BULLETIN OF THE

KOREAN CHEMICAL SOCIETY

VOLUME 5, NUMBER 4, AUGUST 20, 1984

# An X-ray Diffraction Study of Na, Ag-A Reduced by Hydrogen. Ag$_3^+$ and Ag$_3^{2+}$ Clusters

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The reduction of vacuum-dehydrated Na$_x$Ag$_{12-x}$-A, $0 \leq x \leq 9.2$, and its reoxidation by O$_2$, have been studied by X-ray powder diffraction. Also, the structure of Na$_6$Na$_6$-A treated with hydrogen at room temperature has been studied by single crystal methods in the cubic space group *Pm*3*m* at 24°C ($a$ = 12.221(2) Å). The diffraction pattern of dehydrated Ag$_{12}$-A reduced by H$_2$ contains only the (111) and (200) reflections of silver metal, indicationg that the zeolite structure has been lost, but the zeolite's diffraction pattern and structural integrity can be fully restored by oxidation with O$_2$ at 100 or 200°C. In contrast, the structures of Na$_x$Ag$_{12-x}$-A, $x$=4.5 and 9.2, were not destroyed by treatment with hydrogen. Dehydrated Na$_6$Ag$_6$-A treated with 50 Torr of hydrogen gas at 24°C for 30 minutes has 6 Na$^+$ and 1.27 Ag$^+$ ions at 6-ring sites. These Ag$^+$ ions are associated with 2.54 Ag$^0$ atoms to form 1.27 Ag$_3^+$ clusters per unit cell. Also found were 0.7 Ag$_3^{2+}$ clusters per unit cell near the 8-rings. The structure was refined to the final error indices $R_1$ = 0.134 and $R_2$ (weighted) = 0.147, using 168 independent reflections for which $I_0 > 3\sigma(I_0)$.

## Introduction

Metal clusters are of interest because of their importance in catalysis. Silver clusters are likely to be good models for clusters of other elements. Zeolites containing both Ag$^0$ and Ag$^+$ are important in partial oxidation processes such as the formation of ethylene oxide from ethylene and oxygen.[1] Partially decomposed, fully Ag$^+$-exchanged zeolite A,[2,3] containing a hexasilver cluster coordinated to eight Ag$^+$ ions in a fraction of its sodalite units,[4] exposed to oxygen and then amonia, partially oxidizes the ammonia to form the saturated hydronitrogens, triazane (N$_3$H$_3$) and cyclotriazane (N$_3$H$_5$).[5] Ag$^+$-exchanged zeolite Y was found to cleave water into hydrogen and oxygen by a photochemically induced redction of Ag$^+$, followed by the oxidative thermal desorption of hydrogen.[6]

Ag$^+$ ions in zeolite are very sensitive to chemical treatment. Upon dehydration of Ag$^+$-exchanged zeolite A and of the faujasite type zeolites, autoreduction of Ag$^+$ ions occurs with formation of small metal clusters[2,3] and of silver microcrystallites outside the zeolites.[2,3,7]

Ag$^+$ in zeolite A can be reduced by treatment with reducing agents. Tsutsumi and Takahashi reported that Ag$^+$ ions in zeolite Y are reduced to bulk clusters of Ag$^0$ after treatment with alcohols and alkylbenzene.[8] Ag$^+$ ions in Ag-A, Ag-X, and Ag-Y are also reduced by treatment with carbon monoxide.[9] Beyer, Jacobs, and Uytterhoeven reported that polynuclear cations of mean or approximate compositiosition Ag$_3^+$ form upon partial reduction of dehydrated fully Ag$^+$-exchanged zeolite Y.[7] Hydrogen uptake by silver chabasite produced Ag$_4^{2+}$ and Ag$_3^+$ clusters according to epr measurements. In Ag, Na-Y, Ozin *et al.* identified Ag$_5^{4+}$, Ag$_5^{3+}$, and Ag$_5^{2+}$ clusters on the walls of the supercages using fluorescence emission an excitation,diffuse optical reflectance and epr spectroscopy.[11]

