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Paramagnetic Silver Clusters in Ag–NaA Zeolite: Electron Spin Resonance and Diffuse Reflectance Spectroscopic Studies

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Abstract: Paramagnetic silver clusters generated in activated Ag–NaA zeolite by γ-irradiation at 77 K or by H_2 reduction at 295 K have been studied by electron spin resonance (ESR) and diffuse reflectance spectroscopy. Depending on the silver content in the zeolite, neutral Ag_3^0 or monovalent Ag_6^+ clusters were identified by ESR. They are formed during radiolysis by electron capture from diamagnetic Ag_3^+ or Ag_6^{2+} species, respectively. In Ag_1–NaA zeolite the transformation of Ag_3^0 to Ag_6^+ clusters has been followed by ESR and related to the reaction between Ag_3^+ and Ag_3^0 in the same sodalite cage of the zeolite structure. Diffuse reflectance spectra of the same zeolite sample show some correlation between the optical bands and paramagnetic silver clusters identified by ESR. The mechanism of silver clustering in the sodalite cage of Ag–NaA zeolite based on the present ESR and optical data and earlier X-ray diffraction and far infrared studies is discussed.

Small metal clusters of platinum group metals or copper, silver, and nickel supported on various solids appear to have significant potential in heterogeneous catalysis.[1] Small silver clusters in zeolites have been extensively studied in recent years with various experimental techniques such as X-ray diffraction,[2-4] electron spin resonance (ESR),[5-7] and optical spectroscopy.[8-13] In activated silver A zeolite depending on the activation temperature and initial silver content the formation of trimeric and hexameric silver species has been proposed on the basis of X-ray diffraction data.[4] The presence of Ag^+–Ag^0–Ag^+ linear clusters has been associated with a yellow color of the zeolite and an absorption band at 445 nm. A band at 510 nm has been assigned to two Ag_3^{2+} clusters interacting in the sodalite cage of the zeolite structure.

Applying Fourier transform far infrared spectroscopy to Ag–NaA zeolite Ozin et al.[12] studied the reduction of Ag_3^{2+} species by H_2 in the temperature range 293 to 413 K. They postulated a reversible redox process

$$Ag_3^{2+} \underset{O_2}{\overset{H_2}{\rightleftharpoons}} Ag_3^0$$

occurring in the presence of H_2 or O_2. One limitation of these interpretations is related to the fact that no ESR spectra were observed for activated Ag–NaA samples although paramagnetic Ag_3^{2+} species were postulated. In a more recent paper Ozin et al.[7] proposed the interesting transformation of a trimeric cluster (Ag_3^{x+}) to a hexamer pseudocluster $(Ag_3^{x+})_n$ without specifying specific numbers for the charges of the postulated silver species.

The objective of this work was to use γ-irradiation at 77 K to render the silver clusters, present in activated Ag–NaA zeolite, paramagnetic and identifiable by ESR. The ESR spectra of silver zeolites activated under various conditions as well as those subsequently exposed to H_2 at room temperature were also studied. Comparative optical absorption studies were carried out in order to correlate the optical bands to the paramagnetic silver species generated by γ-irradiation.

Experimental Section

Linde NaA zeolite (4A), after repeated washing with 0.1 M sodium acetate, was ion exchanged with 0.8 mM, 4 mM, and 20 mM $AgNO_3$ to obtain samples with 0.25, 1, and 5 Ag^+ per unit cell, respectively. The subscript on Ag in Ag–NaA indicates the number per unit cell. The exchange was carried out at room temperature in aqueous solution for 17 h. The material was handled and stored in the dark. the silver content was obtained by commercial atomic absorption analysis.

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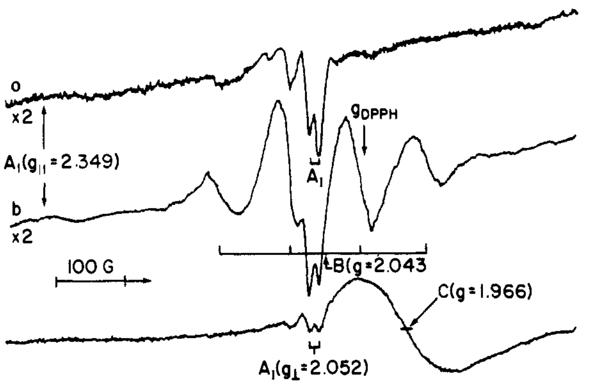

Figure 1. ESR spectra at 77 K of Ag_1–NaA zeolite for (a) an activated sample (after oxidation with prolonged evacuation at 723 K), (b) an activated sample exposed to H_2 at room temperature for 1.5 h, and (c) the same sample as in spectrum b evacuated at room temperature for 0.5 h and subsequently at 473 K for 0.5 h.

