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Crystallographic Evidence for the Reduction of CO in Partially Dehydrated Silver Zeolite A

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The crystal structure of Ag^+-exchanged zeolite A vacuum-dehydrated at 370 °C and then treated with carbon monoxide at 23 °C has been determined by single crystal x-ray diffraction methods in the cubic space group *Pm*3*m* at 23(1) °C; a = 12.116 (2) Å. The structure was refined to the final error indices R_1 = 0.061 and R_2 (weighted) = 0.068 using 349 independent reflections for which $I>3\sigma(I)$. 3.6 Ag^+-CO complexes, where -CO may represent -CHO or -CH_2OH, were found in each large cavity. By coordination to silver atoms followed by reaction with $Ag°$ and H^+ within the zeolite, carbon monoxide has been partially reduced. In about 28% of the sodalite units, a $Ag_6(Ag^+)_2$ cluster may be present. In about 37% of the sodalite units, three Ag^+ ions are found on threefold axes where they may be bridged by three water molecules. The remaining 35% of the sodalite units are empty of silver species. Two Ag^+ ions per unit cell are associated with 8-ring oxygens. The remaining *ca* 3 Ag^+ ions per unit cell have been reduced during the synthesis and have migrated to form small silver crystallities on the surface of the zeolite single crystal.

Introduction

Hydrated Ag^+-exchanged zeolite A undergoes partial decomposition when heated under vacuum to form, within its sodalite unit, uncharged molecular Ag_6 clusters, each of which is stabilized by coordination within a cube of eight Ag^+ ions.[1,2] The number of silver clusters in seven separate crystallographic determinations has been found to depend upon the dehydration time and temperature.[2] Hermerschmidt and Haul also identified $(Ag_6)^{n+}$ ($n \leq 6$) clusters in the sodalite cavity of dehydrated Ag^+-exchanged zeolite A using esr spectroscopy[3] and their results were duplicated by Grobet and Schoonheydt.[4] This was reverified by the careful work of Morton and Preston who did esr measurements on isotopically pure samples of Ag-A.[5]

When ethylene is sorbed by dehydrated Ag_{12}-A,[6] the Ag_6 molecules are hardly effected: their number remains the same, and the Ag-Ag distances decrease from slightly greater to slightly less than that in silver metal.[6] Ethylene acts as a titrating agent which forms lateral π complexes with two of the eight 6-ring[7] Ag^+ ions; the remaining six Ag^+ ions remain firmly complexed to the ligand molecule Ag_6.

As a continuation of the study of the unusual chemistry of silver ions, silver clusters, and molecules within zeolite A, a carbon monoxide sorption complex of partially dehydrated Ag_{12}-A was prepared and its crystal structure determined. It was initially hoped that CO gas would reduce some of the Ag^+ ions in zeolite A to form Ag atoms and clusters which might be examined crystallographically. If Ag^+ were not reduced by CO, the structure of some Ag^+–C≡O complexes might be learned.

Experimental

Crystals of zeolite 4*A* were prepared by Charnell's method.[8] A single crystal about 0.08 mm on an edge was lodged in a fine capillary. $AgNO_3$ (0.05 M) was allowed to flow past the crystal at about 1.0 cm/sec for 3 days. Since the exchange of Ag^+ for Na^+ has been shown to be facile and complete after much milder treatment, complete exchange was assured in this case.[1,2,9] The clear, colorless hydrated Ag^+-exchanged crystal was dehydrated for 2 days at 370 °C and 2×10^{-6} Torr. Under these conditions, most water molecules should be removed, affording open channels and coordinately unsaturated Ag^+ ions for reaction with CO; simultaneously relatively few Ag atoms should have been generated,[1,2] so the zeolite should have suffered little or no damage. After the crystal was cooled to 21(1) °C, it was treated with *ca* 740 Torr of CO gas (Union Carbide, research grade). Microscopic examination showed that it had become dark grey. After 1 hr, the crystal, still in its CO atmosphere, was sealed in its capillary by torch.