Recently, dehydrated crystals of Ag$_{12}$-A treated with hydrogen at 24°C and 150°C were studied.[12] In both cases, the zeolite diffraction pattern was lost and only powder diffraction lines from small crystals of silver metal were seen. Another $Ag_{12}$–A crystal was dehydrated in oxygen gas at 400°C, exposed to hydrogen at 330°C, and treated with oxygen at 330°C. This time the diffraction pattern was quite good, indicating that this crystal, which had been damaged and which had lost silver initially, had repaired itself and had readsorbed silver during the final oxygen treatment. The resulting black-brown crystal contained 11 $Ag^+$ ions and approximately 0.56 $Ag^0$ atoms per unit cell. The color of crystal indicated that it was coated with $Ag_2O$, accounting thereby for the remaining 0.44 silvers.[12] The crystal structure of vacuum-dehydrated $Na_{7.4}Ag_{4.6}$–A treated with $H_2$ at 350 °C, followed by evacuation of $H_2$ at 350 °C, showed that some $Ag^+$ ions were reduced and that $Ag_5^{3+}$ clusters had formed in the large cavity. These silver clusters were associated with 8-ring and 6-ring oxide ions.[4, 13]

Continuing this work, we studied the stability of the $H^+$ form of zeolite A by X-ray diffraction $Na_{12-x}Ag_x$–A ($0 \leq x \leq 9.2$) treated with $H_2$ and then $O_2$, and the structure of the silver clusters by determining the crystal structure of $Na_6Ag_6$–A treated with $H_2$.

## Experimental Section

(*a*) *X-Ray Powder Diffraction.* A sample of $Na_{12}$–A was supplied by the Linde Division of Union Carbide. Portions were exchanged for approximately for a week by a static method[14] using 0.1 *M* $AgNO_3$. After exchange, they were filtered, washed,and air dried, all in darkness. The chemical compositions, determined by atomic absorption spectrometry, were $Ag_{12}$–A, $Ag_{7.5}Na_{4.5}$–A, and $Ag_{2.5}Na_{9.5}$–A.
These sample were dehydrated at 300°C and $10^{-4}$ Torr for one day. X-ray diffraction experiments were performed under following conditions.

X-Ray source: Cu K$\alpha$. power: 15 mA and 35kV. Scan speed: 4°/min. Detector: scintillation counter. The X-ray diffraction patterns are shown in Figures 1 and 2.

(*b*) *Determination of the Structure of a Single Crystal.* To a portion of the powder sample of composition $Ag_{7.5}Na_{4.5}$–A prepared above, a few large crystals of zeolite A prepared by Charnell's method,[15] were added with enough water to submerge all solid particles. It was hoped that large single crystals of similar composition would result at equilibrium, but the actual composition of the crystal studied appears to be $Na_6$ $Ag_6$–A. Equilibrium was apparently not achieved.[14]

An 80 $\mu$m single crystal was selected and lodged in a fine capillary. This clear colorless, hydrated partially $Ag^+$–exchanged zeolite crystal was dehydrated at 350°C for 41 hours and $5 \times 10^{-5}$ Torr. The crystal was then treated with *ca* 50 Torr of $H_2$ has at 24 (1)°C for 30 minutes. The hydrogen was evacuated, and the crystal, still under vacuum, was sealed in its capillary by torch. Microscopic examination showed that the crystal had turned black. Diffraction intensities were then measured at 24°C.

The cubic space group *Pm3m* (no systematic absences) was used instead of *Fm3c* for reasons described previously.[4a, 16, 17] A Syntex four-circle computer-controlled diffractometer with a graphite monochromator and a pulse-height analyzer was used throughout for preliminary experiments