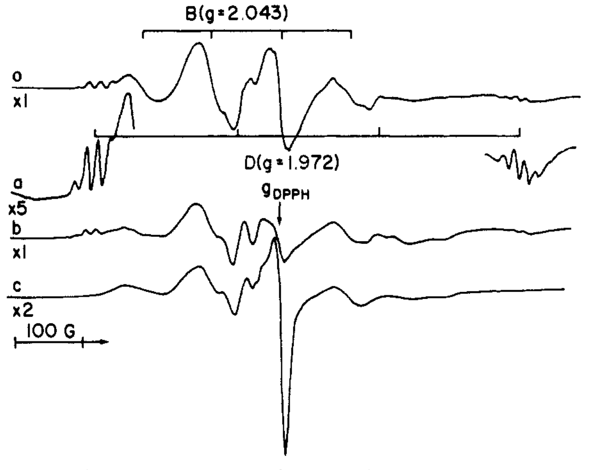

Figure 2. ESR spectra at 77 K of activated Ag_1–NaA zeolite exposed to H_2 at room temperature for 1.5 h, subsequently evacuated for 24 h at room temperature, and γ-irradiated at 77 K with a 1-Mrad dose: (a) a sample annealed to room temperature for 30 s, (b) for 2 h, and (c) exposed to air at room temperature for 10 min.

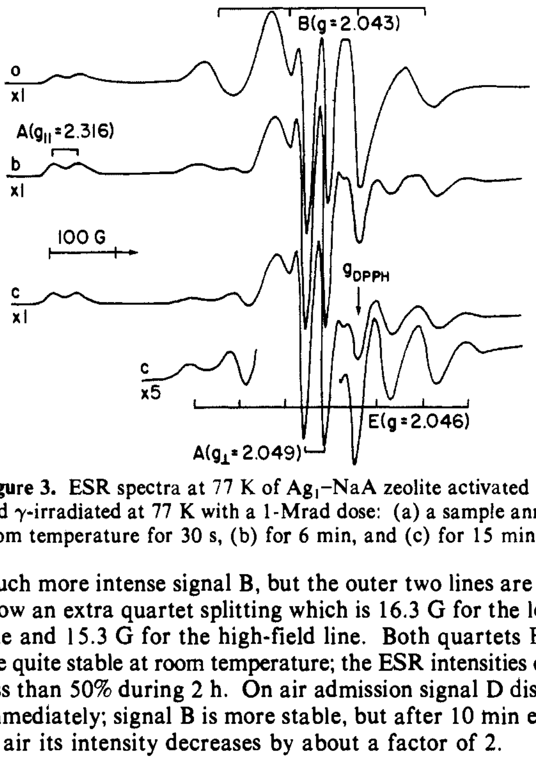

Figure 3. ESR spectra at 77 K of Ag_1–NaA zeolite activated at 723 K and γ-irradiated at 77 K with a 1-Mrad dose: (a) a sample annealed at room temperature for 30 s, (b) for 6 min, and (c) for 15 min.

The filtered and washed zeolite samples were placed into 10 mm o.d. Pyrex tubes connected to 3 mm o.d. Spectrosil quartz ESR tubes or to a quartz, flat cylindrical optical cell. Both setups were equipped with valves for vacuum treatment and gas admission. The samples were gradually heated in vacuo for 18 h up to 723 K and then with oxygen for 3 h also at 723 K and evacuated at the same temperature overnight (~18 h). Some samples were slowly heated in flowing oxygen to 723 K and then degassed also at 723 K. Samples prepared in both ways will be referred to as "activated". The activated samples were reduced by 300 Torr of H_2 at room temperature or by γ irradiation at 77 K with a dose of 1 Mrad. Samples exposed to H_2 were transferred to ESR tubes or optical cells for ESR or diffuse reflectance measurements. Samples for γ-irradiation were sealed off in vacuo at less than 10^{-4} Torr before irradiation.

ESR spectra at 77 K were measured on an E-4 Varian spectrometer at 9.2 GHz. The diffuse reflectance spectra were recorded over the wavelength of 200–600 nm on a Perkin-Elmer 330 spectrophotometer equipped with a Hitachi integrating sphere accessory with a wavelength range of 200^+ to ~800 nm. The spectra were reported as recorded. Transformation by a Kubelka–Munk function was investigated and found to not significantly change the spectral shape in this wavelength range. A Gammacell 220 ^{60}Co source with a dose rate of 1.12 Mrad h^{-1} was used for γ-irradiation.

Results

ESR Characteristics of Ag–NaA. The ESR spectra of Ag–NaA recorded at different stages of activation treatment depend very little on the zeolite silver content. The major ESR signal which appears after heating in vacuo up to 723 K is anisotropic signal A_1 shown in Figure 1a with $A_\perp = 13.8$ G, $A_\parallel = 40.1$ G, $g_\perp = 2.052$, and $g_\parallel = 2.349$. Its intensity does not change on subsequent oxidation and evacuation at 723 K and is almost independent of silver content. Besides the line assigned to signal A_1 several other lines spread over 500 G are observed in activated Ag–NaA, especially for samples with higher silver content. The lines are weak and the spectral pattern is rather complex so no assignment has yet been made.

