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# Silver Clusters and Chemistry in Zeolites

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## Contents

## 1. Introduction

A new era of nano-structured materials is emerging. The stringent requirements for novel optical and electronic materials with precisely defined nanoparticle size, geometry, and dimensionality are stimulating an exponential growth in research in this area. A focus of this research has been on the synthesis and characterization of clusters in matrices (*e.g.* in polymers, in zeolites, and in noble gas and other glasses), in the vapor phase, and in colloidal solution.[1-8]

The group VIII transition metals, Ni, Pd, and Pt, have been extensively studied because of their pronounced catalytic activity.[9-11] These three metals, and others of lesser catalytic importance including rhodium, iridium, and silver, are cubic closest packed. It is partly for this reason that silver clusters have been a well-studied model in recent years. Additionally, a better understanding of the nucleation process of cluster formation, and of the transition in properties from molecular aggregates of metal atoms to the bulk metal, can follow from the study of silver clusters.

The spectroscopic work done on silver clusters trapped in solid noble gas matrices at low temperature has been extensively reviewed by Ozin,[12] and Henglein has done the same for photochemical studies of colloidal silver particles in solution.[8,13] This article will review the chemistry of silver in zeolite hosts, including the synthesis and structures of silver clusters.

Zeolites are a class of materials which have crystallographically well-defined channels and cavities. Although originally defined as aluminosilicates with anionic frameworks, the definition of zeolites has expanded to include silicates, aluminophosphates, silicoaluminophosphates, gallosilicates, titanosilicates, metallosulfides, metallo-oxides, *etc.*[14,15] Many of these new members of the zeolite family have neutral frameworks. The framework structures of zeolites are composed of assemblages of $SiO_4$, $AlO_4$, $PO_4$, or other tetrahedra which share vertices to form the basic building units.[16] The simplest of these are the *n*-rings, e.g. 4-rings, 6-rings, 8-rings, and 12-rings, where *n* is the number of oxygens in a ring. A 6-ring, for example, is a 12-membered ring whose aperture is defined by the van der Waals radii of six oxygen atoms. Figure 1a, for example, is composed of 4-rings and 6-rings. Double-4-rings (D4R's) consist of two parallel eclipsed 4-rings joined together by four bridging oxygens to give a near cube of eight tetrahedral atoms with an oxygen near the middle of each edge: Figure 1b contains double-4-rings. Other common units in these structures are double-6-rings (D6R's, see the hexagonal prisms in Figure 1c), double-8-rings (D8R's, see the octagonal prisms in Figure 1d), the sodalite cavity (Figure 1a) which may be viewed as a fundamental building unit for zeolite A (Figure 1b) and faujasite (zeolites X and Y) (Figure 1c), the α-cage (at the center of Figure 1b, and at the corners and center of Figure 1d), and the

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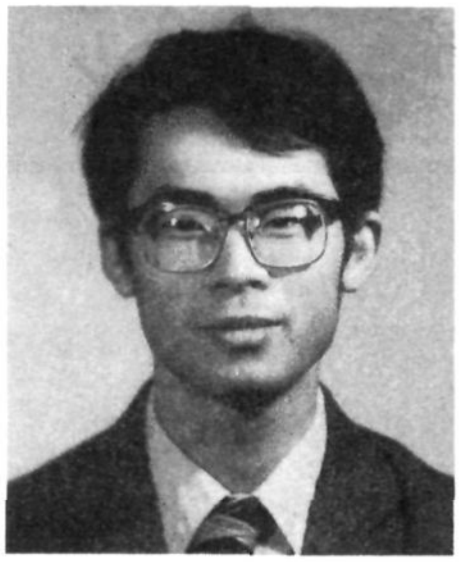
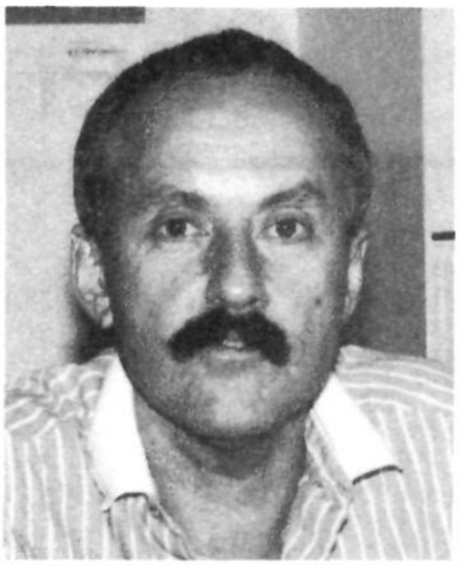


Tao Sun was born in the south of China, but grew up in the very north near the Russian border. He taught high school for three years after graduation from a teachers' college. In 1987, he obtained his M.S. degree in heterogeneous catalysis from the Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan. For three years, he worked in the Research and Development department of the Jinling Petrochemical Corporation in Nanjing. He obtained his Ph.D. in physical chemistry from the University of Hawaii in 1993. He is interested in the synthesis and characterization of heterogeneous catalysts and nano-structured porous materials.



Karl Seff grew up on a chicken farm near Petaluma, CA. He received his B.S. degree in chemistry from U.C., Berkeley, in 1959, and his Ph.D. from M.I.T. in 1964 under David P. Shoemaker. After three years with Kenneth N. Trueblood at U.C.L.A., he joined the faculty at the University of Hawaii, where he is now Professor of Chemistry. Using X-ray and pulsed-neutron crystallography, he studies the chemistry which occurs within zeolites. A typical experiment would involve ion-exchange and dehydration of a single crystal, followed by treatment or sorption under well-defined conditions, and finally structure determination. Cation positions, neutral and charged metal and binary clusters, small molecule and free radical complexes, and metallic continua are identified.

supercage (at the center of Figure 1c). Several typical zeolite structures are shown in Figure 1, parts b–e.

Most zeolites contain exchangeable cations in their channels and cavities, as needed to balance the anionic charge of their frameworks. They may also contain easily removable and replaceable guest molecules such as water or organic molecules. Organic templates used in zeolite synthesis, typically alkylammonium ions, are usually not removable except by decomposition or oxidation.[16] Zeolites can show high catalytic activity and high specific selectivity toward reactants, reaction intermediates, and products. This gives them wide utility in the petrochemical industry as catalysts. In addition, they are very selective sorbents for gas- and liquid-phase separations.

In recent years, zeolites have found new uses as hosts for the preparation of supersmall (less than one unit cell in extent) or superlattice [more (often much more) than one unit cell in extent] metal and semiconductor clusters in a new rapidly developing subfield of solid-state materials science.[19–21] A wide range of metal or binary compound clusters and of organometallic or coordination compounds has been entrapped in different types of zeolites.[19,20,22,23] These composite materials have found numerous applications, including size/shape selective catalysis,[22,24–27] gas separation and purification,[28] and electro- and photocatalysis.[9]

The following are some reasons for studying silver zeolites:

(1) $Ag^+$ is the *only* noble monopositive cation that forms a mononuclear species with appreciable stability in water.[29] No hydrolysis occurs. Of all the noble metals, only $Ag^+$ can be exchanged, easily and completely, into zeolites from aqueous solution. Stoichiometric ion exchange, impossible to achieve for most cations, is frequently observed for $Ag^+$.

(2) The reversible oxidation–reduction of silver in zeolites provides an excellent model system for studying the mechanism of formation of noble metal clusters within zeolite channels and cavities. It is also an excellent model for studying the catalytic mechanism for the dehydrogenation of hydrocarbons.

(3) Hydrated silver zeolites are light-sensitive materials. It was recently proposed that silver zeolites incorporated into membrane electrodes may be used to photocatalyze the splitting of water.[11] This may become commercially important on a large scale in the future.

(4) Various silver sodalite materials prepared by Ozin and Stucky[30,31] demonstrate that silver halosodalites may be used to fabricate organized assemblies of $(Ag_4X)^{3+}$ clusters. Interactions among these clusters directly affect the optical properties of these materials. They are potential candidates for light-write and light-erase materials, and they may also have application as pressure or chemical sensors.

## 2. Structures and Chemistry of Silver Clusters in Zeolites

It has been shown by a variety of techniques that small silver clusters, neutral or charged, form and are stabilized in the cavities and channels of zeolites A, X, and Y, chabazite, mordenite, and Rho.

### 2.1. Silver Clusters in Zeolite A

Zeolite A (Figure 1b) may be viewed as an assemblage of truncated octahedra, each composed of 24 tetrahedra (Figure 1a). These are variously referred to as cubo-octahedra, sodalite cavities, or $\beta$-cages. These cubo-octahedra are octahedrally joined at 4-rings by four bridging oxygens.