X-Ray Data Collection. The cubic group *Pm*3*m* (no systematic absences) was used throughout this work for reasons

Table 1. Positional, Thermal[a], and Occupancy Parameters of Dehydrated Ag_{12}-A Treated with CO Gas

Atom	Wyc. Pos.	x	y	z	[b]β_{11} or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	[c]Occupancy varied	fixed
(Si,Al)	24(*k*)	0	1829(2)	3664(2)	35(2)	27(1)	23(1)	0	0	13(3)	—	[d]24.0
O(1)	12(*h*)	0	1990(10)	5000	80(10)	80(10)	31(6)	0	0	0	—	12.0
O(2)	12(*i*)	0	3020(6)	3020(6)	58(8)	29(4)	29(4)	0	0	10(10)	—	12.0
O(3)	24(*m*)	1111(5)	1111(5)	3231(7)	70(4)	70(4)	51(6)	50(10)	4(9)	4(9)	—	24.0
Ag(1)	6(*e*)	0	0	1652(4)	28(2)	28(2)	15(3)	0	0	0	1.68(2)	1.67
Ag(2)	8(*g*)	2391(2)	2391(2)	2391(2)	42(1)	42(1)	42(1)	12(2)	12(2)	12(2)	3.57(2)	3.60
Ag(3)	8(*g*)	1293(6)	1293(6)	1293(6)	50(3)	50(3)	50(3)	31(8)	31(8)	31(8)	1.10(3)	—
Ag(4)	8(*g*)	1830(20)	1830(20)	1873(20)	6.9(9)						0.5(1)	0.56
Ag(5)	12(*h*)	0	4130(20)	5000	400(40)	130(20)	340(40)	0	0	0	2.04(6)	—
C(1)	8(*g*)	3540(40)	3540(40)	3540(40)	150(40)	150(40)	150(40)	-8(100)	-8(100)	-8(100)	3.7(3)	3.60
O(4)	24(*m*)	2730(100)	4210(30)	4210(30)	400(100)	30(1)	30(1)	-50(90)	-50(90)	-30(60)	4.4(2)	3.60

[a] Positional and isotropic 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 given as the number of atoms or ions per unit cell. [d]Occupancy for (Si) = 12; occupancy for (Al) = 12.

discussed previously.[10-12] Preliminary crystallographic experiments and subsequent data collection were performed with an automated, four-circle Enraf-Nonius CAD-4 diffractometer, equipped with a graphite monochromator. Mo K_α radiation was used for all experiments ($K_{\alpha1}$, $\lambda = 0.70930$ Å; $K_{\alpha2}$, $\lambda = 0.71359$ Å). The cubic unit cell constant, as determined by a least-squares refinement of 25 intense reflections for which $19° < 2\theta < 24°$, is 12.116(2) Å. Reflections from two intensity-equivalent regions of reciprocal space (*hkl*, $h \leq k \leq l$; and *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 a slow scan speed, ranging between 0.150° and 0.260° in ω $\min^{-1}$. 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 $2\theta < 70°$ were recorded.

The raw data for each region were corrected for Lorentz and polarization effects, including that due to incident beam monochromatization; the reduced intensities were merged; and the resultant estimated standard deviations were assigned to each averaged reflection by the computer programs, PAINT and WEIGHT.[13] An absorption correction was judged to be unimportant ($\mu = 3.6$ mm^{-1}), and was not applied. Of the 853 pairs of reflections examined, only the 349 whose net counts exceeded three times their corresponding esd's were used in structure solution and refinement.