An ESR spectrum of activated Ag_1–NaA zeolite reduced with H_2 at room temperature is shown in Figure 1b. After hydrogen admission an isotropic quartet B with $A = 101$ G and $g = 2.043$ develops slowly and even after 1.5 h of exposure to H_2 its intensity is low. Sample evacuation at room temperature does not change the ESR spectrum, but subsequent evacuation at 473 K for 0.5 h eliminates quartet B and produces a broad singlet C with $g = 1.966$ and a peak-to-peak derivative line width of about 140 G.

If Ag_1–NaA reduced by H_2 at room temperature is evacuated at the same temperature and then γ-irradiated at 77 K, the intensity of signal B is increased by about one order of magnitude compared to the intensity in hydrogen reduction (see Figure 2a). Signal B recorded after γ-irradiation seems to have a slightly larger hyperfine splitting of $A = 102$ G, but $g = 2.043$ and the line intensity ratio of about 1:3:3:1 are the same as those for H_2 reduced samples.

Reduction by H_2 also produces a new quartet D with $A = 208$ G and $g = 1.972$. The central two lines are superimposed on the much more intense signal B, but the outer two lines are not and show an extra quartet splitting which is 16.3 G for the low-field line and 15.3 G for the high-field line. Both quartets B and D are quite stable at room temperature; the ESR intensities decrease less than 50% during 2 h. On air admission signal D disappears immediately; signal B is more stable, but after 10 min exposure to air its intensity decreases by about a factor of 2.

Signal D is not observed if Ag_1–NaA zeolite is γ-irradiated directly after activation without any H_2 treatment (see Figure 3). In this case, besides quartet B the ESR spectrum reveals an anisotropic signal A with $A_\perp = 30.1$ G, $A_\parallel = 36.6$ G, $g_\perp = 2.049$, and $g_\parallel = 2.316$. The intensity of signal A is more than two orders of magnitude bigger than signal A_1. Also, the ESR parameters are slightly different from those of signal A_1. Quartet B in γ-irradiated activated Ag_1–NaA (without H_2 treatment) is not stable on thermal annealing at room temperature and transforms to isotropic septet E with $A = 67.6$ G and $g = 2.046$. The changes are rather fast, and the quartet is not seen after 15 min of annealing. Simultaneously the zeolite color changes from salmon to brick-red. This transformation does not take place in activated and γ-irradiated $Ag_{0.25}$–NaA zeolite where signal B on thermal annealing slowly decays without any spectral changes. Septet E is more stable at room temperature than quartet B in samples treated by H_2 before γ-irradiation. Its intensity decreases about twofold after 16 h of annealing at room temperature.

The ESR spectra of activated Ag_5–NaA zeolite exposed to H_2 at room temperature or y-irradiated at 77 K are shown in Figure 4 and 5, respectively. After H_2 admission into the sample an

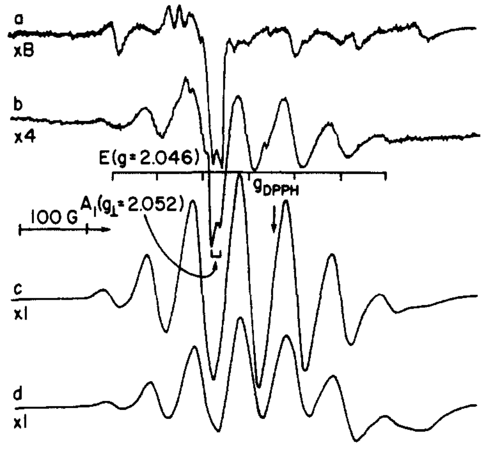

Figure 4. ESR spectra at 77 K of Ag_5–NaA zeolite: (a) an activated sample (after oxidation with prolonged evacuation at 723 K) and (b) an activated sample exposed to H_2 at room temperature for 5 min, (c) for 1 h, and (d) for 1.5 h.

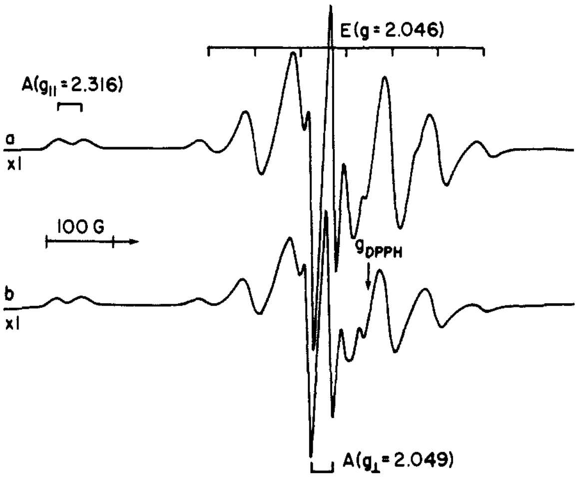

Figure 5. ESR spectra at 77 K of Ag_5–NaA zeolite activated at 723 K and γ-irradiated at 77 K with a 1-Mrad dose: (a) a sample annealed at room temperature for 30 s and (b) a sample exposed to air at room temperature for 2 h.