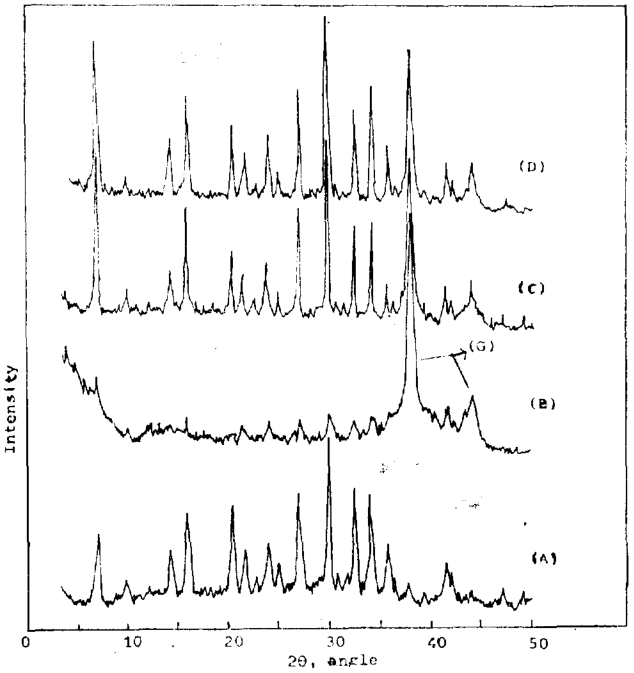

**Figure 1.** X-Ray diffraction of $Ag_{12}$–A; (A) $Ag_{12}$–A dehydrated at 300°C under $10^{-4}$ mmHg; (B) Dehydrated $Ag_{12}$–A treated by flowing $H_2$ gas; (C) Hydrogenated $Ag_{12}$–A treated by flowing $O_2$ at 200°C; (D) Hydrogenated $Ag_{12}$–A treated by flowing $O_2$ at 100 °C; (G) These peaks are (111) and (200) diffractions of silver metal.

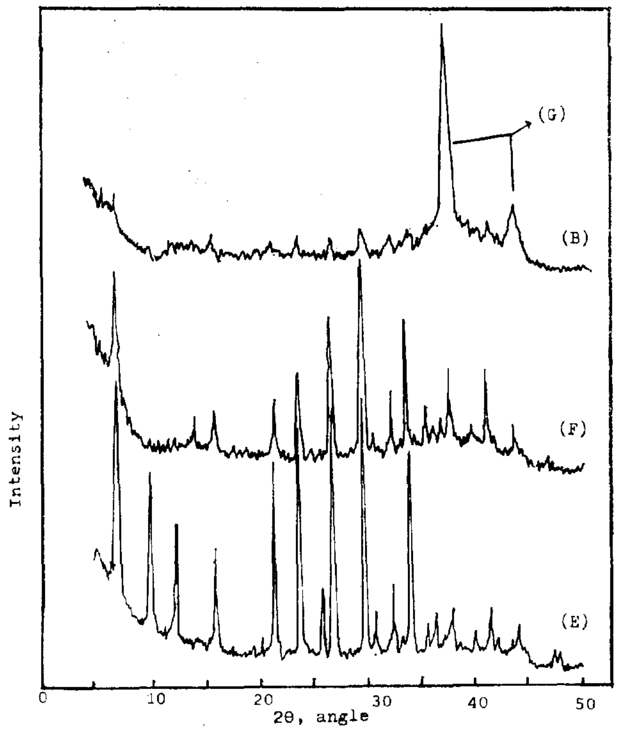

**Figure 2.** X-Ray diffraction of $Na_{12-x}Ag_x$–A; (E) Dehydratde $Na_{9.2}Ag_{2.8}$–A treated by flowing $H_2$; (F) Dehydrated $Na_{4.5}Ag_{7.5}$ –A treated by flowing $H_2$; (B) Dehydrated $Ag_{12.0}$–A treated by flowing $H_2$; (G) These peaks are (111) and (200) diffractions of silver metal.

and for the collection of diffraction intensities. Molybdenum radiation ($K\alpha_1$, $\lambda=0.70930$ Å; $K\alpha_2$, $\lambda=0.71359$ Å) was used. The cell constant, $a=12.221(2)$ Å, was determined by a least-squares treatment of 15 intense reflections for which $20° < 2\theta < 24°$ using $K\bar{\alpha}$, $\lambda=0.71073$ Å. The $\theta$-$2\theta$ scan technique was used. Each reflections was scanned at a constant rate of 2.0 deg $\text{min}^{-1}$ from 1.0° (in $2\theta$) below the calculated $K\alpha_1$ peak to 1.0° above the $K\alpha_2$ maximum. Background intensity was counted at each end of the scan range for a time equal to half the scan time. The intensities of three reflections in diverse regions of reciprocal space were recorded after every hundred reflections to monitor crystal and instrument stability. Only small, random fluctuations of these reflections were noted during the course of data collection.

The intensities of all lattice points for which $2\theta > 70°$ were recorded. Although few reflections were significantly greater than background for high $2\theta$ value, this limit was selected to allow the data set to be more complete.