### 2.1.1. Silver Clusters in Completely $Ag^+$-Exchanged Zeolite A (Ag-A)

In 1962, dehydrated Ag-A was found to be very sensitive to even small amounts of moisture.[32] Upon

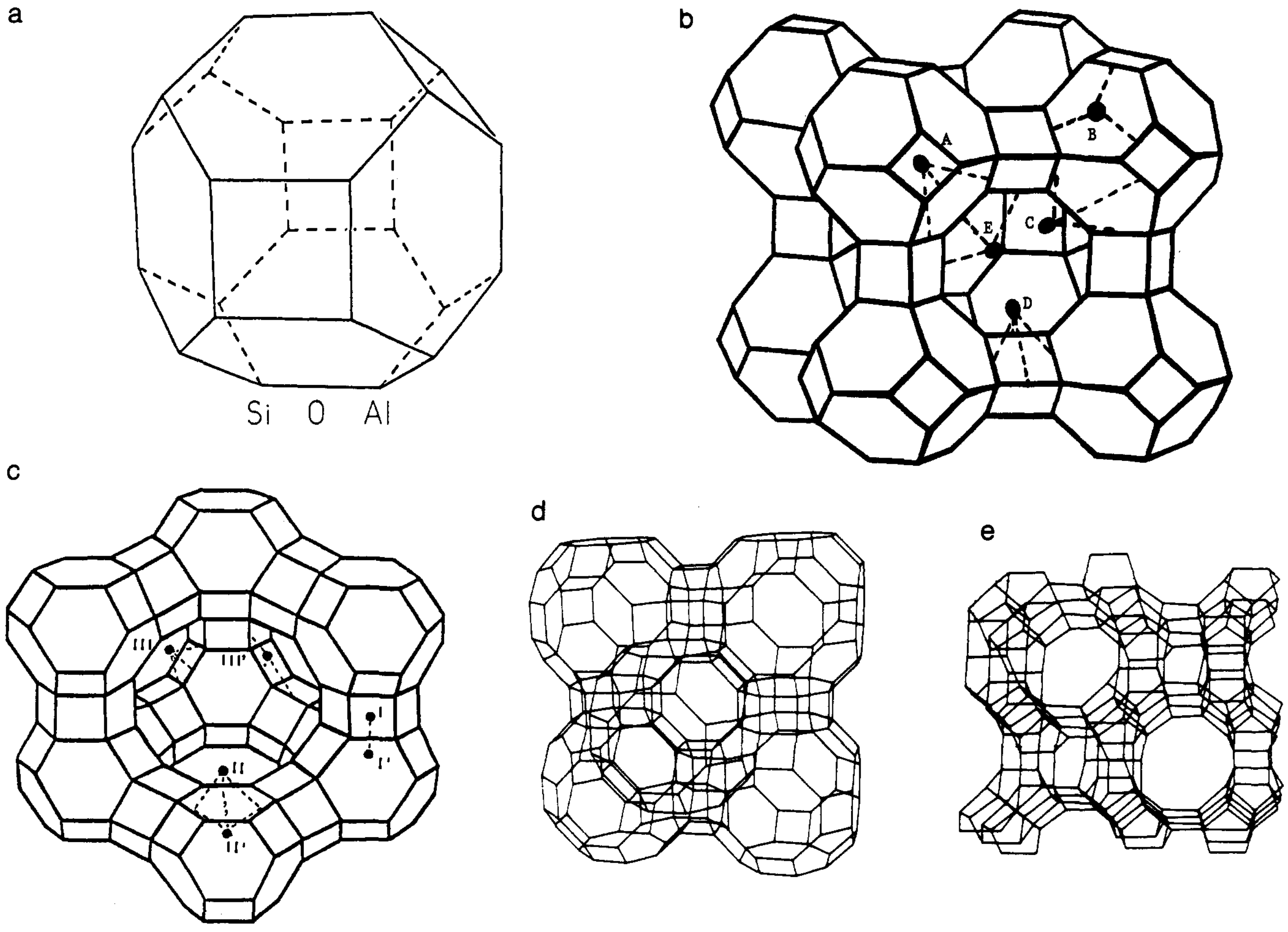


**Figure 1.** Framework structures of a sodalite cavity (a) and of zeolite A (b), faujasite (synthetic faujasite is called zeolite X or zeolite Y) (c), Rho (d), and mordenite (e). Extraframework cation positions in zeolite A (b) are labeled with letters, and those in faujasite (c) are labeled with Roman numerals. (Parts a and b are reprinted from ref 17. Copyright 1993 AAAS. Parts d and e are reprinted from ref 18. Copyright 1992 Butterworth-Heinemann, a division of Reed Publishing (USA), Inc.)

absorption of water, the brick-red color of dehydrated Ag-A changed to orange, then to yellow, and finally to white. No explanation for this phenomenon was given at that time.

In 1977, Kim and Seff observed these and other color changes in fully $Ag^+$-exchanged zeolite A during dehydration at high temperature under high vacuum. In gold-colored single crystals, they found, by single-crystal X-ray diffraction techniques, the uncharged octahedral hexasilver clusters, $Ag_6^0$, in the sodalite cavities. Each hexasilver cluster was stabilized by coordination to eight silver cations in 6-rings (Figure 2).[33,34] The neutral charge was assigned because the Ag–Ag distances were the same as those in silver metal and because of the relatively long silver to oxygen distances, *ca.* 2.8 Å, substantially longer than typical intrazeolitic $Ag^+–O^{\delta-}$ distances, *ca.* 2.25 Å. Although this charge assignment was not completely conclusive, these silvers were, at least substantially, reduced.

The hexasilver cluster is closest packed, like a small unit of the structure of silver metal itself, and has the same symmetry, $O_h$, as its host, the sodalite cavity. Crystallographic results disclosed that as the conditions of vacuum dehydration, such as temperature and time, were increased, the number of silver cations reduced increased from one to nearly four of the 12 per unit cell. The almost spherical thermal parameters of the silver atoms indicated that they were each relatively well surrounded, by contacts with silver cations, other silver atoms, and components of the zeolite framework. This argues for good packing, full occupancy, and high symmetry, *i.e.* hexasilver in a fraction of the sodalite cavities rather than smaller clusters which would occupy all of the sodalite units. Because of the occupancy of

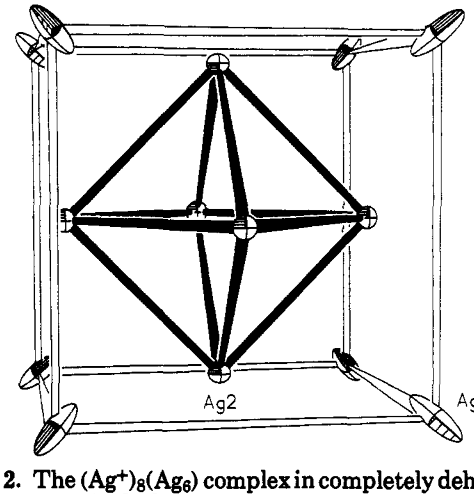


**Figure 2.** The $(Ag^+)_8(Ag_6)$ complex in completely dehydrated Ag-A. The octahedral $Ag_6$ molecule, stabilized by coordination to eight $Ag^+$ ions is shown. The framework atoms of the sodalite cavities are not shown for clarity. Ellipsoids of 20% probability are shown. (Reprinted from ref 34. Copyright 1978 American Chemical Society.)

the reduced Ag position (opposite 4-rings in the sodalite cages of Ag-A) was fractional, this work did not provide complete crystallographic proof for the existence of these hexasilver molecules. The crystallographic results do require, however, that the structures of clusters with five or fewer silver atoms be octahedral with one or more, respectively, vertices missing. These species would have sharply fewer Ag–Ag bonds per atom than hexasilver and would therefore be far less stable. Such species are unlikely to exist unless kinetics prohibits further agglomeration.

The color changes were attributed to a charge-transfer interaction between $Ag^+$ and framework oxygens by Seff and Kim.[33,34] It was noted that, in silver compounds, as the Ag–O bond becomes shorter and more covalent, the color of the compound changes from colorless (Ag–O = 2.48–2.51 Å),[35–37] to golden yellow (2.34 Å), to brown-black (2.05 Å).[38] This explanation was supported by UV/vis transmission spectra of the dehydration and rehydration processes in highly $Ag^+$-exchanged zeolite A.[39] Consistent with this, from the reversible transitions between the three forms of Ag-A observed in dehydration and rehydration processes, Karge attributed the three absorption bands (455, 535, and 585 nm) to three different hydration states of Ag-A. An extended Hückel quantum-chemical calculation showed that the color change correlated with charge transfer from framework oxygens to silver cations; the lowest energy transition in Ag-A was a charge transfer from an orbital localized mainly on framework oxygens to that of a silver ion in a 6-ring.[40] After nearly all of the water is lost, further changes in color must be attributed to the increasing extent of $Ag^+$ reduction (to the formation of silver clusters). The shortest Ag–O bonds and the darkest colors occur when little or no water is retained and little or no $Ag^+$ has been reduced.

It was found that the crystalline X-ray diffraction pattern of dehydrated Ag-A was entirely lost upon exposure to hydrogen gas at 297 or 323 K; only powder diffraction lines from small crystallites of silver were seen.[41,42] However, the full diffraction patterns of Ag-A powder[41] and a Ag-A single crystal,[42] lost upon $H_2$ reduction, remarkably returned after treatment with $O_2$, indicating that the framework structures had been restored. In the single-crystal work, the full integrity of the single-crystal framework had been restored. However, only about 11 $Ag^+$ ions per unit cell were located in the repaired crystal structure,[42] showing that the repair was not quite complete.

In Kim and Seff's reports,[33,34] the elongated thermal parameters of the $Ag^+$ cations in 6-ring planes were viewed as true thermal motion. However, they may also indicate the presence of two different $Ag^+$ positions: one would be partially reduced and would bind to the reduced silver atoms in the sodalite cavities; the other would be $Ag^+$ ions which did not participate in such an interaction. This was essentially the only crystallographic argument for the existence of linear $Ag_3^{2+}$ clusters (*vide infra*).