isotropic septet E with A = 67.6 G, g = 2.046 G, and a line intensity ratio of 1:4.4:10.1:12:9.6:5:1.1 appears immediately in the presence of H_2. High gain did not reveal any additional lines. The ESR intensity slowly increases with time, reaching a maximum after about 1 h of exposure to H_2. Longer contact time decreases the septet intensity and the broad line C becomes visible. If the same sample is evacuated at room temperature for 24 h to remove H_2 and is γ-irradiated at 77 K, the main ESR features are a broad line C with overlapped signals A and E. Irradiation at 77 K of activated Ag_5–NaA, not exposed previously to H_2, yields septet E with approximately the same intensity and the same spectral parameters as in the sample reduced by H_2 (see Figure 5). The main difference is due to the presence of a very intense signal A in γ-irradiated zeolite. The intensities of signals A and E do not change during 1 h of thermal annealing at rom temperature. In the presence of air the intensity of signal E decreases about twofold during 2 h, indicating a much higher stability of septet E compared to quartet B in an oxygen atmosphere.

Ag_5–NaA zeolite was also γ-irradiated after activation at 483 K. The ESR spectrum recorded after 30 s of annealing at room temperature shows the same septet E as in zeolite activated at 723 K. In Ag_5–NaA activated at lower temperature signal E is much less stable at room temperature than for higher activation temperature and decays completely during 2 h.

ESR spectra of a hydrated Ag_5–NaA sample γ-irradiated at 77 K are shown in Figure 6. Directly after irradiation, besides the intense signal A, a complex spectrum of at least 7 lines is seen. The ESR intensity decreases dramatically after 2 min of annealing

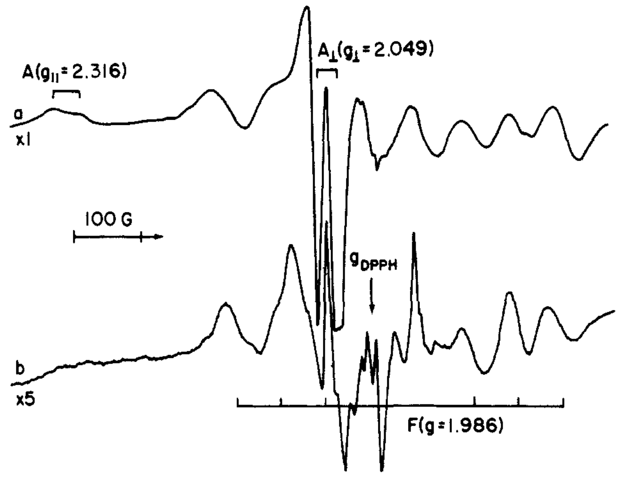

Figure 6. ESR spectra at 77 K of hydrated Ag_5–NaA zeolite γ-irradiated at 77 K with a 1-Mrad dose: (a) a sample annealed at room temperature for 30 s and (b) for 3 min.

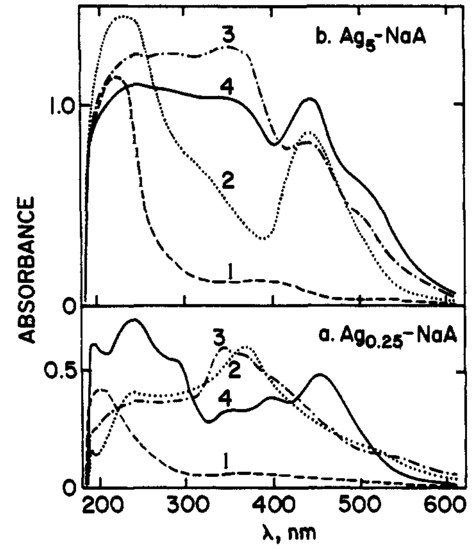

Figure 7. Diffuse reflectance spectra of Ag–NaA zeolite recorded at room temperature: (a) $Ag_{0.25}$–NaA, (b) Ag_5–NaA; (1) an air-dried hydrated sample, (2) a sample evacuated while raising the temperature to 503 K over 6 h, (3) the same sample as in (2) following raising the temperature to 723 K for 12 h, and (4) a sample oxidized for 3 h at 723 K and evacuated at the same temperature for 17 h.

at room temperature. Signal A disappears completely as well as several other lines present in the initial spectrum revealing several narrow lines at $g \sim 2$ and a much wider spectrum F which we believe could be interpreted as a doublet of isotropic triplets with g = 1.986, doublet splitting ~348 G, and triplet splitting ~64 G.

Reflectance Spectra of Ag–NaA. In contrast to the ESR spectra which do not show major changes during activation treatment, the reflectance spectra of Ag–NaA are distinctly different at various stages of activation. The reflectance spectra of $Ag_{0.25}$–NaA and Ag_5–NaA zeolite recorded at different activation stages are shown in Figure 7.