Structure Determination. Full-matrix least-squares refinement was initiated using the atomic parameters of the framework atoms ((Si,Al), O(1), O(2) and O(3)) of dehydrated and partially decomposed Ag_{12}-A.[1,2] Anisotropic refinement of the framework atoms converged to an R_1 index, $(\Sigma|F_o - |F_c||)/\Sigma F_o$, of 0.43 and a weighted R_2 index, $(\Sigma w(F_o-|F_c|)^2/\Sigma wF_o^2)^{1/2}$ of 0.50. A difference Fourier synthesis revealed one large threefold-axis peak at Ag(2) (see Table 1). Anisotropic refinement including these Ag^+ ions converged to $R_1 = 0.29$ and $R_2 = 0.33$. From successive difference Fouriers, silver atoms and ions at Ag(1), Ag(3), Ag(4) and Ag(5) were located (see Table I). Including these cation positions in anisotropic refinement yielded convergence at $R_1 = 0.067$ and $R_2 = 0.088$. A subsequent different Fourier synthesis revealed at (0.359, 0.359, 0.359) of height 0.9(3) eÅ^{-3}, and another at (0.277, 0.416, 0.416), of height 0.9(2) eÅ^{-3}. The first peak refined as 3.7 carbons and the second as 4.4 oxygens (see Table 2). The alternative assignment, *i.e.*, first peak oxygen and second carbon, increased the R value by 0.003; also the resulting thermal ellipsoid for the more firmly bound atom became unrealistically larger.

Table 2. Selected Interatomic Distances(Å) and Angles(deg)[a] of Dehydrated Ag_{12}-A Treated with CO Gas

(Si,Al)-O(1)	1.631(3)	O(1)-(Si,Al)-O(2)	111.7(5)
(Si,Al)-O(2)	1.640(4)	O(1)-(Si,Al)-O(3)	111.6(4)
(Si,Al)-O(3)	1.687(4)	O(2)-(Si,Al)-O(3)	107.8(3)
Ag(1)-O(3)	2.700(7)	O(3)-(Si,Al)-O(3)	106.0(3)
Ag(2)-O(3)	2.418(5)	(Si,Al)-O(1)-(Si,Al)	166.7(9)
Ag(3)-O(3)	2.369(9)	(Si,Al)-O(2)-(Si,Al)	146.8(4)
Ag(4)-O(3)	2.100(10)	(Si,Al)-O(3)-(Si,Al)	136.6(5)
Ag(5)-O(1)	2.610(20)	O(3)-Ag(1)-O(3)	59.8(3)
Ag(5)-O(2)	2.760(10)	O(3)-Ag(2)-O(3)	97.4(2)
Ag(1)-Ag(4)	3.147(2)	O(3)-Ag(3)-O(3)	100.1(2)
Ag(1)-Ag(1)	2.830(5)	O(3)-Ag(4)-O(3)	120.0(5)
Ag(2)-C(1)	2.41(4)	O(3)-Ag(2)-C(1)	120.0(2)
C(1)-O(4)	1.51(8)	Ag(2)-C(1)-O(4)	105(3)
		Ag(1)-Ag(4)-Ag(1)	53.4(3)

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

From the interatomic distances among Ag(1), C(1), and O(4), it was clear that Ag^+-CO complexes had formed. Therefore the occupancy numbers of C(1) and O(4) were constrained to equal that of Ag(2). The lowest error indices were obtained when the occupancies at Ag(1), and C(1), and O(4) were 3.6.

The final R_1 and R_2 values are 0.061 and 0.068. All shifts in the final cycle of least-squares refinement were less than 0.2% of their corresponding esd's. A final difference Fourier function showed one insignificant peak of height 4.3(10) eÅ^{-3}

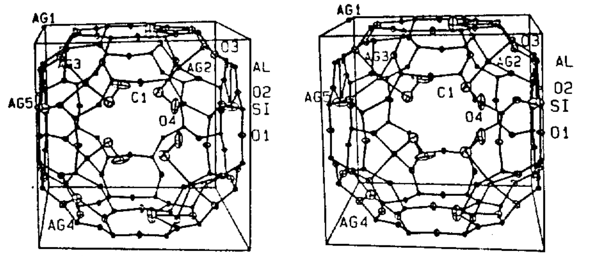

Figure 1. A stereoview of a large cavity of dehydrated Ag_{12}-A treated with CO gas. Four Ag^+-CO complexes (either Ag^+-CHO or Ag^+-CH_2OH) are shown in the large cavity. About 60% of the unit cells have this arrangement. The remaining 40% contain three such Ag^+-CO complexes. Ellipsoids of 20% probability are used.