The mechanism of silver reduction and the interactions of silver clusters with absorbate gas molecules in Ag-A and Ag,Na-A were investigated in detail by Jacobs, Uytterhoeven, and Beyer.[41] A temperature-programmed desorption (TPD) experiment on hydrated Na,Ag-A showed that water was the main desorption product at low temperature, but that oxygen gas was evolved at higher temperatures, above 400 K. As no hydroxyl groups were detected by IR, the following "autoreduction" mechanism was proposed for Ag-A:

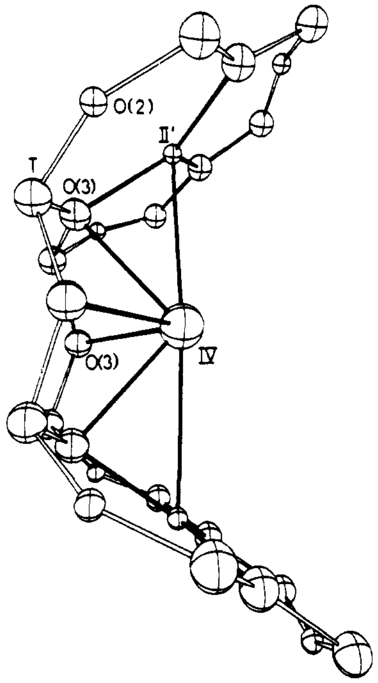
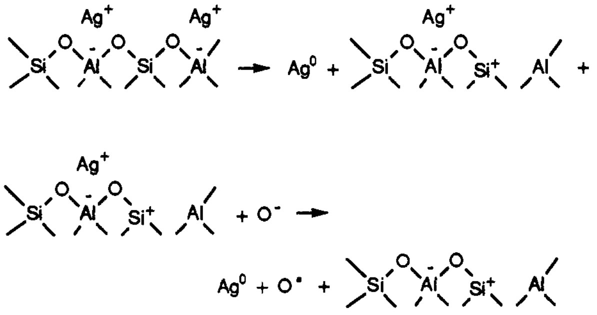


**Figure 3.** Representation of the coordination of the $Ag_3^{2+}$ cluster in dehydrated Ag,Na-A. The Ag species are two at II' about one at IV. Ellipsoids of 50% probability are shown. The higher thermal motion at IV indicates that this silver atom is less firmly held than those at II'. An artificial temperature factor of $1 \times 10^{-2}$ nm$^2$ was used for Ag(II'). (Site II' in ref 43 is site A in Figure 1b.) (Reprinted from ref 43. Copyright 1981 Butterworth-Heinemann, a division of Reed Publishing (USA), Inc.)



(1)

(2)

$$2O^\bullet \rightarrow O_2 \qquad (3)$$

The overall stoichiometry of this reaction can be represented symbolically as

$$2Ag^+ + ZO^{2-} \rightarrow {}^1/_2O_2 + 2Ag^0 + Z \qquad (4)$$

Where $ZO^{2-}$ represents a zeolite framework and highlights one of its oxygens, and Z represents a zeolite framework with a missing oxygen link, *i.e.* with a Lewis acid site.

Contrary to Kim and Seff's model, Jacobs *et al.*[41] proposed the existence of isolated linear $Ag_3^{2+}$ clusters (see Figure 3) in the sodalite cavities because "an $Ag_8^{8+}$-($Ag_6^0$) cluster in the sodalite cage is rather improbable, since its formation in low exchanged forms would result

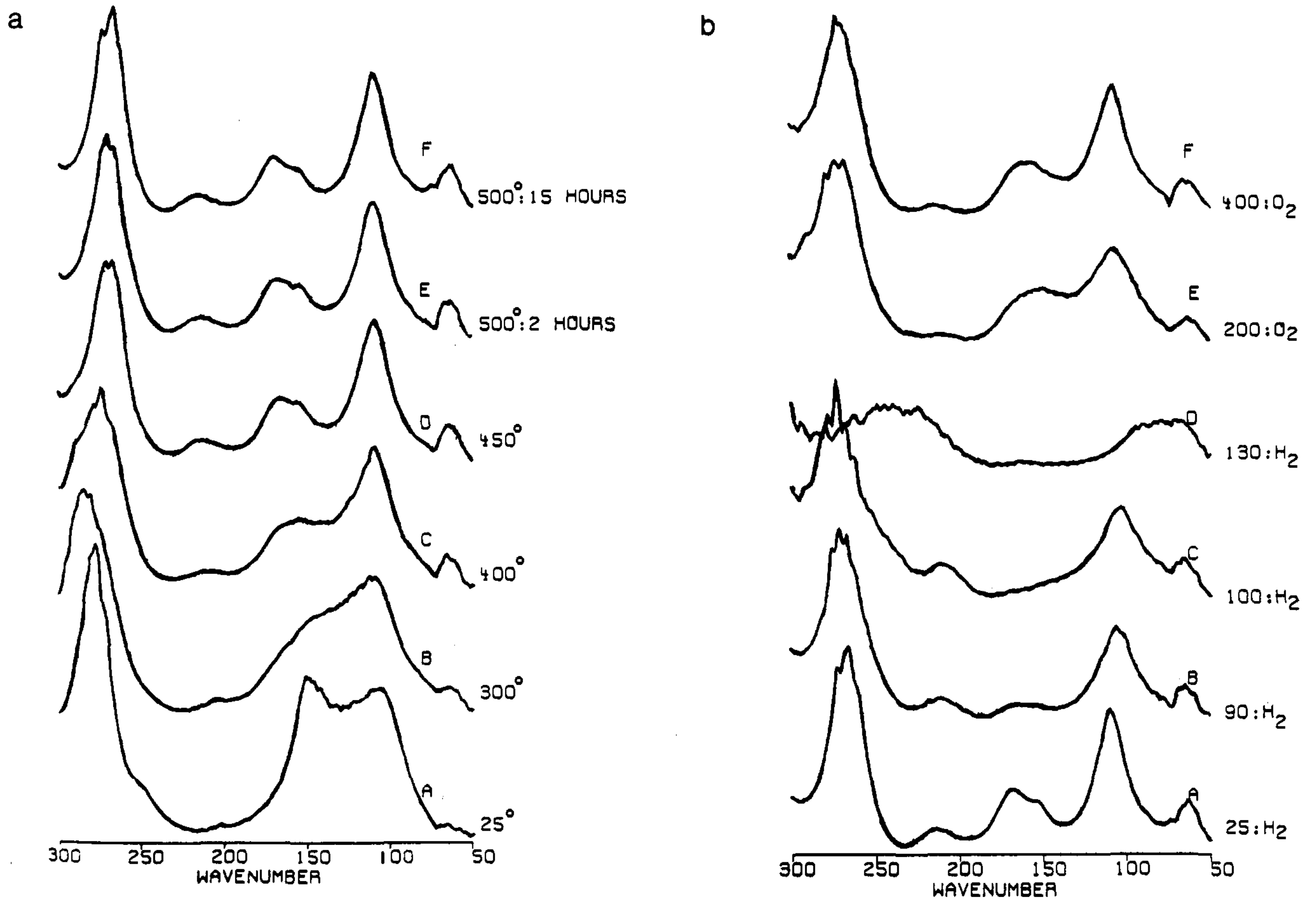


**Figure 4.** The far-IR absorbance spectra of Ag-A: (a) during vacuum dehydration at the indicated temperature (in °C) and (b) during $H_2/O_2$ reduction–oxidation at the indicated temperature (in °C). (Reprinted from ref 50. Copyright 1985 American Chemical Society.)

in segregation of cations: part of the crystal should contain only Na$^+$ cations, while aggregation of charged silver should occur at a few other spots". Because no OH groups were observed in IR spectra, they concluded that no reduction of Ag$^+$ cations had occurred upon exposure of Ag-A to hydrogen at room temperature, which was inconsistent with both the qualitative (Ag powder diffraction lines) and the quantitative (structural) crystallographic results.[41,42]

This Ag$_3^{2+}$ cluster in Na,Ag-A was then reported to be present in Ag-A also. A series of structure refinements and optical measurements on zeolite powder and on single crystals of Ag-A were carried out to support the presence of isolated and 2–4 interacting Ag$_3^{2+}$ clusters in the sodalite cavities.[43–45] Using powder X-ray diffraction data, Gellens and co-workers refined Ag$^+$ ions in the 6-rings at two positions, sites A and B (see Figure 1b).[43,44] Attempts by Kim and Seff[33,34] to refine these positions using single-crystal data did not support Gellen's result. Because of the redundancy in $h^2 + k^2 + l^2$, Gellen's refinement using powder data was necessarily less reliable (this work predates Rietveld methods[46]). Refinement of these same positions by Gellens using single-crystal diffraction data[45] was not successful either: the overlap of the displacement ellipsoids led one thermal parameter to become unusually high. In this single-crystal structure refinement, the occupancy ratio of Ag(site A)/Ag(site D, a position for reduced silvers) = 1.60, a vlaue intermediate between the theoretical extremes of 2 for a linear triplet and 1.33 for a hexasilver cluster, respectively. The nature of the silver clusters in zeolite A had not been clarified.

However, it was clear from Gellens' work that the extent of Ag$^+$ cation reduction depends on the dehydration temperature.[43] A yellow color appeared at 378 K, which was assigned to isolated linear Ag$_3^{2+}$ clusters. The brick-red color which appeared at more severe dehydration conditions was attributed to 2–4 interacting Ag$_3^{2+}$ clusters. He believed that the color changes were due to the formation of silver clusters inside the sodalite cavities and that the color shifted from yellowish to brick-red as the size of the clusters increased.

A diffuse-reflectance spectroscopic study[47] and a molecular orbital calculation[48] were carried out for the purpose of better understanding the electronic and the physical structure of these linear trisilver clusters. The calculated electronic transition energies within trisilver clusters deviated widely from that found in the observed spectra. Because such a calculation was very difficult to do, the optical absorption assignments could only be based on comparisons with available data.

Ag-A and Ag,Na-A were extensively studied by Ozin using far IR techniques.[49–53] The whole process of the formation of silver clusters (Figure 4) was followed. Bands at 149 and 110 cm$^{-1}$ were assigned by Ozin to the stretching modes of an isolated Ag$_3^{2+}$ cluster, and bands at 168, 153, 110 and 63 cm$^{-1}$, to skeletal modes of Ag–Ag interaction between Ag$_3^{2+}$ clusters.

The existence of hexasilver clusters was confirmed by ESR observations of the reduction process in Ag-A by Hermerschmidt and Haul,[54] followed by those of

Schoonheydt.[55,56] No ESR signals were detected after vacuum dehydration of Ag-A at 673 K. A characteristic, isotropic seven-line spectrum appeared in Ag-A when dehydrated Ag-A was exposed to hydrogen gas at temperatures below 293 K. This signal was not stable in the presence of hydrogen gas at room temperature. Upon further hydrogen reduction, the reduced silver atoms migrated out of the sodalite cages and aggregated on the external surface of the zeolite. The *g* value of the seven-line ESR spectra was 2.053 with a hyperfine coupling constant $A = 7.23$ mT and a line width $\Delta H_{pp} = 3.07$ mT. This suggested that a zeolite cavity contained six equivalent silver nuclei. The only reasonable interpretation for this ESR resonance in Ag-A was the formation of a charged highly symmetric hexasilver cluster inside a sodalite cage, like the neutral hexasilver cluster proposed by Kim and Seff.[33,34]

The structure and environment of two interacting linear trisilver clusters, as proposed by Uytterhoeven,[41] are not very different from that of octahedral hexasilver, and might have been responsible for this seven-line ESR signal. This explanation was dismissed because further hydrogen reduction should have generated more complex trisilver cluster interactions as proposed by Gellens.[43,44] The observed seven-line ESR signal would then be changed, but this was in disagreement with Hermerschmidt and Haul's experimental results:[54] further reduction by hydrogen at higher temperature only decreased the intensity of this signal without showing new signals for intermediate silver clusters.