In hydrated Ag–NaA zeolite independent of silver content only an absorption at 210 nm is observed. In $Ag_{0.25}$–NaA this absorption is shifted to 220 nm after the sample is heated in vacuo at 503 K and a new band at 370 nm is seen. After activation at 723 K this band shifts to 340 nm and disappears on oxidation at 723 K. The reflectance spectrum then shows two maxima at 220 and 450 nm. The $Ag_{0.25}$–NaA sample in the temperature range 403–723 K is yellow-green and after oxidation is yellow-orange. The hydrated Ag_5–NaA zeolite, which is a little bit gray, becomes canary-yellow after being heated at 503 K in vacuo. The reflectance spectrum then shows two absorption bands at 220 and 440 nm. Heating in vacuo at 723 K changes the zeolite color to

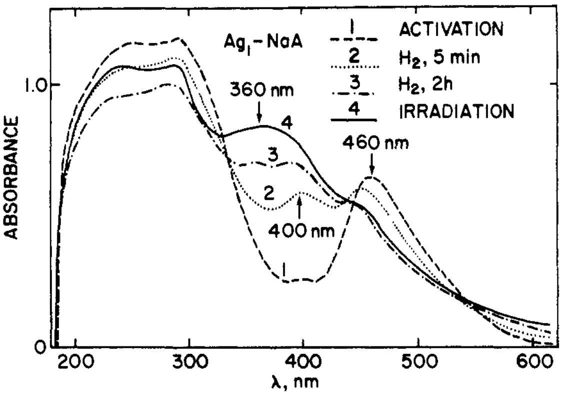

Figure 8. Diffuse reflectance spectra of Ag_1–NaA zeolite recorded at room temperature: (1) a sample activated at 723 K, (2) an activated sample exposed to H_2 at room temperature for 5 min and (3) for 2 h, and (4) the same sample as in (3) evacuated at room temperature for 17 h and subsequently γ-irradiated at 77 K.

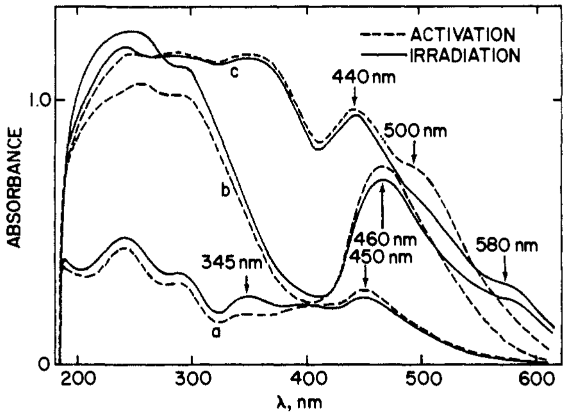

Figure 9. Diffuse reflectance spectra of Ag–NaA zeolite recorded at room temperature: (a) $Ag_{0.25}$–NaA, (b) Ag_1–NaA, (c) Ag_5–NaA; (1) samples activated at 723 K and (2) activated samples γ-irradiated at 77 K with a 1-Mrad dose and annealed for 10 min at room temperature.

brown-yellow. This change is associated with the appearance of a very broad absorption in the range 200–350 nm and a shoulder in the red part of the spectrum at about 510 nm. After oxidation and evacuation at 723 K the broad absorption from 200–350 nm decreases whereas the band at 440 nm and the shoulder at 510 nm show increased intensity.

The reflectance spectra of activated Ag_1–NaA zeolite exposed to H_2 at room temperature for various periods of time and subsequently γ-irradiated after H_2 evacuation are shown in Figure 8. Activated Ag_1–NaA shows a broad absorption in the range 200–300 nm and a peak at 460 nm. Immediately after H_2 admission the absorption at 400 nm appears while the broad absorption at 200–300 nm and the peak at 460 nm decrease. After 2 h of exposure to H_2 the peak at 460 nm is seen as a shoulder on the broad absorption band with two maxima at 360 and 400 nm. Hydrogen evacuation at room temperature does not change the reflectance spectrum, but subsequent γ-irradiation at 77 K with 10 min of annealing at room temperature distinctly increases the absorption in the 360–400-nm region. The band at 360–400 nm is nearly stable at room temperature and disappears on exposure to air within a few minutes. A similar band at 350 nm shows up also in activated $Ag_{0.25}$–NaA zeolite after γ-irradiation but with much lower intensity. An activated Ag_1–NaA zeolite is salmon color, and in the presence of H_2 it slowly becomes sandy-yellow. After H_2 evacuation the color is yellow-green, and this does not change after γ-irradiation (see Figure 9).

