Silver Ions in Zeolite A are Reduced by H_2 only at High Temperatures when 8-Rings are Blocked by Cs^+. Crystal Structures of Dehydrated Ag_9Cs_3-A Treated with H_2 at 23, 310, and 470°C

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The structures of dehydrated Ag_9Cs_3-A treated with hydrogen gas at three different temperatures have been determined by single-crystal X-ray diffraction techniques. Their structures were solved and refined in the cubic space group $Pm3m$ at 23(1) °C. All crystals were ion exchanged in flowing streams of aqueous $AgNO_3/CsNO_3$ with a mole ratio 1:3.0 to achieve the desired crystal composition. The structures treated with hydrogen at 23°C (a = 12.288(1) Å) and 310°C (a = 12.291(2) Å) refined to the final error indices R_1 = 0.091 and R_2 = 0.079, and 0.065 and 0.073, respectively, using the 216 and 227 reflections, respectively, for which $I > 3\sigma(I)$. In both of these structures, eight Ag^+ ions are found nearly at 6-ring centers, and three Cs^+ ions lie at the centers of the 8-rings at sites of D_{4h} symmetry. One Ag° atom, presumably formed from the reduction of a Ag^+ ion by an oxide ion of a residual water molecule or of the zeolite framework during the dehydration process, is retained within the zeolite, perhaps in a cluster. In these two structures hydrogen gas could not enter the zeolite to reduce the Ag^+ ions because the large Cs^+ ions blocked all the 8-windows. However, hydrogen could slowly diffuse into the zeolite and was able to reach and to reduce about half of the Ag^+ ions in the structure only at high temperature (470°C). The silver atoms produced migrated out of the zeolite framwork, and the protons generated led to substantial crystal damage.

Introduction

Ag^+ ions in zeolite A are easily reduced by H_2, even at 25 °C, and the reduced Ag atoms or clusters can be easily reoxidized to Ag^+ by O_2[1]. Hydrogen uptake by Ag-chabazite produced, $(Ag_4)^{2+}$ and $(Ag_3)^+$ clusters according to epr measurements[2]. The reduction in Ag-mordernite was similar to that in Ag-chabazite and also led to the formation of charged clusters[2]. In the structure of dehydrated Ag_6Na_6-A[3] treated with 50 torr of H_2 at 23°C, 1.27 $(Ag_3)^+$ clusters and 0.7 $(Ag_3)^{2+}$ clusters per unit were found in the large cavity[4]. In the structure of $Na_{7.4}Ag_{4.6}$-A, vacuum dehydrated and treated with H_2 at 350°C, $(Ag_6)^{3+}$ clusters of low symmetry were found in the large cavity.[5,6]

Hydrated Ag_{12}-A undergoes partial autoreduction upon dehydration and heating to form uncharged molecular Ag_6 clusters, each of which is within a cube of eight Ag^+ ions and near the plane of a 6-oxygen ring[7,8]. The number of silver clusters in 7 separate crystallographic determinations has been found to depend upon the dehydration time and temperature[8] Hermerschmidt and Haul also indentified Ag_n^{n+} ($n \leq 6$) clusters in the sodalite cavity of dehydrated Ag^+-exchanged zeolite A using epr spectroscopy[9] and their results were duplicated by Grobet and Schoonheydt[10]. This was reverified by the careful work of Morton and Preston who did esr measurements on isotopically pure samples of Ag-A[11]. These clusters of $(Ag_6)^c$, stabilized by coordination to 8 Ag^+ ions, may also be viewed as $(Ag_{14})^{8+}$. Gellens et al. proposed from their X-ray powder diffraction studies of variously treated dehydrated Ag^+-exchanged zeolite A, that linear Ag_3^{3+} clusters have formed: each consists of an Ag° atom, opposite a 4-ring in the sodalite cavity, bound between two Ag^+ cations located at the framework six-rings[12].

Recently several structures of dehydrated Cs_xAg_{12-x}-A ($8 \geq x \geq 2$) were determined[13,14]. It was seen that the first three Cs^+ ions per unit cell selectively occupy the 8-ring sites (symmetry D_{4h}), filling that equipoint and fully blocking the 8-windows. The present study was initiated to see the temperature dependency on the reduction of Ag^+ ions in zeolite A by H_2 molecules. It will be also interesting to study how Cs^+ ions in these 8-oxygen ring sites behave in the H_2 treatment. Futhermore, because of the high scattering powers of Cs^+ and Ag^+, precise and reliable crystallographic determinations should be easy to achieve.