Standard deviation were assigned to individual reflections according to the formula,

$$\sigma(I) = (\mathrm{w}^2(\mathrm{CT}+B_1+B_2) + (pI)^2)^{1/2}$$

where CT is the total integrated count, $B_1$ and $B_2$ are the background counts, $I$ is the intensity, and w is the scan rate. The value of $p=0.02$ was found to be appropriate for the intrumentation used.[18] Of the 874 symmetry independent reflections measured, 168 had intensities greater than three times their standard deviations, and only these were used in subsequent structure determination. The intensities were corrected for Lorentz and polarization effects;[19] the contribution of the monochromator crystal was calculated assuming it to be half-perfect and half-mosaic in character. Absorption ($\mu=1.96$ $\text{mm}^{-1}$) was judged to be negligible and a correction for it was not applied.[20]

(c) *Structure Determination.* Full-matrix least-squares refinement was initiated with the atomic coordinates of the ethylene sorption complex of $Ag_{12}$-A.[21] The model consisted of all framework positions (Si, Al), 0(1), 0(2), and 0(3)) and a $Ag^+$ position with occupancy variable at a 6-ring site. Convergence occurred with $R_1=(\Sigma|F_0-|F_c||)/\Sigma F_0=0.32$ and $R_2=(\Sigma w(F_0-|F_c|)^2|\Sigma wF_0{}^2)^{1/2}=0.35$.

A subsequent difference Fourier synthesis revealed two important peaks of heights 5.6 and 5.9 $e\text{Å}^{-3}$, esd=0.323 $e\text{Å}^{-3}$, at (0.24, 0.24, 0.5) and (0.19, 0.19, 0.19), respectively. Simultaneous positional and anisotropic thermal parameter refinement, except for Ag(2) and Na(1) which were refined isotropically, converged to $R_1=0.21$ and $R_2=0.23$. The occupancy at Na(1) refined 6.2(7) and was fixed at 6.0. A subsequent difference Fourier synthesis revealed four peaks at (0.36, 0.5, 0.5), (0.09, 0.39, 0.5), (0.33, 0.33, 0.33), and (0.16, 0.36, 0.5) with heights of 1.4 to 2.6 $e\text{Å}^{-3}$, esd=0.24 $e\text{Å}^{-3}$. Only the second and third peaks were stable in least-squares refinement reducing $R_1$ to 0.143 nd $R_2$ to 0.149.

The $Ag^+$ ions can be distingushed from $Na^+$ ions because of the following reasons. Firstly, their atomic scattering factors are quite different, 46 $e^-$ for $Ag^+$ *vs.* 10 $e^-$ for $Na^+$. Secondly, their ionic radii are different, $Ag^+=1.26$ Å and $Na^+=0.97$ Å. Also the approach distances between those ions and zeolite oxide ions in dehydrated $Na_{12}$-A[22] and partially decomposed[2,3] have been determined and indicative. Thirdly, not like $Na^+$ ions, $Ag^+$ ions are easily reduced by $H_2$ and some reduced $Ag^\circ$ atoms may be located far from framework oxide ions. These $Ag^0$ atoms may be closely bound to another Ag ions or $Ag^0$ atoms to form silver clusters. Finally, the requirement that 12 metals or ions be found does not allow the major positions to refine to acceptable occupancies with the alternative assignment of ionic identities.

Occupancy refinements of Ag(1), Ag(2), Ag(3), ag(4), and Na(1) converged to 1.3 (2), 2.4(2), 0.8(2), 1.8(3), and Na (1) (see Table 1). It appeared that the occupancy numbers of Ag(1) and Ag(3) were about one half those of Ag(2) and Ag(4), respectively. The distance between Ag(1) and Ag(2) is 3.30 Å. The approach distance of Ag(2) to the framework oxide ion O(1) is 3.07 Å and that of Ag(1) to the framework O(3) is 2.50 Å. This shows that Ag(1) is an $Ag^+$ ion and that Ag(2) is an $Ag^\circ$ atom. They appear to form $Ag_3{}^+$ clusters. Therefore, the occupancy number of Ag(1) was contrained to maintain at one-half that of Ag(2) in least-squares refinements. Similarly (see discussion), the occupancy number of Ag (3) was reset to one-half that of Ag (4). The final refinement, using anisotropic thermal parameters for all positions except Ag(3) and Ag(4) which were refined isotropically, converged at $R_1=0.134$ and $R_2=0.147$. The largest peak on the final difference Fourier synthesis (esd=0.15 $e\text{Å}^{-3}$) appeared at (0.22, 0.22, 0.5) with height 1.8 ($6^{23}$) $e\text{Å}^{-3}$, and appears to be residual electron density at Ag(2).