The reflectance spectra of Ag–NaA zeolite with different silver content measured after activation and after subsequent γ-irradiation at 77 K are shown in Figure 9. In all cases the irradiated samples were annealed at room temperature for 10 min before the optical measurements. After γ-irradiation the salmon color Ag_1–NaA sample becomes brick-red and a new absorption band in the red part of the spectrum with a maximum near 580 nm is observed. The same absorption appears in γ-irradiated Ag_5–NaA samples, but in this case it is associated with the nearly complete decay of a band at 510 nm. The band at 580 nm is nearly stable at room temperature if the samples are kept under vacuum. On air exposure it slowly disappears, and after 2 h its intensity is about twofold lower. The Ag_5–NaA sample which after activation at 723 K is brick-red becomes brownish after γ-irradiation.

Discussion

It is well proven by x-ray diffraction studies that during vacuum thermal dehydration of silver zeolite A or Y a redistribution of silver ions takes place accompanied by partial autoreduction of Ag^+ by reaction with water at temperatures up to 523 K or with lattice oxygen at higher temperature.[3,15] The degree of silver reduction in fully exchanged Ag–NaA activated at 600 K was estimated to be almost 8% by Jacobs et al.[15] on the basis of lattice oxygen desorption. Silver atoms produced by autoreduction can interact with other Ag^0 atoms or Ag^+ ions to form silver clusters. Kim and Seff,[16,17] interpreting their X-ray data of activated Ag_{12}–A single crystal, proposed the formation of an octahedral cluster of six silvers, Ag_6^0, located in the sodalite cage of the zeolite structure. Gellens et al.,[3,4] using X-ray diffraction and reflectance spectroscopy for powdered, activated Ag_{12}–A, were able to distinguish trimeric silver clusters formed by low-temperature activation (yellow sample) and pseudohexameric clusters in samples activated above 520 K (brick-red sample). Both clusters are located in the sodalite cages. The trimer was envisaged as Ag^+–Ag^0–Ag^+ with Ag^0 fixed at site 4 opposite a four-membered Al/Si ring and two Ag^+ located at two S2′ sites associated with Si/Al six-rings but extending into the sodalite cage. The silver–Silver bond length was estimated as 0.285–0.300 nm. At higher temperature two or more trimers can be formed in the same sodalite cage and they are assumed to interact with each other. The Ag_3^{2+} cluster was associated with the yellow zeolite color and absorption bands at 445 and 300 nm whereas the brick-red color and absorption bands at 360 and 510 nm were assigned to Ag_6^{n+}. Karge,[9] using ultraviolet/visible transmission spectroscopy, observed three different forms of activated Ag_{12}–A characterized by distinct optical bands in the visible region with maxima at 455 nm (yellow form), 535 nm (orange form), and 585 nm (brick-red form). The transition between these three forms was completely reversible, depending on the degree of dehydration. A possible dependence between the degree of dehydration and cluster formation has been discussed. The far infrared (IR) studies on hydrogen-reduced silver A zeolites indicate the formation of a neutral Ag_3^0 silver cluster in Ag_6–NaA[12] and of a hexamer Ag_6^{n+} in Ag_{12}–A zeolite.[14]

In spite of the large number of papers on silver clustering in zeolites the ESR data on paramagnetic silver clusters are very limited. No ESR spectra were observed for autoreduced Ag–NaA zeolite. Narayana and Kevan[7] observed spectra of Ag_3^+ in hydrated Cs_7Na_5–A zeolite and Ag_3^{2+} in hydrated NaY zeolite after γ-irradiation at 77 K. Hermerschmidt and Haul[6] observed a seven line isotropic ESR spectrum (A = 72.3 G and g = 2.053) in activated Ag–NaA exposed to hydrogen at room temperature. The spectrum was assigned to Ag_6^{n+} clusters located in the sodalite cage. The Ag_6^{n+} signal is not stable at room temperature and slowly transforms to a broad singlet, $\Delta H_{pp} \sim 100$ G, which was interpreted as a magnetic resonance absorption of conduction electrons in small silver crystallites.

Paramagnetic silver clusters have been observed and identified in various frozen solutions and several other matrices. In 1966 Shields[18] observed ESR spectra of γ-irradiated frozen solutions

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of $AgNO_3$ in water and in small alcohols. Besides the ESR doublet of Ag^0 atoms he observed Ag_2^+ triplet with $A(^{109}Ag_2^+) \sim 300$ G, $A(^{107}Ag_2^+) \sim 260$ G, and $g = 1.973$. An Ag_2^+ species with similar ESR parameters was stabilized in vitreous calcium metaphosphate after γ-irradiation.[19] Symons et al.[20,21] have characterized various paramagnetic silver clusters Ag_2^+, Ag_3^{2+}, and Ag_4^{3+} formed after low-temperature γ-irradiation and thermal annealing of frozen benzene and methyl cyanide solutions containing $AgClO_4$ or $AgNO_3$. The g values of all studied clusters are smaller than 2.00, and the A values, although to some extent dependent on the matrix, decrease nearly proportionally to the cluster nuclearity. An equilateral triangular structure for Ag_3^{2+} and a tetrahedral structure for Ag_4^{3+} have been proposed. Recently, Symons and Stevens[22] correlated the growth of optical absorptions at 265 nm (ethanol solution) and at 290 nm (aqueous solution) with the growth of a Ag_4^{3+} ESR signal during thermal annealing at γ-irradiated frozen solutions of $AgClO_4$ in ethanol and water.