Experimental

Crystals of zeolite 4A were prepare by Charnell's method[15]. Each of three single crystals (0.08 mm on an edge) was lodged in a fine glass capillary.

To prepare exchanged crystals of composition Ag_9Cs_3-A an exchange solution of $AgNO_3$ and $CsNO_3$ in the mole ratio of 1 to 3.0, with a total concentration of 0.05 M, was used. This ratio is obtained by interpolation in a straight-line region of the binary ion-exchange selectivity curve for Ag^+ and Cs^+. That it is linear here is shown by the work of Lin[16]. The points used were taken from the recently determined crystal structures of $Ag_{10}Cs_2$-A and $Ag_{8.65}Cs_{3.35}$-A which were prepared using exchange solutions in which $AgNO_3/CsNO_3$ was 1:1 and 1:5, respectively[14].

Ion exchange was accomplished allowing the solution to flow past each crystal at a velocity of approximately 1.0 cm/sec for 3 days. After exchange, each crystal remained colorless. Crystals 1 and 2 were then dehydrated at 370°C and 1×10^{-6} Torr for 40 hrs. Crystal 1 was then treated with ca 100 Torr of zeolitically dried H_2 gas at 23°C for 30 minutes, evacuated, and sealed off in its calillary by torch. Microscopic examination showed that this crystal had become redish yellow. Crystal

Table 1a. Positional, Thermal[a], and Occupancy Parameters of Dehydrated Ag_9Cs_3-A Treated with H_2 at 23°C

	Wyckoff position	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy varied	Occupancy fixed
(Si, Al)	24(**k**)	0	1841 (7)	3705 (5)	9 (6)	11 (6)	8 (5)	0	0	4(10)		24.0[d]
O(1)	12(**h**)	0	2190(17)	5000	105(32)	−24(15)	−5(16)	0	0	0		12.0
O(2)	12(**i**)	0	2973(14)	2973(14)	32(17)	22(14)	22(14)	0	0	7(35)		12.0
O(3)	24(**m**)	1117(8)	1117 (8)	3362(12)	13 (8)	13 (8)	23(15)	5(20)	18(15)	18(15)		24.0
Ag(1)	8(**g**)	1863(4)	1863 (4)	1863 (4)	101 (4)	101 (4)	101 (4)	163 (8)	163 (8)	163 (8)	8.1(2)	8.0
Cs(1)	3(**c**)	0	5000	5000	163(29)	91 (7)	91 (7)	0	0	0	2.9(1)	3.0
Ag(2)	6(**e**)	0	0	1720(49)	97	97	163	0	0	0	0.9(1)	1.0

Table 1b. Positional, Thermal[a], and Occupancy Parameters of Dehydrated Ag_9Cs_3-A Treated with at 310°C

	Wyckoff position	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy varied	Occupancy fixed
(Si, Al)	24(**k**)	0	1834 (6)	3701 (5)	21 (6)	22 (6)	0 (4)	0	0	14(14)		24.0[d]
O(1)	12(**h**)	0	2212(16)	5000	42(21)	−1(16)	21(18)	0	0	0		12.0
O(2)	12(**i**)	0	2966(12)	2966(12)	0(15)	36(12)	36(12)	0	0	17(33)		12.0
O(3)	24(**m**)	1132(8)	1132 (8)	3372(11)	18 (7)	18 (7)	21(13)	10(19)	19(13)	19(13)		24.0
Ag(1)	8(**g**)	1874(3)	1874(3)	1874 (3)	77 (2)	77 (2)	77 (2)	11(19)	11(19)	11(19)	7.9(1)	8.0
Cs(1)	3(**c**)	0	5000	5000	152(12)	108 (6)	108 (6)	0	0	0	2.6(1)	3.0
Ag(2)	6(**e**)	0	0	1684(25)	18(11)	18(11)	50(29)	0	0	0	1.0(1)	1.0

[a] Positional and anisotropic thermal parameters are given $\times 10^4$. Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter. 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 β_{ii} values using the formula $\mu_i = 0.225a(\beta_{ii})^{1/2}$. [c] Occupany for (Si) = 12; occupancy for (Al) = 12. [d] Occupancy factors are given as the number of atoms or ions per unit cell.

2 was treated with ca 200 Torr of H_2 gas at 310°C for 30 minutes, evacuated at 310°C for 30 minutes, and sealed off in its capillary; it had become black. Crystal 3 was dehydrated at 360°C and 1×10^{-6} Torr for 60 hrs. It was then exposed to 200 Torr of zeolitically dried H_2 gas and the temperature was increased gradually over a two hour period to 470°C. After 10 minutes, H_2 was evacuated and, after cooling to 25°C, the crystal was sealed off in its capillary by torch. This third crystal had become charcoal black.