The goodness-of-fit, $(\Sigma w(F_0-|F_c|)^2/(m-s))^{1/2}$, is 5.38; m (168) is the number of observations, and s(34) is the number of variables in least-squares. All shifts in the final cycle were less than 5% of their corresponding esd's.

The final structural parameters are presented in Table 1. Interatomic distances and angles are given in Table 2. A likely atomic arrangement in a particular unit cell is shown in Figure 3.

The quantity minimized in least-squares is $(\Sigma w(F_0-|F_c|)^2)$ and the weights ($w$) are the reciprocal squares of $\delta$ ($F_0$), the standard deviation of each observed structure factor. Atomic scattering factors[24] for $O^-$ and $(Si, Al)^{1.75+}$ (the average of $Si^\circ$, $Si^{4+}$, $Al^\circ$, and $Al^{3+}$), $Ag^+$, and $Ag^\circ$ were used. All scattering factors were modified to account for the real components ($\Delta f'$) of the anomalous dispersion correc-

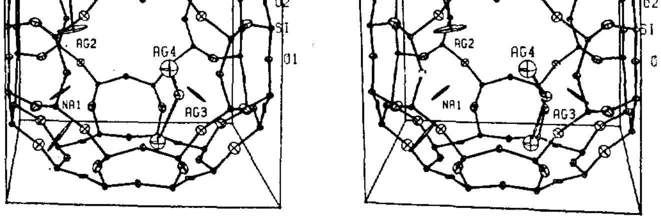

**Figure 3.** A stereoview of the large cavity. Ellipsoid of 20% probability are used.

**TABLE 1: Positional, Thermal,[a] a and Occupancy Parameters of dehydrated $Na_6Ag_6$–A treated with 50 Torr of $H_2$**

| | Wyckoff Position | $x$ | $y$ | $z$ | $\beta_{11}$[b] or $B_{iso}$[c] | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | Occupancy fantor[d] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (Si,Al) | 24($k$) | 0 | 1827(10) | 3696(9) | 29(11) | 18(9) | 17(10) | 0 | 0 | 5(17) | 24.0[e] |
| 0(1) | 12($h$) | 0 | 2231(31) | 5000 | 42(37) | 32(37) | 20(33) | 0 | 0 | 0 | 12.0 |
| 0(2) | 12($i$) | 0 | 2886(24) | 2886(24) | 2(30) | 62(26) | 62(26) | 0 | 0 | 24(74) | 12.0 |
| 0(3) | 24($m$) | 1079(17) | 1079(17) | 3386(22) | 95(20) | 95(20) | 59(32) | 12(69) | 36(42) | 36(42) | 24.0 |
| Ag(1) | 8($g$) | 2312(25) | 2312(25) | 2312(25) | 53(30) | 53(30) | 53(30) | 83(57) | 83(57) | 83(57) | 1.27 |
| Ag(2) | 12($j$) | 2495(26) | 2496(26) | 5000 | 854(194) | 854(194) | 34(31) | 1655(389) | 0 | 0 | 2.54 |
| Na(1) | 8($g$) | 1940(81) | 1940(81) | 1940(81) | 421(107) | 421(107) | 421(107) | 828(228) | 828(228) | 828(228) | 6.0 |
| Ag(3) | 8($g$) | 3289(45) | 3289(45) | 3289(45) | 4.4(27) | | | | | | 0.7 |
| Ag(4) | 24($l$) | 770(88) | 3977(91) | 5000 | 11.8(457) | | | | | | 1.4 |

[a] Positional and anisotropic thermal parameters are given $\times 10^4$. Numbers in parentheses are the estimated standard deviationa in the units of the least significant digit for the corresponding parameter. See Figures for the identities of the atoms. The anisotropic temperature factor= exp $[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$; [b] Root–mean–square displacements can be calculated from $\beta_{ii}$ values by the formula $\mu_i = 0.255\ a\ (\beta_{ii})^{1/2}$; [c] Isotropic thermal parameter in units of Å$^2$; [d] Occupancy factors are given as the unmber of atoms or ions per unit cell; [e] Occupancy for (Si) = 12; occupancy for (Al) = 12.