Howard and Preston[23] reported the ESR identification of a neutral silver cluster Ag_3^0 which was produced at 77 K by co-condensation of ^{107}Ag atoms and C_6D_6 on the cold surface of a rotating crystal. The analysis of the silver isotropic spectrum led to the following ESR parameters—$A(2) = 295$ G, $A(1) = 38.5$ G, and $g = 1.9622$—and to the conclusion that Ag_3^0 is most probably bent with unpaired electrons localized mainly in valence s atomic orbitals of the terminal atoms. Neutral Ag_5^0 clusters were prepared by the same technique.[24] The ESR of Ag_5^0 in aromatic hydrocarbon matrices at 77 K consists of a triplet of multiplets and was analyzed in terms of $A_\parallel(2) = 212$ G, $A_\perp(2) = 210$ G, $g_\parallel = 2.002$, and $g_\perp = 2.085$. A trigonal bipyramid was proposed as the pentamer structure. The Ag_3^0 cluster was also obtained by codepositing atomic silver with excess nitrogen at 4.2 K.[25] The ESR spectrum was characterized by an axially symmetric spin Hamiltonian with $g_\parallel = 1.9933$ and $g_\perp = 1.9558$ and, for $^{107}Ag_3^0$, $A_\parallel(1) = 310.8$ G with $A_\perp(1) = 310.1$ G and $A_\parallel(2) = 76.0$ G with $A_\perp(2) = 72.66$. The triangular structure of Ag_3^0 was proposed with a spin population of 51% on one nucleus and 12% on each of the other two nuclei.

Activated Ag–NaA. Our present examinations of activated Ag–NaA samples with various silver contents indicate that the concentration of paramagnetic silver species after activation is very low and close to the sensitivity limit of ESR. The anisotropic signal A_1, the major feature in the ESR spectrum of activated Ag–NaA, probably is due to Ag^{2+} cations. The ESR parameters of A_1 agree well with those of the divalent silver ion. The same samples studied by reflectance spectroscopy show a variety of absorption bands which change depending on the silver exchange level and the treatment conditions. The characteristic absorption bands of activated Ag–NaA with maxima around 450 and 300 nm assigned previously to Ag_3^{2+} are certainly due to diamagnetic silver clusters as well as the band at 510 nm.

Activated Ag–NaA Exposed to H_2 or γ-Irradiated. Ag^{2+} Cations. In all γ-irradiated, activated Ag–NaA samples we observed an anisotropic ESR signal with parameters close to those of the A_1 signal but with much higher signal intensity. This intense signal is designated as signal A. A spectrum with similar parameters was recorded after room temperature γ-irradiation of Ag–X zeolite and was assigned to Ag^{2+} cations located in the supercages.[26] It is interesting that Ag^{2+} cations which are formed very efficiently after γ-irradiation of activated Ag_1–NaA zeolite are nearly absent if the sample is exposed to H_2 before γ-irradiation (compare Figures 2a and 3a). This observation suggests that also in Ag–NaA zeolite Ag^{2+} cations are located in the supercages. Ag^{2+} most probably originates from Ag^+ as a result of direct electron loss or hole capture. In the supercages, Ag^+ cations are easily reduced by H_2, yielding Ag^0 which migrates to the surface and forms silver microcrystallites. Thus, subsequent γ-irradiation does not form Ag^{2+} because the Ag^+ precursors have already reacted and are largely absent.

Ag_3^0 and Ag_3^{2+} Clusters. Hydrogen reduction or γ-irradiation of Ag_1–NaA lead to ESR signal B with $A \sim 101$ G and $g = 2.043$. According to our best knowledge this signal has not been observed in any matrices containing silver. The line intensity ratio close to 1:3:3:1 and spectrum isotropy imply interaction with three equivalent silver nuclei. To exclude the possibility that signal B is not a sextet (binomial ratio 1:5:10:10:5:1) with the outer lines too small to be observed, we checked spectrum B at very high gain and did not see any additional outer lines.

The trimeric silver clusters can possess different charges and different structures. Two out of three trimeric clusters Ag_3^{2+} and Ag_3^0 are paramagnetic, and each one can have linear or bent structures. The ESR parameters of the Ag_3^{2+} cluster stabilized in frozen toluene solution[20] with $A = 203$ G and $g = 1.973$ are completely different from the parameters of signal B. However, signal D observed in γ-irradiated Ag_1–NaA samples which were previously treated by H_2 has a g value and splitting very similar to that of Ag_3^{2+} in frozen toluene. Signal D shows the extra quartet splittings, distinctly visible on the outer lines, which were also observed in the Ag_3^{2+} spectrum in frozen toluene and related to the combination of interactions with $(^{109}Ag_3)_3$, $(^{109}Ag)_2$ + $(^{107}Ag)_1$, $(^{109}Ag)_1$ + $(^{107}Ag)_2$, and $(^{107}Ag)_3$. On the basis of these similarities we assign signal D to a Ag_3^{2+} cluster with a bent structure as originally proposed.[20] Ag_3^{2+} has to be located in the supercage because it decays immediately in the presence of O_2.