Diffraction intensities were then collected at 24°C. The cubic space group ***Pm3m*** (no systematic absences) was used instead of ***Fm3c*** throughout this work for reasons discussed previously[17].

4-circle computer-controlled diffractometer, equipped with a pulse-height analyzer and a graphite monochromater, was used, with Mo $\mathbf{K}_1$ radiation ($\mathbf{K}\alpha_1$, $\lambda = 0.70930$ Å, $\mathbf{K}\alpha_2$, $\lambda = 0.71359$ Å). The unit cell constant as determined by a least-squares refinement of 15 intense reflections for which $19°<2\theta<24°$, are 12.288(1) Å for crystal 1 and 12.292(2) Å for crystal 2. On a rotation photograph of crystal 3, the (111) and (002) powder lines of Ag could be clearly seen, and the single-crystal pattern was weak. Its unit-cell constant (11.85(12) Å) was imprecisely determined by a least-squares refinement of six (001) reflections.

Data collection was done by methods described previously[18,19] except that only one unique region of reciprocal space was examined at a scan rate (ω) of 2° min^{-1} in 2θ for crystal 1 and 2, and 0.5° min^{-1} for crystal 3. An absorption correction was judged to be negligible ($\mu = 3.3$ mm^{-1}) and was not applied[21].

All unique reflections for which $2\theta<65°$ for crystal 1 and $2\theta<60°$ for crystal 2 were examined by counter methods. For third crystal, all unique reflections for which $2\theta<35°$ were examined. Only those for which $I>3\sigma(I)$ were used for structure solution and refinement. These amounted 216 of 742 reflections examined for crystal 1.227 of 612 reflections for crystal 2 and 31 of 150 reflections for crystal 3, respectively.

Structure Determination

Crystal 1. It was expected that the formula of crystal 1 would be Ag_9Cs_3-A. Therefore, full-matrix least-squares refinement[20] was initiated using the atomic parameters of the framework atoms [(Si, Al), O(1), O(2), and O(3)] with eight Ag^+ ions at 6-ring sites and three Cs^+ ions at 8-ring sites and with one Ag^0 atom at (0.0, 0.0, 0.17) as was found in dehydrated $Ag_{4.7}Cs_{7.3}$-A and dehydrated Ag_{12}-$A^{7,8}$. Full-matrix least-squares refinement with anisotropic parameters quickly converged to the error indices.

$$R_1 = \Sigma\,||F_o| - |F_c||/\Sigma F_o = 0.089$$

$$R_2 = [\Sigma\,\omega\,(F_o - |F_c^2|)/\Sigma\,\omega F_o^2]^{1/2} = 0.078$$

Subsequently, the occupancies at Ag(1), Ag(2), and Cs(1) were refined to 8.01(2), 0.85(8), and 2.90(6), respectively. These occupancies were reset and fixed at Ag(1) = 8, Ag(2) = 1 and Cs(1) = 3, by the assumption of stoichiometry and the need to locate 12 monovalent ions or atoms in the unit cell. A final error indices are $R_1 = 0.091$ and $R_2 = 0.079$. A final difference Fourier function revealed two peaks at (0.0, 0.0, 0.0) (density = 4.8(13) eÅ^{-3}) and also at (0.12, 0.12, 0.12) (density = 3.3(5) eÅ^{-3}).

Table 2. Selected Interatomic Distances (Å) and Angles (deg)[a] of Ag_xCs_{12-x}-A

	Ag_9Cs_3-A + H_2 at 23°C	Ag_9Cs_3-A + H_2 at 310°C
(Si, Al)-O(1)	1.647(8)	1.663(8)
(Si, Al)-O(2)	1.656(19)	1.66(2)
(Si, Al)-O(3)	1.689(8)	1.69(1)
Ag(1)-O(3)	2.25(9)	2.25(1)
Ag(2)-O(3)	2.80(5)	2.86(2)
Cs(1)-O(1)	3.45(2)	3.42(1)
Cs(1)-O(2)	3.52(2)	3.53(2)
Ag(2)-Ag(2)	2.99(6)	2.93(3)
O(1)-(Si, Al)-O(2)	107.8(10)	106.8(9)
O(1)-(Si, Al)-O(2)	112.2(6)	111.9(5)
O(2)-(Si, Al)-O(3)	107.8(6)	107.4(5)
O(3)-(Si, Al)-O(3)	108.7(6)	111.1(8)
(Si, Al)-O(1)-(Si, Al)	149.8(15)	145.6(14)
(Si, Al)-O(2)-(Si, Al)	155.8(13)	155.9(11)
(Si, Al)-O(3)-(Si, Al)	142.5(12)	141.9(8)
O(3)-Ag(1)-O(3)	120.0(17)	120.0(5)
O(1)-Cs(1)-O(2)	45.0(3)	45.0(2)