According to Ozin's assignments of the spectra in Figure 4, parts a and b, the far-IR spectra of silver–silver skeletal modes were the same in Ag-A either after vacuum dehydration above 673 K or upon hydrogen reduction at 298 or 363 K. If so, these results, combined with Hermerschmidt and Haul's ESR results, indicated that octahedral hexasilver had formed during the dehydration process, but that it was an ESR quiet species, $Ag_6^{n+}$ ($n = 0, 2,$ or 4). Upon hydrogen reduction of vacuum-dehydrated Ag-A, ESR active $Ag_6^{n+}$ clusters ($n$ = 1, 3, or 5) formed.

Optical absorption, mass spectroscopy, static magnetic susceptibility, ESR, and gas adsorption were used by Texter *et al.* in an extensive study of Ag-A.[57,58] They concluded that the predominant charged silver clusters formed in Ag-A during mild autoreduction were not paramagnetic. Their magnetic susceptibility measurement contradicted the earlier assignment of cationic $Ag_3^{2+}$ clusters, and indicated that the paramagnetic $Ag_3^{2+}$ cluster was not an intermediate in the dehydration process. This result, as well as the long-standing failure to detect an active linear $Ag_3^{2+}$ species by ESR, disproved the existence of $Ag_3^{2+}$ clusters in the sodalite cages of Ag-A.

Subsequently, a $Ag_3^{+}$ intermediate cluster was proposed to replace the $Ag_3^{2+}$ model.[60] This proposal required the partial reduction of its terminal 6-ring silvers and was in direct conflict with the crystallographic results: the terminal 6-ring silvers bonded strongly to framework oxygens. The bond distance was much shorter than the sum of the radii of $Ag^+$ and $O^{2-}$, which indicates that these silvers are simply cations and are not partially reduced. Additionally, the proposed percentage of reduced silvers in Ag-A at 673 K would be at least 34% if $Ag_3^{+}$ clusters had formed. This number was far higher than the 8% reported by Jacobs.[41]

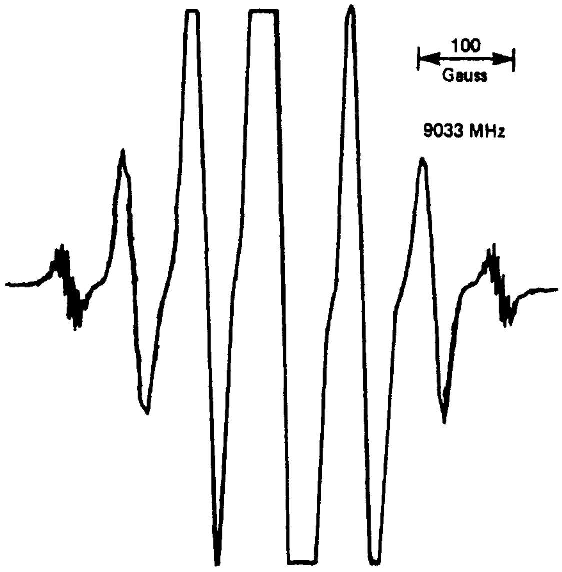


**Figure 5.** First-derivative ESR spectrum at 77 K of the $Ag_6^{+}\cdot 8Ag^{+}$ cluster trapped in the sodalite cavity of Ag-A. (Reprinted from ref 62. Copyright 1987 Butterworth-Heinemann, a division of Reed Publishing (USA), Inc.)

Morton and Preston[61] carefully studied $\gamma$-irradiated Ag-A by ESR and detected three paramagnetic silver clusters: $Ag_2^{+}$, $Ag_3^{2+}$, and $Ag_6^{+}$. Unlike the assignment of the linear trisilver clusters, they found that their trisilver cluster had four isotropic lines, indicating the equivalency of the three silver nuclei. They concluded that this trisilver cluster was cyclic with a $^2A_1'$ electronic configuration in $D_{3h}$ symmetry. Hückel and *ab initio* calculations showed that *cyclo*-$Ag_3^{2+}$ was more stable than linear $Ag_3^{2+}$.[61] Considering the hyperfine anisotropy, bonding, and Jahn–Teller distortion of seven isotropic ESR lines, Morton and Preston assigned the charge of the octahedral $Ag_6$ clusters in their sample to be +1, a highly reduced silver cluster.

They also observed a remarkable superhyperfine signal for the $Ag_6(Ag_8^{8+})$ cluster[62] (Figure 5) in an ESR experiment done with a $^{109}$Ag-isotope-enriched sample. Nine superhyperfine splitting lines were observed at the first and the last hyperfine ESR signals. This superhyperfine interaction was from the eight $Ag^+$ cations surrounding the central hexasilver cluster. It was the first ESR experiment to provide information about the first coordination sphere of the $Ag_6$ cluster in silver zeolites without using a modulation method. In their report, they stated that the ESR evidence confirmed that the coordination number of the hexasilver clusters was variable, as had been found by Kim and Seff in their crystal structure of the ethylene sorption complex of Ag-A[63] and that it depended upon the extent of reduction.

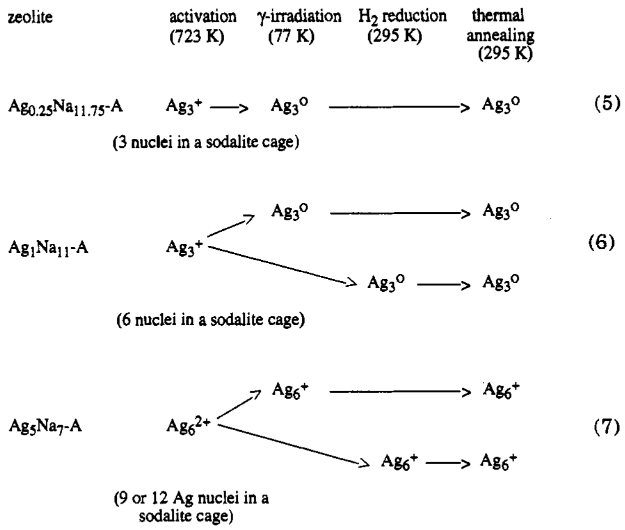
Kim and Seff's crystallographic results showed that as the coordination number of hexasilver decreases from 8 to 6 to 2, the Ag–Ag distance in the $Ag_6^0$ clusters decreases from 2.928(4) to 2.850(4) to 2.830(5) Å.[34,63,64] The Ag–Ag distance in bulk silver is 2.889 Å. This small and possibly insignificant effect (the esds quoted do not include possible systematic errors) indicates that the bonding is strongest within the least coordinated hexasilver cluster and that the bond length in isolated $Ag_6^0$ would be significantly less than that in bulk silver. The greater the number of coordinating $Ag^+$ ions, the more bonding density is drawn away from the central hexasilver molecule.

It gradually became clear that hexasilver clusters in the sodalite units of completely $Ag^+$-exchanged zeolite A are relatively stable intermediates. Silver particles formed on the external surface of the zeolite upon further reduction, indicating that $Ag_6^0$ is not stable within the zeolite unless it can coordinate to $Ag^+$ ions. Because the reduction of fully Ag-exchanged zeolite A by hydrogen was very fast, the kinetics of the reduction, migration, and aggregation of silver species could not be followed by ESR.

### *2.1.2. Silver Clusters in Partially $Ag^+$-Exchanged Zeolite A (Ag,M-A)*

Schoonheydt reasoned that silver cluster formation might be much slower in partially Ag-exchanged zeolite A because the alkali metal cations might hinder the migration of reduced silver atoms.[55] Electron-transfer processes, likely to be responsible for the anomalously high mobility of $Ag^0$, should be disrupted by alkali metal ions. If so, intermediates in the mechanism of silver cluster formation could be trapped and identified by physical methods. Also the reaction kinetics of cluster formation could be slow enough to be easily measurable by ESR and other experimental techniques. In addition, zeolite A has a tolerance for $H^+$ exchange, up to *ca.* 40%, so that the reduction of $Ag^+$ by $H_2$ to give $H^+$ and silver clusters does not necessarily need to lead to the destruction of the zeolite A framework.[65] Indeed, after dehydration at 573 K, crystals of composition $Ag_{7.5}Na_{4.5}$-A and $Ag_{2.8}Na_{9.2}$-A[66] were not destroyed by hydrogen reduction at room temperature. Bent $Ag_3^+$ and $Ag_3^{2+}$ clusters were located crystallographically in the large cavities of $Ag_6Na_6$-A (dehydrated at 623 K and treated with hydrogen at room temperature). A $(Ag_6)^{3+}$ cluster of low symmetry was found in the large cavity of $Ag_{4.6}Na_{7.4}$-A treated with hydrogen at 623 K.[67]

Kevan reported that silver atoms are stabilized in hydrated $Ag_{0.7}Na_{11.3}$-A which had been exposed to $\gamma$-irradiation at 77 K.[60,68–70] The modulation of the ESR signal revealed that each reduced silver atom is at the center of a 6-ring and is coordinated by two water molecules, one in the sodalite cavity and the other in the large cavity. Water molecules were found to play a critical role in the stabilization of the reduced silver atoms in this zeolite. Bent paramagnetic $Ag_3^{2+}$ clusters[69] were also found in the large cavity, but they were destroyed immediately in the presence of oxygen, an indication that this cluster was in a location very accessible to $O_2$. As the silver content of the zeolite increased, $Ag_6^+$ clusters showing the characteristic isotropic seven-line ESR signal became more easily detectable. However, Kevan believed that the isotropic seven-line ESR signal did not necessarily arise from six equivalent silver species, and that its interpretation depended on the specific structure and symmetry of the cluster, which should be probed by a suitable molecular-orbital calculation. He proposed the following for the formation of $Ag_6^+$ clusters in $Ag_mNa_n$-A ($m + n = 12$):



Three initial zeolite A compositions, given in the first column, were treated as the arrows indicate with reference to the headings of the remaining columns, to give the intermediate and final silver clusters shown. This study led Kevan to conclude that both the neutral linear $Ag_3^0$ and the $Ag_6^+$ clusters occupy sodalite cavity sites. (Readers are reminded that $Ag_6^0$ is ESR silent and cannot be identified directly by ESR methods, even if it predominates overwhelmingly.)