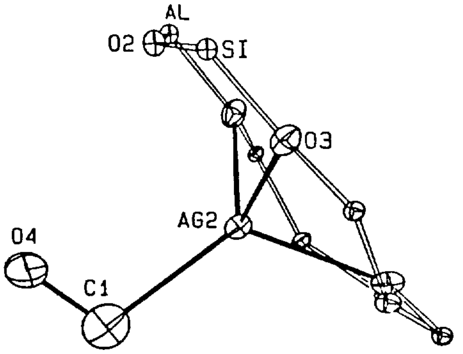

Figure 2. One of 3.6 Ag^+-CO complexes (either Ag^+-CHO or Ag^+-CH_2OH) in the large cavity of each unit cell. Ellipsoids of 40% probability are used. Selected bond lengths and an angle are Ag(2)-C(1) = 2.40(3) Å, C(1)-O(4) = 1.52(8) Å and Ag(2)-C(1)-O(4) = 104 (3)°.

at the origin.

The full-matrix least-squares program used in structure determination minimized $\Sigma w|\Delta F|^2$; the weight w of an observation was the reciprocal squares of $\sigma(F_o)$, its standard deviation. Scattering factors[14] for Ag^0, Ag^+, C^0, O^0, O^-, 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. Al lscattering factors were modified to account for anomalous dispersion.[15]

The final structural parameters are presented in Table 1 and interatomic distances and angles are given in Table 2.

Discussion

In the structure of dehydrated fully Ag^+-exchanged zeolite A treated with CO gas, 3.6 Ag^+ ions at Ag(2) lie on threefold axes of the unit cell and are recessed 1.203(1) Å into large cavity from (111) planes at O(3). Compared to fully dehydrated partially decomposed Ag_{12}-A,[1,2] each of these ions has moved *ca* 1.08 Å further into the large cavity to coordinate to its ligand. The length of the Ag(2)-O(3) bond has increased from 2.25 Å in vacuum-dehydrated fully Ag^+-exchanged zeolite A to 2.418(5) Å in this structure (see Table 2). Also, the O(3)-Ag(2)-O(3) angle has decreased accordingly from the trigonal planar value of 120(1)° to 97.4(2)° after complexation. The O(3) position used must be an average; chemically all O(3)'s cannot be precisely equivalent.

The carbon at C(1) and oxygen at O(4) are located deep inside the large cavity (see Figures 1 and 2). Each of the 3.6 Ag^+ ions at Ag(2) is complexed to one C(1)-O(4) species. The C(1)-O(4) distance, 1.51(8) Å, appears to be too long when compared to other carbon-oxygen bond distances; 1.131 Å in CO molecules, 1.209 Å in H_2CO, 1.427 Å in CH_3OH.[16] However the esd of this bond length is high, so it is acceptable, albeit somewhat uninformative. That it is so much longer than the CO triple bond length, and that AgCO is bent, indicate that reduction of CO has occurred. The Ag^+-C distance (2.41(4) Å) is a little shorter than that in the Ag^+-ethylene complex (2.54 Å).[17]

The Ag(2)-C(1)-O(4) angle is 105(3)°. In the structure of the CO sorption complex of Co_4Na_4-A, the Co-C-O angle is 180°.[18] In the molecular structure of the $(\eta\text{-}C_5H_5)Re(PPh_3)NO(CHO)$, the Re-C-O angle is 128.1°, the C-O distance in the formyl group is 1.220(12) Å and the Re-C distance is 2.055(10) Å.[19] Considering the geometry of the Ag-CO complex, we may propose as one possibility that 3.6 Ag^+-CHO complexes per unit cell may have formed inside the large cavity by the following steps:

$$Ag^+\text{---}\underset{H}{\overset{H}{O}}\text{---}Ag^+ \dashrightarrow 2\,Ag^0 + 2\,H^+ + 1/2\,O_2 \quad \text{(dehydration)}$$

$$Ag + CO \dashrightarrow Ag(CO) \quad \text{(sorption)}$$

$$Ag(CO) + H^+ \dashrightarrow Ag^+\!-\!C\!\overset{\nearrow O}{\underset{\searrow H}{}} \quad \text{(reaction)}$$