**TABLE 2: Selected Interatomic Distances(Å) and Angles (deg)[a]**

| | | | |
|---|---|---|---|
| (Si,Al)–O(1) | 1.67(2) | | |
| (Si,Al)–O(2) | 1.64(3) | | |
| (Si,Al)–O(3) | 1.64(2) | | |
| Na(1)–O(3) | 2.31(10) | | |
| Ag(1)–O(3) | 2.50(4) | | |
| Ag(2)–O(1) | 3.07(3) | | |
| Ag(3)–O(3) | 3.82(6) | | |
| Ag(4)–O(1) | 2.33(11) | | |
| Ag(1)–Ag(2) | 3.30(3) | | |
| Ag(3)–Ag(4) | 3.8(1) | | |
| O(1)–(Si,Al)–O(2) | 110(2) | | |
| O(1)–(Si,Al)–O(3) | 112(1) | | |
| O(2)–(Si,Al)–O(3) | 107(1) | | |
| O(3)–(Si,Al)–O(3) | 106(2) | | |
| (Si,Al)–O(1)–(Si,Al) | 146(0) | | |
| (Si,Al)–O(2)–(Si,Al) | 165(2) | | |
| (Si,Al)–O(3)–(Si,Al) | 147(2) | | |
| O(3)–Ag(1)–Ag(2) | 64(1) | Ag(4)–Ag(3)–Ag(4) | 147(3) |
| Ag(2)–Ag(1)–Ag(2) | 82(1) | O(3)–Ag(1)–O(3) | 106(2) |
| | | O(3)–Na(1)–O(3) | 119(4) |
| | | O(1)–Ag(4)–O(2) | 58()2 |

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

tion.[25]

## Results and Discussion

(*a*) *X-Ray Powder Studies.* In our previous work[12], two dehydrated crystals of $Ag_{12}$–A treated with 100 Torr of hydrogen at 24°C for 6 days and 400 Torr of hydrogen at 150°C for 2 hours, respectively, gave no crystalline diffraction pattern; only powder lines from small crystals of silver metal could be observed. This indicated that at least some of the $Ag^+$ ions in zeolite A were reduced according to the reaction:

$$2Ag + H_2 \longrightarrow 2Ag^0 + 2H^+$$

The rsulting silver atoms migrated out of the zeolite to form silver metal. However, exposure of the reduced crystal to $O_2$ at 330°C resulted in the complete restoration of its single–crystal diffraction pattern. Furthermore, this reoxygenated crystal yielded a sizeable single–crystal data set, indicating that this crystal, whose aluminosilicate framework had been damaged and which had lost silver initially, had repaired itself and had resorbed silver during the final oxygen treatment. This repair process is unusual in crystallography. The acid forms of zeolite are important in carbonium–ion catalysis; it appears that each acid site involves a substantial local disruption of the framework structure.

To learn whether reduced $Ag_{12}$–A can be similarly regenerated by $O_2$ at temperatures below 330° C, other samples were treated flowing oxygen at 100°C and 200°C, each for 15 minutes. Both immediately became lighter in color, and their crystalline X–ray diffraction patterns were restored (see Figure 1), perhaps by the reaction

$$2H^+ + 2Ag^0 + \tfrac{1}{2}O_2 \longrightarrow 2Ag^+ + H_2O$$

Figure 1 shows that the oxidation is equally effective at 100°C and 200°C. Because the diffraction intensities of C and D are almost the same as those in A, the oxidations at 100°C or 200°C are almost complete, and the resulting structure may be almost the same as that of dehydrated $Ag_{12}$–A.[2,3]

Figure 2 shows that the structure of dehydrated partially $Ag^+$–exchanged zeolite A ($Na_{4.5}Ag_{7.5}$–A and $Na_{9.2}Ag_{2.8}$–A) is not severely damaged by treatment with hydrogen gas. As expected, the damage is greater when the silver content is higher (compare F with 7.5 $Ag^+$ to E with 2.8 $Ag^+$ per unit cell). Some $Ag^+$ ions are, however, reduced to form silver clusters whose structure is discussed in next section.

(*b*) *X-Ray Single Crystal Study.*Zeolite A is an aluminosilicate with the chemical formula of $Na_{12}Al_{12}Si_{12}O_{48}\cdot 27H_2O$ ($Na_{12}A$). The twelve $Na^+$ ions are ion exchangeable, for example, easily with $Ag^+$ ions. The anionic framework, $Al_{12}Si_{12}O_{48}^{12-}$, is relatively rigid. The sodalite unit ($Al_{12}Si_{12}O_{48}$)–a truncated octahedron consisting of 24 tetrahedra can be considered as a basic building unit of framework. Eight sodalite units, stacked in a simple cubic manner and interconnected by bridging oxide ions at O(1), form the large cavity. Each unit cell contains one large cavity and one sodalite unit.