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

Table 3. Deviation of atom (Å) from the (111) Plane at O(3)[a]

	Ag_9Cs_3-A + H_2 at 23°C	Ag_9Cs_3-A + H_2 at 310°C
O(2)	0.25	0.21
Ag(1)	0.0	-0.01
Ag(2)	-2.75	-2.80

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

Both peaks were unstable in least-squares refinment. See Table 1, 2 and 3 for additional information.

Crystal 2. Full-matrix least-squares refinement was initiated with atomic parameters for the atoms of the aluminosilicate framework, Ag(1), Ag(2), and Cs(1) from the structure of crystal 1. Simultaneous positional, occupancy, and anisotropic thermal parameter refinement converged to $R_1 = 0.061$ and $R_2 = 0.060$. The occupancies at Ag(1), Ag(2), and Cs(1) (See Table 1) were refined to 7.9(1), 1.0(1) and 2.6(1), ions or atom per unit cell respectively. These values were reset and fixed at 8, 1, and 3, respectively. The final error indices were $R_1 = 0.065$ and $R_2 = 0.073$. A final difference Fourier synthesis was featureless except for one broad but insignificant peak at (0.0, 0.0, 0.5) with a height of 1.9(4) eÅ^{-3}.

Crystal 3. Least-squares refinement was initiated using the atomic parameters of crystal 2. Since there were only 34 reflections for which $I > 3\sigma(I)$, only the positional parameters of the framework atoms, and the occupancy parameters of Ag(1), Ag(2), and Cs(1) were varied. The occupancy at Ag(2) was refined quickly to zero, while those at Ag(1) and Cs(1) became 4.5(10) and 3.5(6), respectively. This structure could not be studied further because of the paucity of data.

The quantity minimized in the least-squares treatment was $\Sigma\omega\ (F_o - |F_c|)^2$, where the weights ($\omega$) are the reciprocal squares of $\sigma(F_o)$, the standard deviation of each observation. Atomic scattering factors[22,23] for Ag°, Ag$^+$, Cs$^+$, O$^-$ and (Si, Al)$^{1.75+}$ were used. The function describing (Si, Al)$^{1.75+}$ is the mean of the Si°, Si^{4+}, Al°, and Al^{3+} functions. All scattering factors were modified to account for the real component ($\Delta f'$) of the anomalous dispersion correction[24,25]. Bond lengths and selected angles are given in Table 2.

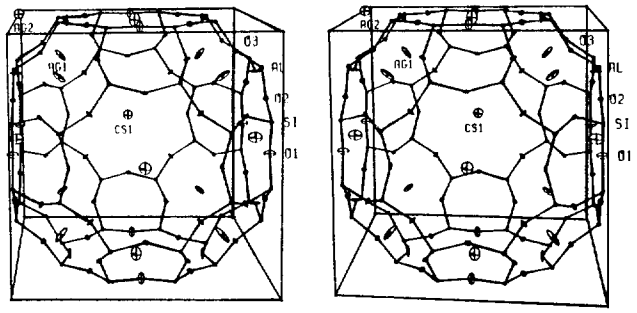

Figure 1. A stereoview of a large cavity of dehydrated Ag_9Cs_3-A is shown using ellipsoids of 20% probability. All 6-rings are filled with Ag$^+$ ions at Ag(1) and all 8-rings are filled with Cs$^+$ ions at Cs(1).

Discussion

When fully Ag$^+$-exchanged zeolite A is dehydrated, the eight Ag$^+$ ions on the threefold-axis move to the centers of the 6-rings to sites of three coordination. The remaining four Ag$^+$ ions are reduced in order, with the least suitably coordinated ions reacting first. Upon heating for 1-10 days at 375 to 450°C, a four-ring Ag$^+$ ion is reduced first, followed in time by the Ag$^+$ ions in 8-rings, but the eight Ag$^+$ ions in 6-rings are not reduced at all. At 475°C, the reduction of Ag$^+$ ions at all sites proceeds rapidly enough to approach completion in 1-2 weeks.