The long carbon-oxygen bond may indicate that the -CHO group has been reduced further by the following reaction:

$$Ag^+\!-\!C\!\overset{\nearrow O}{\underset{\searrow H}{}} + 2Ag + 2H^+ \dashrightarrow Ag^+\text{-}CH_2OH + 2Ag^+$$

In a series of similar steps involving $NaBH_4$, Mo^+-CO can be reduced to MoCHO, $MoCH_2OH$ and $MoCH_3$.[20,21]

The above processes are limited by the availability of H^+ and Ag atoms. More of these might be generated if some CO is oxidized:

$$(Ag^+)_2OH_2 + CO \dashrightarrow 2\,Ag^0 + CO_2 + 2H^+$$

and $$CO + O^{2-}\ \text{(framework)} + 2Ag^+ \dashrightarrow CO_2 + 2Ag$$

(OH_2 and O^{2-} in the reactions above may be replaced by OH^-, due, respectively, to hydrolysis of water and to hydrolysis of (demage to) the zeolite framework.) Accordingly, it is also possible, and more consistent with the C-O bond length observed, that the Ag-CO complexes found, 3.6 per unit cell, are Ag^+-CH_2OH.

The Ag^+ ion at Ag(4) is at a position found in the structure of dehydrated Ag_{12}-A.[1,2] This Ag^+ ion lies on a threefold axis, almost on one of the (111) planes at O(3), and is trigonally coordinated at 2.10(1) Å to three O(3) framework oxygens. For comparison, the sum of the ionic radii of O^{2-} and Ag^+ is 2.58 Å.[22] Therefore these Ag(4)-O(3) bonds are quite short and therefore quite covalent. (The occupancy at Ag(4) is low, so that short distance may be virtual.)

The Ag(1) position is very similar to that of the silver atoms in hexasilver in the structure of dehydrated partially decomposed Ag_{12}-A.[1,2] The occupancy at Ag(1) is 1.67 and that of Ag(4) is 0.56. This may indicate that $Ag_6(Ag^+)_2$ clusters have formed within about 28% of sodalite units (Figure 4).

As the hexasilver molecule changes its coordination num-

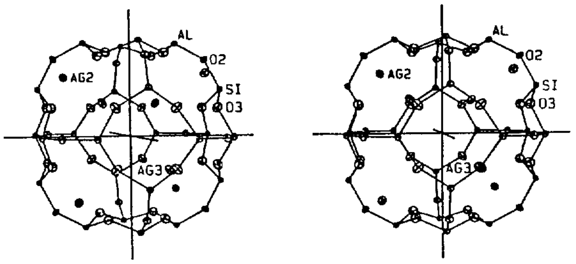

Figure 3. A stereoview of a sodalite unit containing three Ag^+ ions deep within itself, perhaps as $[Ag_3(H_2O)_3]^{3+}$. About 40% of the sodalite units may have this arrangement. Ellipsoids of 20% probability are used.

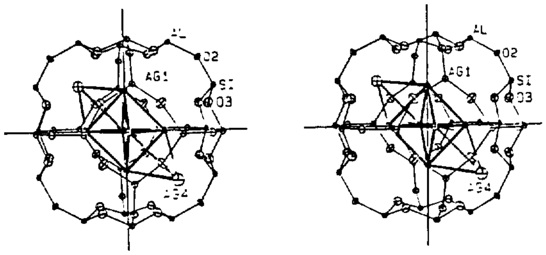

Figure 4. A stereoview of a sodalite unit containing an Ag_6 molecule complexed to two Ag^+ ions is shown. Ellipsoids of 20% probability are used.