Entry into each large cavity can be made from six others, arranged octahedrally, through 16-membered $Al_4Si_4O_8$ ring. The mean diameter of this ring is approximately 4.2 Å and is defined by the ionic radii of the eight oxide ions–for this reason it is called an 8-oxygen ring (or an 8-window). Each sodalite unit is surrounded cubically by eight large cavities and can be entered from each only through a 12-membered $Al_3Si_3O_6$ ring. This ring is called a 6-oxygen ring (or a 6-window).

In the structure of hydrogenated $Na_6Ag_6$-A, 6.0 $Na^+$ ions and 1.27 $Ag^+$ ions lie on two crystallographically different threefold axes of the unit cell near 6-oxygen plane.[4] Two kinds of silver clusters, $Ag_3^+$ and $Ag_3^{2+}$, are found. 1.27 $Ag^+$ ions at Ag(1) and 2.54 $Ag^\circ$ atoms at Ag(2) form 1.27 $Ag_3^+$ clusters per unit cell, and 1.4 $Ag^+$ ions at Ag(4) and 0.7 $Ag^\circ$ atom at Ag(3) form 0.7 $Ag_3^{2+}$ cluster (see Table 1 and 2)

In the structure of vacuum dehydrated fully $Ag^+$-exchanged zeolite A, an uncharged silver cluster, probably the hexasilver molecule, was found at the center of most of its sodalite cavities.[2,3] The number of clusters in the structure was found to depend upon dehydration time and temperature.[2,3] This hexasilver cluster is closely packed and has the natural growth form {111} of silver metal. It is the smallest possible fully developed single crystal of silver. The hexasilver molecule behaves as a Lewis acid with respect to the zeolite framework, accepting electron density and delocalizing it through coordination interactions onto the $Ag^+$ ions on the threefold axes. In this structure, average distance between $Ag^+$ ion and $Ag^0$ atom is 3.31 Å and average distance between $Ag^0$ atom and $Ag^0$ atom is 2.92 Å.[2,3]

In the structure of hydrogenated $Na_6Ag_6$-A, distance between Ag species at Ag(2) and its nearest oxide ion at O(1) is 3.07(3) Å. This distance is much longer than 2.58 Å,[26] which is a sum of ionic radius of $Ag^+$ ion and that of $O^{2-}$ ion, so that the Ag species is not likely an $Ag^+$ ion. Also the position at (0.249, 0.249, 0.5) is unfavorable for $Ag^+$ ion[2,27] and its occupancy number is unusually high for the $Ag^+$ ion, indicating that this must be Ag atom position. The distance between Ag species at Ag(1) and O(3) is 2.50 Å, indicating Ag species at Ag(1) is an ion, $Ag^+$. $Ag^+$ ions at Ag(1) occupy axes near 6-ring, and are recessed by 0.98 Å into the large cavity from (111) plane at O(3). Comparing this structure with fully dehydrated $A_{12}$-A[2,3] each of $Ag^+$ ions at Ag(1) is displaced by 0.82 Å into the large cavity to coordinate Ag species at Ag(2). The distance between Ag species at Ag(2) and Ag ion at Ag(1) is 3.30 Å. This is too long to be $Ag^0$-$Ag^0$ bond distance and too short to be an unmoderated $Ag^+$-$Ag^+$ contact distance ($Ag^0$ to $Ag^0$ distance in natural Silver is 2.89Å). This must be $Ag^0$-$Ag^+$ coordination contact distance. This also indicates that Ag species at Ag(1) is an ion, $Ag^+$ ion and that at Ag(2) is a reduced $Ag^0$ atom.

The distance between Ag species at Ag(3) and its nearest oxide ion at O(3) is 3.82 Å which is too long to be an $Ag^+$ ion to oxide ion distance. This indicates that Ag species at Ag(3) are silver atoms. Silver species at Ag(4) are associated with 8-ring oxide ion, and the distance between Ag(4) and its nearest oxide ion at O(1) is *ca* 2.33 Å. This indicates that the silver species at Ag(4) are the ions, $Ag^+$. The distance between Ag(3) and Ag(4) is 3.8 (1) Å. This is much longer than distance between Ag(1) and Ag(2). However, considering the bond orders of two clusters, this bond distance is reasonable. $Ag_3^+$ cluster can be considered as a three-center two electron bond while $Ag_3^{2+}$ can be considered as a three-center one electron bond (electron configuration of Ag is {Kr} $4d^{10}5s$). Bond order of one $Ag^0$-$Ag^+$ bond in $Ag_3^+$ cluster is one half while that of $Ag_3^{2+}$ cluster is one quarter. Therefore, $Ag^0$-$Ag^+$ bond in $Ag_3^{2+}$ cluster is much diffuser than $Ag^0$-$Ag^+$ bond in $Ag_3^+$ cluster.[28]

