.

any further.

Dehydrated Ag₉₂-X at 350°C. Full-matrix least-squares refinement was initiated by using the atomic parameters of framework atoms of the previous dehydrated Ag₉₂-X at 300 ℃. Anisotropic refinement of the framework atoms converged to an unweighted R_1 index of 0.51 and a weighted R_2 index of 0.58, respectively.

A difference Fourier function revealed two large peaks at (0.0, 0.0, 0.0) and (0.246, 0.246, 0.246) with heights of 14.5 and 8.7 eÅ⁻³. These two peaks were stable in least-squares refinement. Isotropic refinement including the Ag⁺ ions at Ag(1) and Ag(4) positions converged to $R_1 = 0.392$ and $R_2 = 0.473$ with occupancies of 16.5(2) and 16.3(3), respectively (see *Table* 1).

A subsequent difference Fourier synthesis showed the positions of Ag species at Ag(2), (0.082, 0.082, 0.082), with peak height 13.2 eÅ⁻³ and Ag⁺ ions at Ag(3), (0.182, 0.182, 0.182), with peak height 9.7 eÅ⁻³. These were stable in least-squares refinement, and anisotropic refinement of framework

atoms and isotropic refinement of Ag(2) and Ag(3) converged to $R_1=0.141$ and $R_2=0.134$ with occupancies of 27.7(8) and 16.8(4), respectively.

A subsequent difference Fourier synthesis showed the positions of Ag^+ ions at Ag(5), (0.42, 0.06, 0.05), with peak height 2.7 $e\text{Å}^{-3}$ and Ag^+ ions at Ag(6), (0.41, 0.125, 0.125), with peak height 2.6 $e\text{Å}^{-3}$. Simultaneous positional and isotropic thermal parameter refinement with varied occupancy numbers converged to the error indices $R_1=0.121$ and $R_2=0.105$. Anisotropic refinement of the framework atoms and of Ag species at Ag(1), Ag(2), Ag(3), and Ag(4) except for Ag(5) and Ag(6) which were refined isotropically converged to $R_1=0.096$ and $R_2=0.085$ (see Table 1). The occupancy numbers of Ag(1), Ag(2), Ag(3), Ag(4), Ag(5), and Ag(6) per unit cell were refined to 16.5(2), 27.7(8), 16.8 (4), 16.3(3), 6.6(5), and 5.5(3), respectively. The occupancies of Ag(1), Ag(3), Ag(4), Ag(5), and Ag(6) were fixed except for Ag(2) at the values shown in Table 1.

All shifts in the final cycles of least-squares refinement were less than 0.1% of their corresponding standard deviations. The final error indices converged to $R_1=0.096$ and $R_2=0.085$. (The structure was refined to the final error indices $R_1=0.130$ and $R_2=0.091$ with 473 reflections for which $I>1\sigma(I)$.) The final difference function was featureless except for a peak at (0.277, 0.973, 0.777) of height 0.74 $e\text{Å}^{-3}$. This peak was not within bonding distance of any other atom, and was not considered further.

Atomic scattering factors[20,21] for Si, Al, O^-, Ag^0, and Ag^+ were used. All scattering factors were modified to account for anomalous dispersions.[22] The final structural parameters and selected interatomic distances and angles are presented in Table 1 and 2, respectively.

DISCUSSION

Zeolite X, a synthetic version of the mineral faujasite, has an open, negatively charged framework (see Fig. 1). Its framework structure is composed of 192 corner-shared SiO_4 and AlO_4 tetrahedra per cubic unit cell; $a\cong25.0\text{ Å}$.[23] If the number of Al

Table 2. Selected interatomic distances(Å) and angles (deg)[a] for dehydrated Ag_{92}-X