Hydrated Ag,Cs,Na-A ($Cs_7Na_5$-A with *ca.* 0.7 $Ag^+$ per unit cell exchanged into it) was $\gamma$-irradiated at 77 K, followed by annealing at 273 K for 20 s. A $Ag_4^{3+}$ cluster was detected by ESR at 77 K, but it was destroyed by dehydration.[70] Wasowicz and Michalik[71] interpreted this to be indicative of a $Ag_3^{2+}$ cluster interacting with a $Ag^+$ ion in an elongated manner in the sodalite cavity. The same cluster was found when $Ag_6^{n+}$ clusters in Ag,Na-A were exposed to water vapor. In the hydrated form, water molecules coordinate strongly to silver species to limit the diffusion of reduced silver atoms.[68]

The process of $Ag_6$ cluster formation during hydrogen reduction was studied by Schoonheydt[59] using ESR. He found that the initial rate of formation of $Ag_6$ clusters in Ag,Na-A followed an Arrhenius law with an activation energy in the range of 47–63 kJ/mol, indicating controlled diffusion of alkali metal cations during the formation of silver clusters in Ag,Na-A. In Ag-A, the diffusion rate of the reduced Ag atoms was too fast to be followed, suggesting either electron-transfer processes or very weak interactions between silver atoms and the zeolite framework. There was an induction period for silver cluster formation in Ag,K-A. No silver clusters were observed in the presence of $Cs^+$ or $Ca^{2+}$ cations. $Ag_6$ clusters formed only when two or more $Ag^+$ cations were present per unit cell, in agreement with Kevan's results. The absence of $Ag_6$ clusters in Cs,Ag-A and Ca,Ag-A was understood to result from the difference in labilities between $Cs^+$ or $Ca^{2+}$ and $Ag^+$ cations. He believed that $Cs^+$ and $Ca^{2+}$ were less labile than $Ag^+$ and that these less labile cations were hindering the migration of silver atoms to the reduced silver sites for cluster formation. The mobility of cations in zeolite cavities has been discussed by Stamires[72] and Schoonheydt.[73]

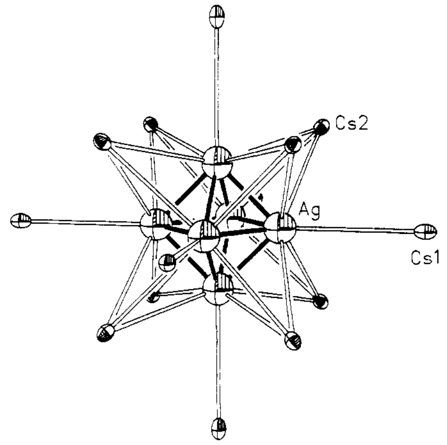


**Figure 6.** The octahedral $Ag_6$ cluster in the large cavity of $Ag_{4.5}Cs_{13.5}$-A. It is stabilized by coordination to six $Cs^+$ ions in a first coordination shell and eight $Cs^+$ ions in a second shell. The framework atoms of the large cavity of zeolite A are not shown for clarity. Ellipsoids of 20% probability are shown.

The crystal structure of Cs,Ag-A, synthesized surprisingly from the reaction of Ca,Ag-A with Cs metal vapor, showed that at relatively mild conditions, 523 K, only $Ca^{2+}$ cations were reduced and replaced by Cs atoms, while the much more electrophylic silver cations were not reduced![74] (The $\mathcal{E}^0$ for the reaction

$$Ag^+ + Cs^0 \rightarrow Ag^0 + Cs^+$$

which had failed to occur is very large, +3.7 V.) These results were explained by noting initially that Cs atoms are too large to pass through 8-rings. Therefore, the oxidation–reduction reaction must have occurred only on the external surfaces of the crystal. Kim and Seff concluded that the relatively covalent Ag–O bonding made $Ag^+$ cations less labile than the ionic $Ca^{2+}$ cations in the zeolite cages. When the Cs-reduction reaction was initiated, only $Ca^{2+}$ could move to the crystal surface to react with Cs atoms, while $Ag^+$, nonlabile at *ca.* 523 K within the fully dehydrated zeolite, could not react. This is in disagreement with Schoonheydt's interpretation of his results.

A remarkable hexasilver cluster was synthesized in the *large cavity* of zeolite A by exposing Ca,Ag-A to rubidium vapor.[75] [*Vide supra* (paragraph 3 of section 2.1.1.) for the arguments for the existence of hexasilver at a fraction of its sites rather than smaller clusters in larger fractions or all of those sites.] Up to five silver atoms (designated to be atoms, or at least more like $Ag^0$ than $Ag^+$, because the Ag–O distances are long) were located crystallographically in the large cavity (which, like the sodalite cavity, has $O_h$ symmetry, assuming Si = Al). Compared to the maximum number of nearly four reduced silver atoms in the sodalite cavity of Ag-A,[33,34] this result was more indicative crystallographically of the formation of hexasilver clusters. In this structure, the proposed hexasilver cluster was coordinated by six $Rb^+$ in the first shell and seven or eight $Rb^+$ in a second shell (similar to that in Figure 6). About 83% of the large cavities of Rb,Ag-A were filled with this type of cluster. This value is quite close to full occupancy of $Ag_6$; a structure with full occupancy would have evenly distributed, isolated, uniform clusters, which may potentially be more suitable for some applications. Subsequently, this hexasilver cluster was synthesized in the large cavity of Na,Ag-A and K,Ag-A by exposure to Cs metal vapor.[76,77] However, when a fully $Ag^+$-exchanged zeolite A single crystal (dehydrated at 623 K at $1 \times 10^{-6}$ Torr) was exposed to alkali metal vapor, no diffraction pattern of zeolite A could be observed at all.[77] It was suggested that residual water molecules, which remain in Ag-A dehydrated at 623 K,[78] may have been responsible, perhaps by the formation of MOH which should be quite corrosive to the zeolite at this temperature.

## 2.2. Silver Clusters in Faujasite Zeolites

Faujasite is the general name for zeolites X and Y and the mineral faujasite. Its aluminosilicate framework may be viewed as an assemblage of sodalite cavities (Figure 1a), of composition $(Si_{24-x}Al_xO_{48})^{x-}$, $0 < x < 12$, which are arranged in space (Figure 1c) like the carbon atoms in diamond. They are joined at alternate 6-rings by six bridging oxygens, one bound to each vertex of Figure 1a, to complete a tetrahedron. This leads to the existence of large supercage cavities and small D6R cavities (Figure 1c). The extra-framework cations which balance the negative charge of the framework occupy various positions (labeled in Figure 1c) dependent on their coordination requirements and ionic radii and on the aluminum distribution in the zeolite framework.

The sodalite unit, which nearly has $O_h$ symmetry in zeolite A, has only $T_d$ symmetry in faujasite. The eight 6-rings, equivalent in zeolite A, become four tetrahedrally arranged single 6-rings (S6R's) and four tetrahedrally arranged D6R's in faujasite, 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. Understandably, studies of the formation of silver clusters in Ag-X and Ag-Y have yielded results very different from those in Ag-A.

Octahedral hexasilver clusters, the most likely reduction intermediates between silver ions in Ag-A and bulk silver metal outside the zeolite, have never been found in Ag-X and Ag-Y by any direct method, except for Ozin's interpretation of spectra taken in the far-IR region.[50]

Eulenberger, Shoemaker, and Keil[79] found that $Ag^+$ ions selectively occupy sites I and II (Figure 1c) in vacuum-dehydrated Ag-Y. About one-third of the site I′ positions (opposite S6R's and inside the sodalite cavity) were also occupied by $Ag^+$ cations. The interactions between silver ions in the sodalite cavity were distant and weak. The distance, $Ag_{(I)}$–$Ag_{(I')}$ = 3.24 Å, was substantially longer than the Ag–Ag distance in silver metal and in Ag-A. The authors did not interpret these positions to indicate that reduction had occurred or that clusters had formed. Consistent with this, the sample they studied was colorless.

Tsutsumi and Takahashi[80] found that $Ag^+$ ions in Ag-Y could easily be reduced to bulk silver clusters (15–30 nm on the external surface of zeolites) by treatment with alkylbenzenes and alcohols. $Ag^+$ ions in Ag-X and Ag-Y were also reduced by treatment with carbon monoxide at 623 K. Riekert[81] found that fully reduced Ag-Y could be reoxidized to produce the original Ag-Y and that the extent of oxidation could be controlled by experimental conditions. Ono got similar results in his study of the $H_2$ reduction of Ag-Y.[82]

The consumptions of hydrogen by $Ag^+$-Y and of oxygen by $Ag^0$-Y were followed by IR and X-ray spectrometry.[83,84] High- and low-temperature reduction mechanisms were reported. At low temperature, hydrogen reduction probably resulted in the formation of $Ag_3^+$ clusters in sodalite cavities. Further reduction was resisted. The reduction rate was found to be limited by cation migration. Above 623 K, large silver particles were found on the external surface of zeolites by powder X-ray diffraction. The high activation energy for this reduction reaction was attributed to the difficulty with which $Ag^0$ atoms at site I migrated out of D6R's.