The reduced Ag° atoms, as they are generated, go to the sodalite-unit sites designated Ag(2) in the present structures. Under the most suitable conditions, 4 Ag° atoms are produced per unit cell and remain in an undamaged zeolite[8]. This has been interpreted as indicating that two-thirds of the sodalite units contain octahedral Ag_6 molecules at their centers while the remaining one-third of the sodalite unit are empty of silver species. This six atom cluster, subsequently verified by esr work[9-11] is stabilized by coordination to 8 Ag$^+$ ions near the centers of 6-rings, and may therefore be viewed as a Ag_{14}^{8+} cluster.

In the structures of crystals 1 and 2, only one Ag$^+$ ion is present at Ag(2). The distances between Ag(2) and the nearest oxide ion at O(3), 2.80(5) Å for Ag_9Cs_3-A treated with H_2 gas at 23°C and 2.86(2) Å for Ag_9Cs_3-A similarly treated at 310°C, are similar to those seen before[7,8] between a neutral silver atom and a framework oxide ion. The possible Ag(2)-Ag(2) distances, 2.99(6) and 2.93(3) Å are about the same as the Ag-Ag bond in silver metal, 2.89 Å[26]. Similar distances were also observed in $Ag_{10}Cs_2$-A (2.94 Å)[14] and in dehydrated Ag_{12}-A (2.92 Å)[7,8]. Under the same experimental conditions, one reduced Ag atom was present in the structure of dehydrated $Ag_{8.65}$-$CS_{3.35}$-A[14] and also in the structure of dehydrated $Ag_{7.6}Na_{4.4}$-A[5]. Therefore this reduced Ag atom would have formed by autoreduction during the dehydration process, and did not require hydrogen to be reduced. It may be that a

neutral cluster has formed in 1/6 of the sodalite units, or that an isolated atom exists in each sodalite, coordinated most attractive among several alternatives to 4 Ag^- ions to give $(Ag_5)^{4+}$, symmetry $4mm$.

The Ag^+ ions at Ag(1) are at the positions as those found in the structure of dehydrated Ag_{12}-A[7,8]. Each Ag^+ ion at Ag(1) lies on a threefold axis and lies exactly on one of eight (111) planes of three O(3)'s for crystal 1 and 2 (Table 3). In crystals 1 and 2, this position is therefore fully occupied. Each Ag^+ ion at Ag(1) is trigonally coordinated at 2.25 Å to three O(3) framework oxygens. As compared to the sum of Ag^+ and O^{2-} radii, 2.58Å[27], three bonds are quite short and therefore quite covalent. The unusually strong interaction implied by this is consistent with the high selectivity that zeolite A shows for Ag^+.

The Cs^+ ions at Cs(1) lie at the centers of 8-oxygen rings. The local symmetry of this site is C_{4h} (D_{4h} in $Pm3m$). Each Cs^+ ion is 3.4 Å from four O(1) oxygens and 3.5 Å from four O(2)'s. As has been observed before in other zeolite A structures, these distances are substantially longer than the sum of ionic radii, 2.99 Å[27].

In the structures of Ag_9Cs_3-A treated with H_2 at 23 and 310°C, hydrogen molecule (kinetic diameter = 2.89 Å)[28] can not enter the zeolite channels because large Cs^+ ions block the 8-ring windows[29]. Therefore Ag^+ ions have not been reduced by hydrogen in these structures. However, at 470°C, hydrogen must have slowly diffused into the zeolite cavities, because about 3.5 of the eight 6-ring Ag^+ have been reduced. The higher thermal vibrations of the Cs^+ ions at the centers of 8-rings at 470°C must have allowed this diffusion to occur. Unfortunately, the reduced Ag^0 atoms produced migrated out of zeolite framework to form small silver crystallities on the surface.

This is consistent with the work of Fraenkel, who reported that $Na_{9.4}Cs_{2.6}$-A is the best composition for the encapsulation of hydrogen gas. According to Fraenkel, $Na_{9.4}Cs_{2.6}$-A can hold as high as 1.5 wt % of hydrogen at 2000 atm. In the encapsulation process, the zeolite is exposed at elevated temperatures to a high pressure of H_2 gas and then the system is cooled. $Na_{9.4}Cs_{2.6}$-A then encapsulates its hydrogen gas, which can be released as needed simply by reheating. In this case 2.6 Cs^+ ions per unit cell keep H_2 from passing through 8-rings at 25°C; in the work reported here, about 3.0 Cs^+ ions have prevented H_2 from passing through 8-rings at 25 and 310°C.

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