	Crystal 1	Crystal 2
Si-O(1)	1.66(3)	1.60(3)
Si-O(2)	1.62(4)	1.68(2)
Si-O(3)	1.62(3)	1.67(2)
Si-O(4)	1.65(3)	1.63(2)
Al-O(1)	1.61(4)	1.66(2)
Al-O(2)	1.69(4)	1.68(2)
Al-O(3)	1.75(3)	1.74(2)
Al-O(4)	1.69(4)	1.68(2)
Ag(1)-O(3)	2.55(3)	2.52(2)
Ag(2)-O(3)	2.76(3)	2.74(2)
Ag(3)-O(2)	2.52(3)	2.47(2)
Ag(4)-O(2)	2.29(3)	2.20(2)
Ag(5)-O(1)	2.62(7)	2.55(8)
Ag(5)-O(4)	3.04(7)	2.86(8)
Ag(6)-O(1)		3.34(3)
Ag(6)-O(4)		2.47(5)
Ag(1)-Ag(2)	3.55(1)	3.51(1)
Ag(2)-Ag(2)	3.02(1)	3.08(1)
Ag(2)-Ag(3)	2.63(1)	2.68(1)
O(1)-Si-O(2)	115(2)	111(1)
O(1)-Si-O(3)	103(2)	106(1)
O(1)-Si-O(4)	111(2)	114(1)
O(2)-Si-O(3)	103(2)	104(1)
O(2)-Si-O(4)	111(2)	108(1)
O(3)-Si-O(4)	113(2)	113(1)
O(1)-Al-O(2)	108(2)	114(1)
O(1)-Al-O(3)	107(2)	102(1)
O(1)-Al-O(4)	112(2)	111(1)
O(2)-Al-O(3)	107(2)	108(1)
O(2)-Al-O(4)	111(2)	110(1)
O(3)-Al-O(4)	112(2)	111(1)
Si-O(1)-Al	147(2)	147(1)
Si-O(2)-Al	139(2)	135(1)
Si-O(3)-Al	130(2)	129(1)
Si-O(4)-Al	142(2)	145(1)
O(3)-Ag(1)-O(3)	96(1)	95.6(6)
O(3)-Ag(2)-O(3)	76.4(9)	76.3(6)
O(2)-Ag(3)-O(2)	95(1)	94.6(7)
O(2)-Ag(4)-O(2)	109(1)	111.1(8)
O(4)-Ag(5)-O(4)	109(2)	113(2)
O(1)-Ag(6)-O(1)	103(1)	

[a]Numbers in parentheses are estimated standard deviations in units of the least significant digit given for the corresponding value.

ions=number of Si ions=96, and Loewenstein's rule[24] is obeyed, the space group of the framework
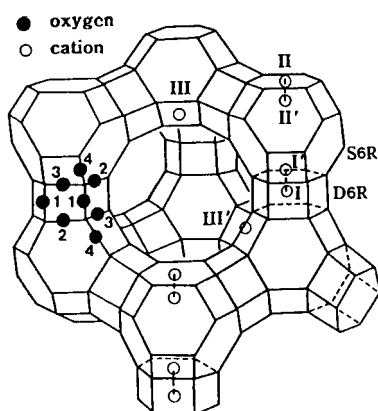
● oxygen
○ cation

Fig. 1. A stylized drawing of the framework structure of zeolite X. Near the center of the each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1 to 4. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that Si substitutes for about 4% of the Al's. Extraframework cation positions are labeled with Roman numerals.

alone is precisely $Fd\bar{3}$.

The basic building unit of zeolite X can be considered to be the sodalite cavity, a truncated octahedron (cubooctahedron) of composition $Si_{12}Al_{12}O_{36}$. Its faces are eight 6-rings (12-membered $Si_3Al_3O_6$ rings whose apertures are defined by the six large oxygens) and six 4-rings (8-membered $Si_2Al_2O_4$ rings). The sodalite units are arranged tetrahedrally in space like the carbon atoms in diamond. Each bonded pair of sodalite units is joined at 6-rings by six additional oxygen atoms, each of which bridges from an Al of one sodalite unit to a Si of the other; only alternating (tetrahedrally arranged) 6-rings of each sodalite unit are used. This leads to the existence of small double 6-ring (D6R) cavities, single 6-rings (S6R's) which were not used in joining, and large supercages. Each supercage has access to four other supercages through near-circular 12-rings (24-membered $Si_6Al_6O_{12}$ rings) and to four sodalite units through 6-rings. Each unit cell contains eight supercages, eight sodalite units, and sixteen D6R's.

The sodalite unit, which nearly has O_h symmetry in zeolite A, has only Td symmetry in zeolite X. The eight 6-rings, equivalent in zeolite A, be-

come four tetrahedrally arranged single 6-rings (S6R's) and four tetrahedrally arranged D6R's in zeolite X, whose sodalite cavity is therefore severely tetrahedrally distorted. The electronegativities of the four types of oxygens in faujasites are necessarily different by symmetry. Of course, the presence of the small D6R cavities and of the larger supercage cavities contribute to give faujasite its unique character.