The preference of $Ag^+$ ions for site I in autoreduced Ag-X and Ag-Y was further confirmed by Gellens *et al.* by powder X-ray methods[43,85] and by Smolin by single-crystal X-ray diffraction.[86] As the Si/Al ratio decreased, 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; none were opposite 4-rings. Gellens found that the maximum number of $Ag^+$ ions in a sodalite cavity of vacuum-dehydrated Ag-X or Ag-Y was 4. However, Smolin found it to be 5.5, which he interpreted to be five $Ag^+$ ions in half of the sodalite cavities and six in the other half. Interactions among the silver ions within the sodalite cavity could not be avoided because of the very short distances involved, 2.92–3.10 Å. Smolin proposed that $Ag_5^{5+}$ clusters without bonding electrons existed (not clusters at all) and that they were distorted monocapped tetrahedra. His $Ag_6$ cluster could not be an undistorted octahedron because the symmetry of zeolite X prohibits that. The refined occupancies of silver ions in Ag-X, determined by Gellens, indicated that $Ag_2$ or $Ag_3$ clusters may have formed.[85]

In fact, silvers opposite D6R's were found off 3-fold axes in a Ag-X single-crystal structure (dehydrated at 723 K, exposed to $O_2$ gas and degassed at 623 K) by Sun.[77] About six silver ions were found per sodalite cavity: site I′ (opposite the D6R's, but slightly off 3-fold axes) is full, and site II′ (opposite S6R's) is half full. $Ag_6^{m+}$, if it has formed, must be a distorted bi-capped tetrahedron. Alternatively, a mixture of clusters from $Ag_4$ to $Ag_8$ which average to six Ag per sodalite cavity might exist. This indicates that tetrahedrally distorted cubic $Ag_8^{n+}$ clusters, which may have formed at low concentration in this crystal, might be present in higher concentration in the sodalite cavities of faujasites with lower Si/Al ratios, as site II′ becomes more fully occupied by silver.

The redox reactions of Ag-Y with hydrogen and oxygen were followed by powder X-ray diffraction.[85] Oxygen treatment of dehydrated Ag-Y under vacuum at 873 K, which had already formed reduced linear $Ag_3^{2+}$ clusters by autoreduction,[70] caused the migration of $Ag^+$ ions into the sodalite units and the D6R's from general positions in the supercages. Linear $Ag_3^{2+}$ clusters formed along the 3-fold axes at sites I′-I-I′. After hydrogen reduction at 348 K, a considerable increase in occupancy at site I′, partly at the expense of site I, was observed. The $Ag_{(I')}$–O bond distance of 2.7 Å, much longer than a normal 2.3 Å Ag–O bond distance, also indicated that $Ag_{(I')}$ had been reduced. Furthermore, the $Ag_{(I)}$–$Ag_{(I')}$ distances increased from 3.1 to 3.4 Å because of this reduction, suggesting that interactions among the $Ag_{(I')}$ silvers had become more important than those among silvers in the linear $Ag_3^{2+}$ clusters and indicating that the linear trisilver clusters probably no longer exist at this stage. The average number of silvers per sodalite cavity was four (three at site I′ and one at site II′).

Diffuse optical reflectance and far-IR spectroscopic investigations, coupled with an electron-in-a-box calculation, indicated that $Ag_n^{q+}$ clusters with $n$ probably in the range of 5–13 are preferred in vacuum-dehydrated Ag-Y.[87] These clusters were judged more likely to be in the supercages. However, $^{129}$Xe NMR studies by Fraissard[88] showed that only $Ag^+$ cations are present in the supercages. No clusters were found in the supercages of Ag-X or Ag-Y, with the possible exception of fully $Ag^+$-exchanged zeolite X.

At low $Ag^+$-exchange levels, all silver ions in hydrated Ag-faujasites are easily reduced to generate clusters, leaving no isolated $Ag^+$ ions in the lattice.[89,90] Kevan proposed that the presence of water assisted the diffusion of silver species.[90] $Ag^0$, $Ag_2^+$, and $Ag_3^{2+}$ clusters were easily found by ESR methods in hydrated and dehydrated Ag-Y which had been $\gamma$-irradiated and in Ag-faujasites which had been reduced by hydrogen. A $Ag_4^{3+}$ cluster appeared at 77 K in hydrated $\gamma$-irradiated Ag,Na-Y, but it faded as it warmed to room temperature.

A comprehensive review of the spectroscopic results, photoprocesses, and the support interactions of silver clusters in silver faujasite is available.[12]

## 2.3. Silver Clusters in Other Zeolites

Hydrogen uptake by Ag-exchanged chabazite was measured volumetrically, and three reduction steps were disclosed.[91] The first step at about 373 K led to the formation of $(Ag_2^+)_n$ clusters in a yellowish-brown sample; $(Ag_3^+)_m$ formed in an olive-green sample in a second step at about 473 K; and finally, above 623 K, all $Ag^+$ ions were reduced to give small silver particles. No paramagnetic species were present in the entire process according to ESR measurements, indicating that $n$ in the formation of $(Ag_2^+)_n$ must be an even number.

The redox reactions of silver mordenite (see Figure 1e) with hydrogen and oxygen were studied by Beyer and Jacobs.[92] These reactions were reversible. The kinetics of reduction were essentially the same as for Ag-Y. Upon mild reduction, $Ag^+$ cations in the main pores agglomerated to form $Ag_5^+$ clusters in the channels: this cluster formula was suggested by the hydrogen uptake. It was reported that the reduction of $Ag^+$ by hydrogen was catalyzed by iron impurities in mordenite.

Chemical analysis showed that all $Na^+$ but no $Cs^+$ cations in zeolite $Na_7Cs_3$-Rho (see Figure 1d) could be replaced by $Ag^+$ ions using aqueous ion exchange.[93] Partially $Ag^+$-exchanged $Ag_7Cs_3$-Rho (from $Na_7Cs_3$-Rho) dehydrated under flowing $O_2$ was white, and no ESR signals were detected. The sample changed to light brown after hydrogen reduction at room temperature, and an isotropic five-line ESR signal and a single signal due to metallic particles were observed. These were interpreted to be $Ag_4^{3+}$ and $Ag_n^0$. ESR measurements indicated that $Ag_4^{3+}$ formed very slowly compared to $Ag_6^+$ in Ag-A. Thus Kevan suggested that these clusters were located in octagonal prisms where they blocked 8-rings and hindered the diffusion of hydrogen.

Comprehensive reviews of silver sodalites have been written by Ozin.[19,20] $(Ag_4X)^{3+}$ clusters (X represents halide) in all or part of the sodalite cavities were characterized by synchrotron X-ray powder diffraction, NMR, and various measurements of their optical properties.

### 3. Silver Complexes in Zeolites

Silver cations are Lewis acids and can accept electrons from Lewis bases to form $Ag^+$ complexes in zeolite cavities.

Nearly six $Br_2$ molecules per 12.3 Å unit cell were sorbed into Na-A.[94] These molecules were found to interact neither with oxygens of the anionic framework, nor with the eight of the 12 $Na^+$ cations which could be located crystallographically. Because of this lack of interaction, which makes little chemical sense and which is inconsistent with that found subsequently in related systems, the presence of unlocated water molecules introduced by poor experimental technique is suspected. Similarly, six $Br_2$ molecules were sorbed into Ag-A.[95] In contrast, these $Br_2$ molecules interact strongly with framework oxygens. $Br_2$ sorption caused the decomposition of the hexasilver cluster, *i.e.* the reduced silver atoms migrated out of the zeolite cavities to form larger silver particles on the external surface of the zeolite. $Br_2$ molecules approach 8-ring oxygens of the zeolite framework axially (Figure 7) to form Br–Br–O charge-transfer complexes. Little direct interaction between $Br_2$ molecules and $Ag^+$ cations was seen. This $Br_2$ molecular complex of Ag-A is very similar to the $I_2$ complex of $Ca_4Na_4$-A.[96]

The $Cl_2$ molecular complex of Ag-A[97] is very interesting and is different from that of $Br_2$, although $Cl_2$ also forms charge-transfer complexes with 8-ring oxygens. The Ag atoms in partially reduced Ag-A were reoxidized by $Cl_2$ to form AgCl in the large cavities. The Ag–Cl bond distance was understandably much shorter in this newly formed AgCl molecule than that seen in $Ag^+$-$Cl_2$ complexes. $Ag^+$ ions interact strongly with sorbed $Cl_2$ molecules and some $Ag^+$ bridge between them. No reduced Ag atoms were found inside or outside the zeolite, indicating that the oxidation of Ag atoms by $Cl_2$ was complete.

Crystallographic and ESR studies of ammonia sorption into Ag-A may be consistent. It was reported by single-crystal diffraction that ammonia was converted to triazane and cyclotriazane on Ag-A at room temperature and that hexasilver clusters were destroyed.[98] ESR observation at a lower temperature, 193 K, showed[99] that the hexasilver clusters remained intact and that ammonia molecules were strongly coordinated to $Ag^+$ ions in the 6-ring planes. A positive charge transfer led to a minor increase in the 5s spin population on the silvers of the hexasilver clusters.