ber from eight or six to two Ag^+ ions, its Ag-Ag bond length (the edge length of the octahedron) decreases from 2.92(1) Å in $(Ag_6)(Ag^+)_8$[1,2] and 2.850(4) Å in $(Ag_6)(Ag^+)_6$[17] to 2.830(5) A in $(Ag_6)(Ag^+)_2$. This change is consistent with the diminished ability of the two Ag^+ ions to drawn bonding electron density from the hexasilver molecule by coordination. Supporting this scheme, the Ag^+-Ag^0 interaction, 3.147(2) Å is somewhat less that the corresponding 3.31(1) Å approach in $Ag_6(Ag^+)_8$[1,2] and 3.26(2) Å) approach in $Ag_6(Ag^+)_6$[17], because the electron-rich Ag_6 molecule can act as a stronger base when it is a ligand to fewer Ag^+ ions. These neutral clusters were also seen in structures such as $Ag_{5.5}Tl_{6.5}$-A dehydrated at 440 °C,[23] Ag_{12}-A treated first with H_2 and then O_2, both at 330 °C[24], and $Ag_{12-x}K_x$-A (x = 1.3 and 2.7) dehydrated at 360 °C.[25]

1.1 Ag^+ ions at Ag(3) lie relatively far inside the sodalite cavity, 1.102(4) A from the (111) plane at O(3) (see Table 3). These Ag^+ ions are trigonally coordinated to their respective sets of three O(3) framework oxygens at 2.369(9) Å. Similar Ag^+ ion positions were seen at the structures of hydrated Ag_{12}-A and trihydrated Ag_{12}-A in which three Ag^+ ions are associated with three water molecules to form $[Ag_3(H_2O)_3]^{3+}$ rings.[26] (The water molecules in these rings may have dissociated within the zeolite to give $[Ag_3(H_2O)_2OH]^{2+}$, $[Ag_3(H_2O)(OH)_2]^+$, or $[Ag_3(OH)_3]^0$.) If the Ag^+ ions at Ag(3) participate in such rings, as their position indicates, about 37% of sodalite cavities would be so occupied. However the bridging oxygens of these H_2O's or OH^-'s could not be located in this structure, perhaps because of the low occupancy of their position.

The two Ag^+ ions at Ag(5) are associated with 8-ring oxygens (see Figure 1). The relatively large thermal parameters of the Ag(5) position are consistent with its relatively long and presumably weak interaction with the zeolite framework. It approaches zeolite framework oxide ions at 2.61(2) Å to O(1) and 2.76(2) Å to O(2). Each Ag(5) ion may also approach one or two O(4) oxygens at about 3.4(1) Å.

Table 3. Deviation(Å) of Atoms from the (111) Plane at O(3) of Dehydrated Ag_{12}-A Treated with CO Gas

O(2)	0.411(4)	Ag(1)	-2.660(3)
Ag(2)	1.203(1)	Ag(3)	-1.102(4)
Ag(4)	0.030(15)	C(1)	3.604(30)
O(4)	3.984(69)		

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

Only about nine silver atoms or ions were found per unit cell (see Table 1). Apparently the remaining *ca* 3.0 Ag^+ ions per unit cell were reduced during the synthesis and have migrated out of the zeolite framework to form small silver crystallites on the surface of the zeolite single crystal, accounting for its dark grey color.

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Crystal Structure of Dehydrated Partially Ag^+-Exchanged Zeolite A treated with Cesium Vapor at 250°C