Exchangeable cations, which balance the negative charge of the aluminosilicate framework, are found within the zeolite's cavities. They are usually found at the following sites, shown in *Fig.* 1: site I at the center of a D6R (alternatively called the hexagonal prism), site I' in the sodalite (β) cavity on the opposite side of one of the D6R's 6-rings from site I, site II' inside the sodalite cavity near a S6R entrance to the supercage, site II in the supercage opposite a S6R from site II', site III in the supercage on a twofold axis opposite a 4-ring between two 12-rings, and site III' somewhat off III (off the twofold axis)[25] (see *Fig.* 1).

In both structures, Ag species are found at five and/or six different crystallographic sites.

Sixteen Ag⁺ ions at Ag(1) lie at site I at the center of a double six-oxygen ring (D6R). This 16-fold position is fully occupied. Each Ag⁺ ion at Ag(1) is coordinated by six O(2) oxygen atoms of hexagonal prism at distance of ca. 2.54 Å, which is very similar to the sum of the ionic radii of Ag⁺ and O-2, $1.26 + 1.32 = 2.58$ Å.[26]

Ag species at Ag(2) are located at site I' in the sodalite cavity opposite double six rings (D6R's). Each species at Ag(2) is recessed *ca.* 1.93 Å into the sodalite cavity from its 6-ring plane. This 32-fold position is also fully occupied (this indicates that four Ag species at Ag(2) are present at the every sodalite unit). The distance between Ag(2) and its nearest framework oxide ions, again at O (3), is ca. 2.75 Å, which is almost the same distance between Ag atom and framework oxygen, 2.78 Å in the previous studies.[10,11] Therefore, this species may be a reduced Ag⁰ atom and not a Ag⁺ ion. The distance between Ag(2) and Ag(2) is *ca.* 3.05 (1) Å, which indicates that four Ag atoms in the sodalite unit must form a tetrahedral silver clus-

ter, Ag_4.

The distance between Ag(1) and Ag(2), ca. 3.53 Å, is too long to be a Ag^0-Ag^0 bond (2.89 Å[27] in silver metal) and this distance is close to Ag^+-Ag^0 contact distance of 3.31 Å in Ag-A, and of 3.24 Å in Ag-Y. Therefore the Ag(1)-Ag(2) distance may be an Ag^0-Ag^+ coordination contact distance.

The distance, Ag(1)-Ag(2) ca. 3.53(3) Å, shows clearly that the bonding electron density is predominantly located on the central four silver atoms, although complication requires that some of it be delocalized onto the Ag^+ ions at Ag(1). In the previous study,[28] Ag^+ ions are found to be reduced by the following reaction within sodalite unit.

$$Ag_3(H_2O)_3^{3-} \rightarrow Ag^- + Ag_2(H_2O)^{2+} + 2H_2O$$
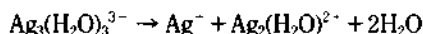
which is the penultimate step of the dehydration process, followed by

$$Ag_2(H_2O)^{2+} \rightarrow 2H^+ + 2Ag + 1/2O_2$$
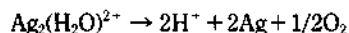
Gellens and Schooheydt studied[12,27,28] Ag^+-faujasite-type zeolites by reflectance spectroscopy. Ag^+-faujasites are autoreduced by dehydration to form uncharged silver cluster and charged di and trisilver clusters in low-Al zeolites. They also found, independent of the Al/Si ratio, that reduction with hydrogen produces Ag atoms which forms uncharged Ag clusters inside or outside the zeolite. It has been shown by a variety of techniques that small silver clusters, neutral and charged silver
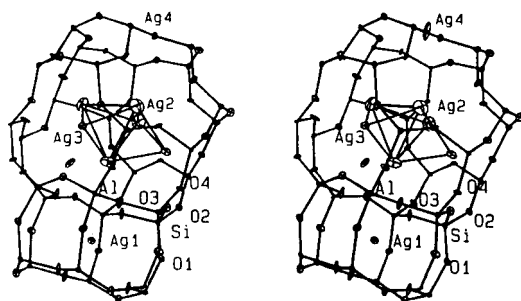