**TABLE 3: Deviation of Atoms (Å) from the (111) Planes at O(3)**[a]

| | |
|---|---|
| Ag(1) | 0.98 |
| Na(1) | 0.19 |
| Ag(2) | 3.05 |
| O(2) | 0.16 |

[a] A positive deviation indicates that the atoms lie on the opposite side of the plane from the origin, *i.e.*, in the large cavity.

The ions at Na(1) lie on the threefold axes of 6-oxygen ring. These ions are all trigonally coordinated, approaching their respective sets of three framework O(3) at 2.31 Å. The bond distance, 2.31 Å, is very similar to 2.32 Å of $Na^+$-O(3) distance in $Na_{12}$-A.[22] Thermal ellipsoids of $Na^+$ ions at Na (1) are very elongated and normal to the 6-ring plane. This indicates that there may be two or more nonequivalent posistions located very closely to each. In this structure, two different kinds of ions and one kind of atom (Ag (1), Na (1), and Ag(3) in Table 1) are located very closely to the threefold axes. Therefore, ions at Na(1) can not be separated into two crystallographically nonequivalent points.

In the structure of $Na_6Ag_6$-A reduced by hydrogen, 6 $Na^+$ ions at Na(1), 1.27 $Ag^+$ ions at 6 Ag(1), 1.4 $Ag^+$ ions at Ag (4), 2.54 $Ag^0$ atoms at Ag(2), and 0.7 $Ag^0$ atom at Ag(3) are located per unit cell. This indicates that *ca* 0.09 silver species have migrated out of the zeolite structure. The color of crystal also indicates that it is coated with silver species, which accounts for the remaining 0.09 silver atoms.

Recently, crystal structure of partially $Ag^+$-exchanged zeolite A, $Na_{7.4}Ag_{4.6}$-A, which were treated with 320 Torr of $H_2$ at 350°C for three hours and evacuated hydrogen at 350°C for $2\frac{1}{2}$ hours, were determined.[13] In this structure, $Ag_5^{3+}$ clusters were found. These silver clusters are associated with 8-ring oxide ions and also 6-ring oxide ions: $Ag^+$-$Ag^\circ$=3.4 Å and $Ag^0$-$Ag^0$=2.94 Å.

It appears that $Ag^+$ ions in zeolite A are easily reduced upon hydrogen treatment to form silver clusters: $Ag_3^+$ and $Ag_3^{2+}$ clusters are formed under mild condition of hydrogen treatment. $Ag_5^{3+}$ clusters are formed under strong condition of hydrogen treatment. Reduced silver can be reoxidized by oxygen treatment and moved into original $Ag^+$ ion positions of the dehydrated $Ag^+$-exchanged zeolite A.

*Acknowledgement.* This work was supported by Korean Science and Engineering Foundation and by the U.S. National Science Foundation (NSF-INT81-13065).

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# A Method for Determining Molecular Weights of Block Copolymers by Gel Permeation Chromatography

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A theory is given for determining the molecular weights of block copolymers from the experimental elution volume in GPC. Interaction effect between a sample of block copolymer and a column packing material as well as the size effect are separately considered for the first time applying the partial exclusion mechanism proposed by Dawkins. The molecular weight determination shows 6% standard–deviation from the molecular weights measured by an osmometric method for eight block copolymers, which is much more improved result than other methods, *e.g.*, the universal plot method (13 %) and the Runyon's method (12 %). The reason which explains the better result is that our theory takes into account the interaction effect correctly.

## Introduction

Gel permeation chromatography (GPC) is one of the most useful tools for characterizing molecular weight distributions of polymeric substances. One of the major separation mechanisms of GPC is a size exclusion, but the other mechanisms shoudl be considered to explain the proper elution behavior of polymer samples. Particularly, for copolymers which have heterocomponents in a single molecule, such as block and graft copolymers, the situation is more complicated.