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The crystal structure of partially Ag^+-exchanged zeolite A, $Ag_{3.2}Na_{8.8}-A$, vacuum dehydrated at 360 °C and then exposed to 0.1 torr of cesium vapor for 12 hours at 250 °C has been determined by single-crystal X-ray diffraction techniques in the cubic space group *Pm3m* (a = 12.262(2)Å) at 21(1) °C. The structure was refined to the final error indexes $R_1 = 0.068$ and $R_2 = 0.072$ by using 338 reflections for which $I_o > 3\sigma(I_o)$ and the composition of unit cell is $Ag_{3.2}Cs_{8.8}$-A. 3 Cs^+ ions lie on the centers of the 8-rings at sites of D_{4h} symmetry. Two crystallographycally different 6-ring Cs^+ ions were found: 1.5 Cs^+ ions at Cs(2) are located inside of sodalite cavity and 4.3 Cs^+ ions at Cs(3) are located in the large cavity. The fractional occupancies observed at Cs(2) and Cs(3) indicate that the existence of at least three types of unit cells with regard to the 6-ring Cs^+ ions. For example, 50% of unit cells may have two Cs^+ ions at Cs(2) and 4 Cs^+ ions at Cs(3). 30% of unit cells may have one Cs^+ ion at Cs(2) and 5 Cs^+ ions at Cs(3). The remaining 20% would have one Cs^+ ion at Cs(2) and 4 Cs^+ ions at Cs(3). On threefold axes of the unit cell two non-equivalent Ag atom positions are found in the large cavity, each containing 0.64 and 1.92 Ag atoms, respectively. A crystallographic analysis may be interpreted to indicate that 0.64 $(Ag_5)^+$ clusters are present in each large cavity. This cluster may be viewed as a tetrasilver molecule $(Ag_4)^0$ (bond length, 2.84Å) stabilized by the coordination of one Ag^+ ion.

Introduction

Numerous investigation have been reported that various types of silver clusters are located in dehydrated fully and partially silver ion exchanged zeolite A, zeolite Y, mordenite, and chabazite.[1-10] The existence of these silver clusters was identified and reconfirmed by many workers using EPR spectroscopy,[6,11-14] reflectance spectroscopy,[15] and FTIR.[16] Ag^+ ions can be reduced by heating, by reaction with reducing agents such as H_2, alcohol, and alkylbenzenes, or by the sorption of metal atoms.[17] Recently, in the structures of dehydrated Ag_6Na_6-A[18,19] treated with 50 torr of H_2 at room temperature, 1.27 $(Ag_3)^+$ clusters and 0.7 $(Ag_5)^{2+}$ clusters per unit cell were found in the large cavity. In the structure of $Ag_{4.6}Na_{7.4}$-A, dehydrated and treated with H_2 at 350 °C, $(Ag_6)^{3+}$ clusters of low symmetry were found in the large cavity.[3,9]

In the structure of fully Cs^+ ion exchanged zeolite A which was prepared by the sorption of cesium metal vapor on dehydrated Na_{12}-A, Na^+ ions were reduced and replaced by Cs vapor and linear cesium clusters $(Cs_3)^{2+}$ and $(Cs_4)^{3+}$, were found.[20]

This work was done to learn whether new silver clusters, or known clusters with unknown structure, could be synthesized for the reaction of $Ag_{3.2}Na_{8.8}$-A with cesium metal vapor as a reducing agent and, if so determine their structures by single-crystal X-ray diffraction techniques.

Experimental

Complete Ag^+ exchange of zeolite 4A single crystals is accomplished by a static method. 0.2g of zeolite 4A (Union Carbide, Lot 494107701161) were allowed to exchange at 24°C with 6-fold excess of 0.05N $AgNO_3$, and the solution was agitated periodically. Each day, the supernatant solution was decanted and a fresh aliquot of 0.05N $AgNO_3$ was added. After 7 days, the zeolite was filtered and dried.

To prepare of Ag_4Na_8-A, samples of Ag_{12}-A and Na_{12}-A were mixed in a 3:1 mole ratio (neglecting water content). To this mixture was added a few large single crystals of zeolite 4A which had been prepared by Charnell's method,[20] with enough water to submerge all solid particles so that at equilibrium the composition of the large crystals would be Ag_4Na_8-A. After 4 days, the water was allowed to evaporate in air at room temperature.

A single crystal 80 μm on an edge was selected and lodged in a fine glass capillary. The hydrated partially Ag^+-exchanged crystal was dehydrated for 48h at 360 °C and 2.0×10^{-6} torr, and then exposed to 0.1 torr of cesium vapor for 12h at 250 °C. After cooling to room temperature, the crystal was sealed off in its capillary by torch. The crystal became metallic black.

Diffraction intensities were subsequently collected at 21(1) °C. The space group *Pm3m* (no systematic absences) was used throughout this work for reasons discussed pre-