Fig. 2. A stereoview of sodalite cavity containing an tetrahedral Ag molecule within a linear of two Ag^+ ions is shown. All D6R's are filled as shown with Ag^+ ions at Ag(1). Four Ag^0 ions at Ag(2), two Ag^+ ions at Ag(3) and two Ag^+ ions at Ag(4) are shown. Ellipsoids of 20% probability are shown.

species are stabilized in the cavities and channels of zeolites A, X, and Y, chabazite, mordenite, and Rho.[29]

The Ag^+ ions at Ag(3) lie at site II' inside sodalite cavity of the six-membered ring in the supercage (site II). This is 32-fold position, but it is only about half occupied. Each Ag^+ ion at Ag(3) coordinates at ca. 2.50 Å to three O(2) framework oxygens, and is recessed ca. 1.31 Å into the sodalite cavity from their oxygen plane. The positions of Ag^+ ions at Ag(3) are close to site I' (distance between site I' and Ag^+ at Ag(3) is ca. 2.66 Å).

Ag(2)-Ag(3) distances, ca. 2.66(1) Å, is almost the same as the sum of ionic radius of Ag^+ and atomic radius of Ag^0, 1.26+1.44=2.70 Å.[29] The probable four-atom cluster forms a tetrahedral Ag_4 cluster and shows the full symmetry of its site, Td, at the center of the sodalite cavity (see Fig. 2 and 3). Each of two Ag^+ ions at Ag(3) coordinates to three Ag^0 atoms of Ag_4 cluster to form Ag_6^{2+} cluster. The Ag_6^{2+} cluster is stabilized by charge delocalization, with some additional electron density from the bridging Ag(3) silver ions. The nearly spherical but large thermal ellipsoids (see Fig. 2 and 3) observed for the atoms of the silver clusters in the structures indicate that these atoms are loosely held in place.

The preference of Ag^+ ions for site I in Ag-X and Y was further confirmed by Gellens et al. by powder X-ray methods.[13,14] As the Al/Si ratio increased, the occupancy of Ag^+ ions in the sodalite units (at I' and II') increased. All silvers in the sodalite cavities of Ag-X and Ag-Y were on 3-fold axes. Gellens found that the maximum number
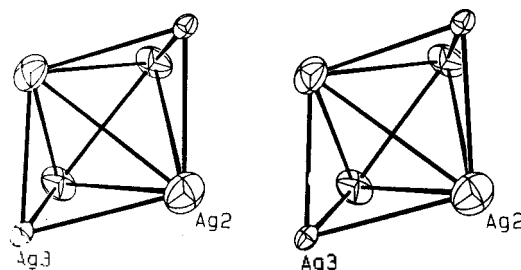

Fig. 3. The tetrahedral Ag_4 molecule, stabilized by coordination to two Ag^+ ions is shown. Ellipsoids of 20% probability are shown.

of Ag^+ ions in a sodalite cavity of vacuum dehydrated Ag-X or Ag-Y was 4, the same number as the present work.

About sixteen Ag^+ ions at Ag(4) lie at site II and are recessed ca. 0.73 Å into the supercage from the single 6-ring plane at O(2). This 32-fold position is also half occupied. The distance between Ag(4) and the nearest oxygen at O(2) is quite short, ca. 2.25 Å, which is the same distance of Ag^+ ion to framework oxygens in the structure of partially decomposed Ag_{12}-A.[10,11] This indicates that the silver species at Ag(4) must be the ions, Ag^+. The angle subtended at Ag(4), O(2)-Ag(4)-O (2) is ca. 110.1°. The present results show that the number of Ag^+ ions at Ag(3) is approximately equal to the number of Ag^+ ions at Ag(4). These positions are 32-fold but only one half of thirty-two such positions are occupied.

An Ag(2)-Ag(4) distance, ca. 4.52 Å, is substantially longer than the Ag(2)-Ag(3) distance, ca. 2.66 Å. The Ag^+ ions at Ag(4) are not associated with Ag^0 atoms at Ag(2).