Crystallographic and ESR studies of the sorption complex of ethylene appear to be inconsistent. $Ag^+$–ethylene complexes were found[63] in the crystal structure of an ethylene sorption complex of Ag-A. Two silver ions per unit cell had moved upon introduction of ethylene to coordinate to ethylene molecules instead of hexasilver. This caused the coordination number of the hexasilver clusters, which coordinate to 6-ring $Ag^+$ ions, to decrease from 8 to 6. The $Ag^+$ ions remained trigonally coordinated to three 6-ring oxygens, and the hexasilver clusters remained intact. Ethylene molecules in the large cavity bound laterally to $Ag^+$ ions along the principal $C_{3v}$ symmetry axis of the zeolite (Figure 8). This bonding is attributed to overlap between the empty $Ag^+$ 5s and the filled ethylene orbitals and so-called back-donation from the filled $Ag^+$ $4d_{xy}$,$4d_{yz}$ orbitals to the empty ethylene $\pi^*$ orbitals as described by Dewar.[100] The expected effects of such bonding on the UV excitation centered at 5.55 eV, corresponding to the $(4d^95s)$ $^1D \leftarrow (4d^{10})$ $^1S$ excitation of $Ag^+$ in $Ag_{0.1}Na_{11.9}$-A, were observed; this provided the first experimental confirmation of the 5s–$\pi$ bonding scheme.[101] However, Morton, Preston, and Tse[99] found no isotropic seven-line signals in the ethylene complex of Ag-A; instead, a new anisotropic ESR signal appeared which was interpreted to be a naked $Ag_6^{4+}$ cluster in the sodalite cavity. It seems that more work is needed to describe the interactions between $Ag^+$ ions and ethylene molecules in zeolite A.

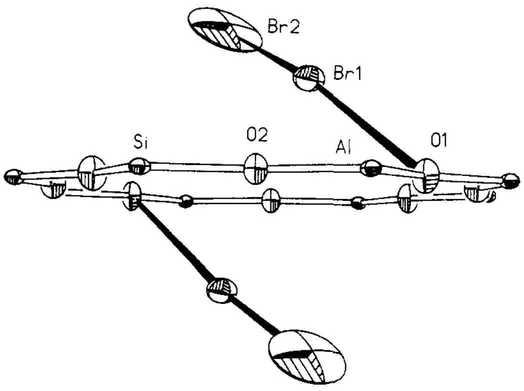


**Figure 7.** Each dibromine molecule interacts strongly by charge transfer with an O(1) oxygen of the zeolite framework. Ellipsoids of 20% probability are shown. (Reprinted from ref 95. Copyright 1978 American Chemical Society.)

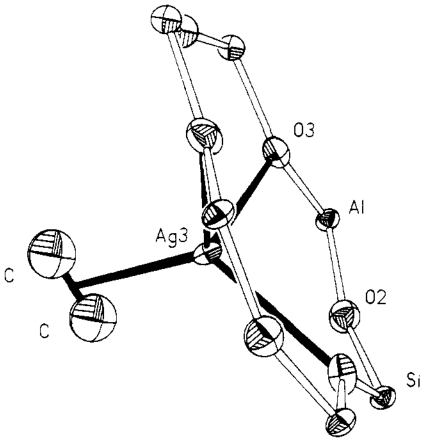


**Figure 8.** A $Ag(C_2H_4)^+$ complex in the large cavity of zeolite A. Ellipsoids of 20% probability are shown. (Reprinted from ref 63. Copyright 1978 American Chemical Society.)

The relative reactivity of various sorbates with hexasilver clusters reported by Wasowicz and Michalik[71] is $CH_3CN \gg H_2O = CH_3OH > C_2H_5OH \gg C_6H_6 = (CH_3)_2C{=}CH_2$. The sorption of $CH_3CN$ immediately destroyed all hexasilver clusters and no ESR signals for any other silver clusters could be detected. The

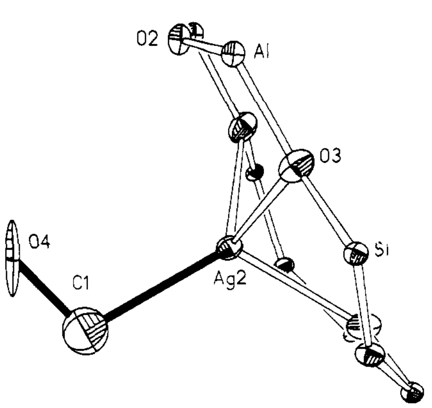
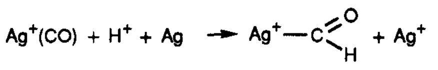


**Figure 9.** A $Ag^+$–CO complex, either $(Ag\text{-}CHO)^+$ or $(Ag\text{-}CH_2OH)^+$, in the large cavity of zeolite A. Ellipsoids of 20% probability are shown. Selected bond lengths and an angle are Ag(2)–C(1) = 2.40(3) Å, C(1)–O(4) = 1.52(8) Å, and Ag(2)–C(1)–O(4) = 104(3)°. (Adapted from ref 64.)

sorption of $CH_3OH$ and $H_2O$ caused $Ag_6$ to be completely converted to an elongated $Ag_3^{2+}\cdots Ag^+$ cluster. The sorption of $C_2H_5OH$ led to a product which contained both $Ag_6$ and $Ag_4^{3+}$. $C_6H_6$ and $(CH_3)_2C{=}CH_2$ are too large to be sorbed, so they had no effect on the hexasilver clusters at all. The mechanism of the interaction of these sorbates with Ag-A depends very much on their polarities and on their molecular sizes and structures.

The interaction of CO with Ag-A has been studied in detail because of the potential application of Ag-A as a photocatalyst for carbon monoxide conversion to higher carbon compounds, and for reduction of carbon dioxide using solar energy.[11] Kim, Song, and Seff[64] determined the crystal structure of Ag-A exposed to CO at room temperature. In this structure, the authors suggested that some of the sodalite cavities were occupied by the almost naked $(Ag_6)^0$ clusters, $(Ag_6^0)(Ag^+)_2$. The CO group was found to be strongly bonded to $Ag^+$ (Figure 9). The Ag–C–O angle was no longer 180°, and the C–O distance was much longer than a C≡O triple bond. These findings indicated that carbon monoxide had been partially reduced, and that $Ag^+$–C–O should be viewed as $(Ag\text{–}CHO)^+$ or $(Ag\text{–}CH_2OH)^+$:



$$Ag^+(CO) + H^+ + Ag \rightarrow Ag^+\text{—}C(=O)H + Ag^+ \qquad (8)$$

Some $Ag^+$ ions were found to be reduced by one of two possible reactions:

$$(Ag^+)_2{\cdot}OH_2 + CO \rightarrow 2Ag^0 + CO_2 + 2H^+ \qquad (9)$$

or

$$CO + O^{2-}\ (\text{framework}) + 2Ag^+ \rightarrow CO_2 + 2Ag^0 \qquad (10)$$

The product Ag atoms migrated out of the zeolite to the external surface.

A similar reduction reaction was proposed by Calzaferri[102,103] on the basis of IR spectroscopy studies. He found that carbon monoxide had two types of adsorption kinetics on Ag-A: fast chemisorption and slow physisorption. Upon brief exposure of Ag-A to CO, an IR absorption band attributed to CO vibration was observed at 2174 $cm^{-1}$, which indicated a fast chemisorption process. Because the CO bond was stabilized by the donation of $\sigma^*(CO)$ electron density to $Ag^+$ in the Ag-CO complex, the stretching vibration frequency of the adsorbed CO showed an increase compared to that in the gas phase. After prolonged exposure of Ag-A to CO, the IR stretching band of CO shifted to 2153 $cm^{-1}$, a result of a slow physisorption process. The interaction of $Ag^+$ ions with CO disappeared completely after hydrogen reduction of Ag-A, indicating no interaction between $Ag^0$ atoms and CO molecules. An IR absorption of $CO_2$ was observed in both hydrated Ag-A exposed to $CO_2$ and Ag-A exposed to CO and $H_2O$. The reduction of $Ag^+$ ions in the presence of CO was found to depend upon the water content of Ag-A. A hypothetical intermediate, $Ag^+\text{–}(CO(OH))^-$, was proposed for the reduction of $Ag^+$ by CO and $H_2O$.[103] This agreed with the mechanism indicated by the crystallographic result: the strong interaction between $Ag^+$ ions and CO molecules led the conversion of CO to a reduced species by reaction with water molecules.

Very similar results were reported for other silver zeolites. Jacobs and Beyer,[41,104] in a comprehensive investigation, correlated the IR absorption of CO to the amount of CO sorbed in Ag-faujasite and Ag-mordenite. It was shown clearly that no CO IR absorption bands appeared after hydrogen reduction at high temperature. In no case was the conversion of CO to $CO_2$ or to any other products indicated in their results, probably because of the absence of $H_2O$.

$CO_2$ adsorption on alkali and alkaline earth cation-exchanged zeolites A and X led to both physisorbed and chemisorbed species.[105,106] IR measurements of $CO_2$ adsorption on unreduced, completely Ag-exchanged zeolite A showed only physisorbed species.[106] An enhanced capacity to retain $CO_2$ was found with partial hydrogen reduction of Ag-A. Unfortunately, no direct IR absorption bands attributed to $CO_2\cdots Ag^+$ or $CO_2\cdots Ag^0$ species were disclosed. It is important to study the interaction of silver zeolite with $CO_2$ because it may provide a solution to difficulties encountered when such materials are used as catalysts for the photoinduced oxidation of water.[11] It has been reported that mechanically activated Ag powder can react with $CO_2$ to produce CO at room temperature:[107]

$$2Ag + 2CO_2 \rightarrow Ag_2CO_3 + CO \qquad (11)$$

but questions regarding this claim remain.

## 4. Applications of Silver Zeolites

Rálek *et al.*[32] were the first to use dehydrated, brick-red Ag-A as a water sensor to detect trace amounts of moisture, on the basis of their observations of color changes from brick-red to orange, to yellow, and finally to white. More recently, Ozin[12,109,110] developed a series of silver or silver halide sodalites, which he speculates may act as chemical, electronic, and optical sensors and may be useful as information storage materials. Because quantum-size I–VII semiconductors confined in sodalite cages might be made with well-defined size and structure and be distributed homogeneously throughout the crystal cages, the sodalite units provide an excellent environment in which to create organized assemblies of clusters for potential application at nanometer dimensions as electronic and optical materials. Like Ag-A, silver halide sodalites are light- and pressure-sensitive materials.[20]

In industry, catalysts used for ethylene epoxidation, consisting of silver deposited on low-surface-area supports, have had very low yields. High-surface-area nonzeolite supports were unsatisfactory due to low selectivity in the final products. An oxidation catalyst was prepared by impregnating samples of natural chabazite and mordenite zeolites with silver nitrate.[111] Catalytic performance was tested at 513 K with a 3% ethylene concentration in air. The results showed that silver zeolites were active and selective in the epoxidation of ethylene and that the selectivity of the products depended on the sizes of the silver crystallites. Metallic aggregation of silver on the external surfaces of zeolites was found, too. Silver mordenite was more active and more selective than silver chabazite in this reaction.

Ozin[112,113] found that $Ag^+$ ions in Ag-Y could activate the dimerization reaction of alkanes under UV–vis irradiation at room temperature. The presence of small charged silver clusters in zeolites enhanced the formation of lattice V-centers under UV irradiation. Subsequently, this lattice V-center activated the C–H bonds of the paraffinic hydrocarbons, abstracted a hydrogen atom to form a lattice hydroxyl group, and led the gaseous alkyl radical $C_nH_{2n+1}$ to dimerize with high selectivity toward the product alkane $C_{2n}H_{4n+2}$. This process, similar to water splitting, was not catalytic: it was a lattice reaction which generated protons, which in turn destroyed the zeolite framework and caused the activity to decrease with irradiation time. Ozin proposed that protons were always generated in this process. If these protons could be removed in this dimerization reaction, research into its potential application in natural gas conversion might progress rapidly.

Matta reported that Ag-faujasites are effective catalysts for the exclusive synthesis of sialosaccharides containing the Neu5Ac$\alpha$2→6 glycosyl linkage.[114] Compared to the traditional synthetic methods for preparing $\alpha$-glycosides of NeuAc, such as methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-2-chloro-2,3,5-trideoxy-D-glycero-$\beta$-D-galacto-2-nonulopyranosate, the synthesis using silver faujasite as a catalyst was very simple and selective. Only $\alpha$-linkages were generated without any side products. It was believed that, during the reaction, silver faujasite was selectively adsorbed onto the $\beta$-face of the glycosyl donor, like $Cl^-$, and thereby allowed the incoming nucleophile to attack only the $\alpha$-face due to steric impedance. Silver faujasite functioned here more like a steric blocking agent than a catalyst.

Qualitative and later quantitative photochemical experiments[115-119] showed that, upon illumination of silver zeolites in aqueous dispersions, the silver ions were reduced to $Ag^0$ atoms and oxygen was evolved. This photoreaction provided an opportunity for exploring the photochemical conversion of solar energy because water splitting, nitrogen fixation, and $CO_2$ reduction all involved the oxidation of oxide in water to molecular oxygen. It was observed that photooxygen production from water with silver zeolites was a self-sensitization reaction.[117-123] That is, the further the reaction proceeds, the more its spectral sensitivity shifts from the initial UV, to the visible, then into the red spectral range. This phenomenon was attributed to the aggregation of reduced silver atoms which became new chromophores at longer wavelengths. As stated earlier, the greatest difficulty in the use of silver zeolites for water splitting is the generation of protons. These protons were difficult to remove from zeolite cation positions and hindered the catalytic reaction.

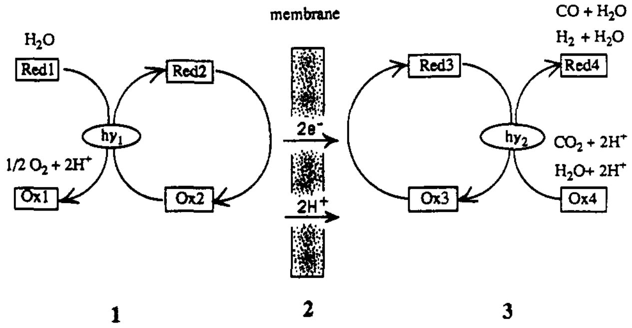


**Figure 10.** A schematic diagram for the photocatalytic splitting of water and the reduction of carbon dioxide. (Adapted from ref 11.)

Calzaferri[11] proposed that this water-splitting reaction could be divided into three physically separate parts (see Figure 10): the oxidation of water to oxygen in reaction 1; the reduction of water to hydrogen in reaction 3; and the coupling of 1 and 3 through a membrane, 2. For the first reaction, they used silver zeolites as catalysts in aqueous dispersion under appropriate conditions. As mentioned earlier, $Ag^+$ ions are reduced and oxygen is generated. Semiconductor particles in a zeolite matrix were used as catalysts for the reduction reaction. The coupling must be accomplished by means of a membrane. For this, they developed a simple and fast technique for preparing a monograin zeolite layer by covalently linking zeolite particles onto an electrode, in which silver redox steps were quasi-reversible.[124] The membrane they prepared coupled a silver zeolite monolayer on the oxidative side to a zeolite monolayer loaded with semiconductor particles on the reductive side. Excitation of semiconductor particles delivered the electrons necessary to reduce water. The holes produced in this process recombined with electrons of the reduced silver atoms. Further exploration of this reaction for solar energy conversion shows great promise.

Below pH = 4, $Cl_2$ was produced when a silver zeolite dispersion in $Cl^-$-containing solution was irradiated at 360 nm.[120] Self-sensitization was observed here also. This photoreaction has potential for solar energy conversion and $Cl_2$ production by directly using sea water, a natural resource. In this reaction, no protons were generated upon silver ion reduction to silver atoms. If the silver atoms can be reversibly oxidized to silver ions which return to the zeolite cages, silver zeolites may be excellent catalysts for this sea water conversion.

The reversible redox properties of silver zeolites have been used to modify traditional electrode surfaces. This redefines the chemical and physical microenvironment at these surfaces and allows heterogeneous electron-transfer reactions to occur.[125] The silver zeolite-modified electrodes have the following advantages: long term stability, especially under reactive, corrosive conditions; molecular selectivity, because zeolites have the ability to selectively absorb some molecules; and three-dimensional complex integrity. Baker and Zhang[126] investigated the electrochemical response of electrodes modified with Ag,Na-Y. In fully $Ag^+$-exchanged zeolite Y, only 20% of the silver cations could be reduced and reversibly reoxidized. The diffusion of silver cations within the zeolite cavity, repulsive interactions among silver ions, and coupled chemical reactions led to a broadened cathodic half-width compared to that of a one-electron reduction process. At low silver-exchange levels, cathodic linear-sweep voltammetry disclosed two electrochemically distinct silver ions which were assigned to sites I and I′. This property can be used to discriminate the redox behavior of ions in electrolytes. Baker found that components of electrolyte solutions can be analyzed using Ag-A-modified electrodes. Calzaferri[123] prepared a silver-exchanged zeolite-modified Pt electrode by linking Na-A as a dense monograin layer onto a Pt electrode followed by $Ag^+$ exchange. SEM pictures disclosed excrescences after 20 cycles of voltammogram measurements, which were identified to be silver particles in the size range of 20–200 nm. These excrescences are likely to shorten the lifetime of the electrodes.

In recent years, extensive studies have been conducted on the phenomenon of the significant enhancement of the Raman signal of molecules adsorbed onto specially prepared metal surfaces, especially silver metal. This is called surface-enhanced raman spectroscopy (SERS). The crucial issues in producing silver particles on substrates involve the control of silver deposition level, aggregation, and long-term stability. Dutta and Robins[127] generated silver clusters on the external surface of zeolites by hydrazine reduction of $Ag^+$-exchanged zeolites. The "snowflake"-like silver particles on the external surface were manipulated using SEM. SERS of molecules absorbed on this silver surface could be detected at nanogram levels. After high-temperature treatment, up to 450 K, the prepared silver zeolite materials were still very stable toward aggregation and continued to exhibit SERS.

## 5. Summary

Silver clusters can be easily synthesized in the cages and channels of zeolites by vacuum dehydration, by reduction with reducing reagents, and by $\gamma$- or X-ray irradiation. The structures, sizes, and charges of the silver clusters are sensitive to the conditions of synthesis and to the structures of the zeolite hosts. The sodalite cages in zeolite A have near $O_h$ symmetry which favors the formation of hexasilver clusters in completely $Ag^+$-exchanged zeolite A. Generally, these hexasilver clusters are stabilized by coordination to silver cations at 6-ring centers. The mechanism for silver reduction is attributed to the self oxidation of framework oxygen (decomposition of the $Ag_2O$ component of the zeolite composition). Reduction by hydrogen leads first to cluster formation and then to the aggregation of silver atoms on the external surface of zeolites. In partially $Ag^+$-exchanged zeolite A, trisilver or tetrasilver clusters can form in sodalite cavities. At very low silver content, weakly bound $Ag^0$ is found.

In reduced faujasites, a linear trisilver cluster, extending from a sodalite cavity through a D6R to another sodalite cavity, is the most favored species. The silvers at the centers of D6R's are the first to be reduced in vacuum dehydration. Near octahedral, nearly closest-packed hexasilver clusters might be present in the sodalite cavities. More intense reduction causes larger silver clusters to form. The largest possible silver cluster in the sodalite cavity of faujasite is projected to be a distorted cube coordinated to eight $Ag^+$ ions: four in D6R's, and four in surrounding large cavities.

X-ray diffraction, ESR, far-IR, MAS-NMR, reflectance-transmittance spectroscopy, and quantum calculation have all proven to be very powerful methods for research into cluster formation in zeolites. EXAFS is able to provide information about local short-range interactions. Yet inconsistencies, often difficult to resolve, and probably based largely on variations in samples and in sample preparation procedures, remain.

Silver clusters are very light sensitive. They may find use as photocatalysts for solar energy conversion, as is being tried in Calzaferri's group, and as optical materials according to Ozin's proposals. The synthesis of hexasilver in 83% of the large cavities of zeolite A suggests that full occupancy is within reach. Zeolites containing clusters are very hopeful candidates for new information storage or optical materials. Future research on the formation and structure of silver clusters in zeolites should focus on the hydrated forms of silver zeolite because this may lead to direct information on water splitting or chlorine evolution from sea water. More advanced quantum-mechanical calculations are necessary to understand the reflectance spectra of silver clusters in zeolite hosts.

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