In the structure of dehydrated Ag_{92}-X at 300 ℃, twelve Ag^+ ions at Ag(5) lie in the supercage at site III'. This is 96-fold position, but this is occupied by only twelve Ag^+ ions. The Ag^+ ions at Ag(5) are also loosely held to framework oxygens Ag(5)-O(1)=2.62(7) Å and Ag(5)-O(4)=3.04(7) Å. These distances are substantially longer than the sum of the ionic radii. Such long interaction distances have been observed previously in supercage (and/or large cavity) of other X and A struc-

tures.[11,30]

In the structure of dehydrated Ag_{92}-X at 350 ℃, the Ag^+ ions at Ag(5) and Ag^+ ions at Ag(6) lie in the supercage at two different III and III' sites, respectively. These positions are 48-fold and 96-fold positions, respectively. In this structure, only 6 Ag^+ ions are found at Ag(5) and only 6 at Ag(6). The Ag^+ ions at Ag(5) bond strongly to framework oxygens (Ag(5)-O(4)=2.55(8) and Ag(5)-O(1)= 2.86(8) Å) and the Ag^+ ions at Ag(6) bond more strongly to the framework oxygens (Ag(6)-O(4)= 2.47(5) and Ag(6)-O(1)=3.34(3) Å) (see Fig. 2, 3, and 4). The comparison of two structures show that the number of Ag^+ ions at Ag(5) at crystal 1 (site III') is approximately equal to the sum of occupancy numbers of Ag^+ ions at Ag^+ at Ag(5) and that at Ag(6) in crystal 2.

Only about twenty-eight silver atoms for crystal 2 were found per unit cell (see Table 1). Apparently the remaining ca. 4.0 Ag^+ ions per unit cell were reduced during the dehydration and have migrated out of the zeolite framework to form small silver crystallites on the surface of the zeolite single crystal, accounting for its black color of the second crystal.

In summary, fully Ag^+-exchanged zeolite X was successfully synthesized and its structure was determined by X-ray diffraction methods. In these structures, all Ag cations are located in the sites I, I', II, II', III and III'. The Ag^+ ions are observed

Table 3. Deviations(Å) of cations from 6-ring planes

	Crystal 1	Crystal 2
at O(3)a		
Ag(1)	−1.61(1)	−1.59(1)
Ag(2)	1.93(1)	1.92(1)
at O(2)b		
Ag(3)	−1.32(1)	−1.30(1)
Ag(4)	0.78(1)	0.67(1)

a A positive deviation indicates that the atom lies in the sodalite unit. b A positive deviation indicates that the atom lies in the supercage.
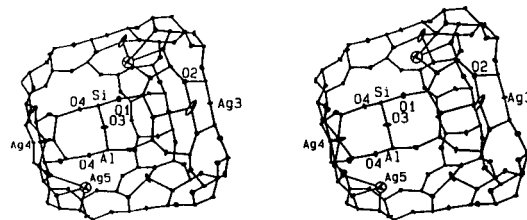

Fig. 4. A stereoview of supercage of dehydrated Ag_{92}-X at 300 ℃. Two Ag^+ ions at Ag(3), two Ag^+ ions at Ag(4) and two Ag^+ ions at Ag(5) are shown. About 50% of supercages may have this arrangement. About 37.5% of supercages may have two Ag^+ ions at Ag(3), two Ag^+ ions at Ag(4) and one Ag^+ ion at Ag(5). The remainder may have three Ag^+ ions at Ag(3), one Ag^+ ion at Ag(4) and one Ag^+ ion at Ag(5). Ellipsoids of 20% probability are shown.
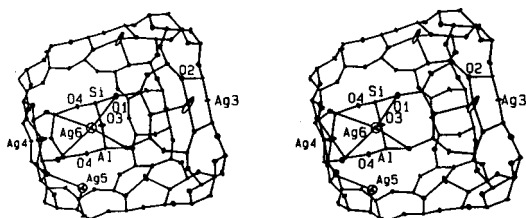
Fig. 5. A stereoview of supercage of dehydrated Ag_{92}-X at 350 °C. All the supercages have two Ag^+ ions at Ag(3) and two Ag^+ ions at Ag(4). About 50% supercages may have one Ag^+ ion Ag(5) and one Ag^+ ion at Ag(6). The remainder may have either one Ag^+ ion at Ag(5) or one Ag^+ ion at Ag(6). Ellipsoids of 20% probability are shown.

almost in all kinds of cavities shown in *Fig.* 2, 3, 4, and 5. The tetrahedral silver cluster, Ag_4 is formed at the center of the every sodalite cavity. At least two six-ring Ag^- ions on sodalite cavity (site II') must necessarily approach this cluster, Therefore, this cluster may be viewed as a distorted octahedral silver cluster, $(Ag_6)^{2+}$.

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