Signal B we assign somewhat tentatively to a neutral Ag_3^0 species. The electronic configurations of Ag_3^0 and Ag_3^{2+} are different, thus one can expect different ESR parameters. However, to better support the assignment of signal B to Ag_3^0, semiempirical calculations are certainly needed, especially if one takes into account the rather dramatic reduction of hyperfine splitting and positive Δg shift for the proposed Ag_3^0 in comparison to Ag_3^{2+}. The reduced hyperfine splitting in signal B suggests that some spin population is elsewhere, perhaps in anisotropic orbitals, but the spectra do not appear very anisotropic. Trial simulations did not indicate any unique conclusions with regard to such possible anisotropy.

Ag_6^+ Clusters. In γ-irradiated Ag_1–NaA, quartet B transforms to septet E on thermal annealing. The same signal E arises in activated Ag_5–NaA directly after hydrogen reduction or after γ-irradiation. A septet with similar ESR parameters was earlier reported[6] in hydrogen-reduced Ag–NaA and was assigned to Ag_6^{n+} ($n = 5, 3, 1$). Septet E shows a positive Δg shift and reduction of hyperfine splitting A in comparison to the value which can be expected from the simple formula $A_x = A_1/x$, where A_1 is the hyperfine splitting constant for a single Ag^0 and x is the number of silver nuclei in the cluster. Taking the lowest value from the values reported in ref 21, $A_1 = 640$ G, the splitting for a hexamer should be higher than 100 G. It seems possible that the reduction of hyperfine splitting and positive Δg shift are characteristic for neutral or nearly neutral silver clusters. If so the most probable candidate represented by signal E would be Ag_6^+. Of course, it is realized that Ag_6^+ is not necessarily expected to have six equivalent Ag atoms; that depends on the specific structure and symmetry which might be probed by suitable molecular orbital calculations. However, we suggest that an Ag_6 species is also mechanistically reasonable as is discussed below.

The ESR parameters of Ag^{2+} and paramagnetic silver clusters stabilized in Ag_1–NaA after γ-irradiation at 77 K or H_2 reduction are tabulated in Table I.

Silver Clustering in Ag–NaA. The formation of linear trimeric clusters during activation of Ag–NaA is well documented by X-ray diffraction studies[3,4] and far-IR spectroscopy.[12,14] The identification of this trimeric cluster as paramagnetic Ag_3^{2+} in activated

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Table I. ESR Parameters of Paramagnetic Silver Clusters and Ag^{2+} in Activated Ag_1–NaA after γ-Irradiation at 77 K

ESR signal	treatment method	species	g^a	A (G)^a
A	γ-irradiation at 77 K	Ag^{2+}	$g_\perp = 2.049$ $g_\parallel = 2.316$	$A_\perp = 30.1$ $A_\parallel = 36.6$
B	γ-irradiation at 77 K or H_2 reduction at 295 K	$Ag_3{}^0$	$g = 2.043$	$A = 102$
C	H_2 reduction at 473 K	$(Ag^0)_n$ crystallities	$g = 1.966$	
D	H_2 reduction at 295 K followed by γ-irradiation at 77 K	$Ag_3{}^{2+}$	$g = 1.9722$	$A = 208$
E	γ-irradiation at 77 K followed by 10 min of annealing at 295 K	$Ag_6{}^+$	$g = 2.046$	$A = 67.6$

[a] The estimated uncertainty in g is ±0.002 G and in A it is ±1 G. The two Ag isotopes were not typically resolved so the only observed A value is given.

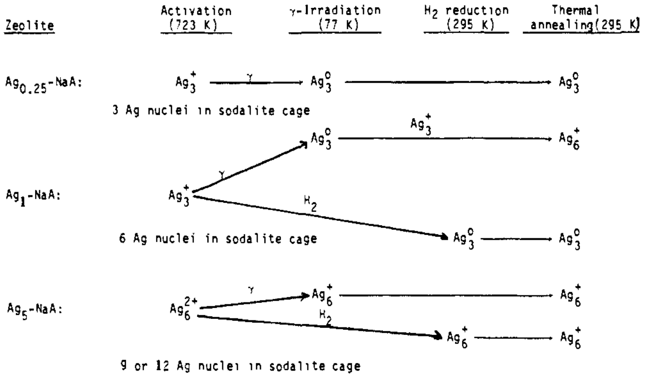
samples cannot be supported by the present ESR studies. However, our assignments of signal B to $Ag_3{}^0$ and signal E to $Ag_6{}^+$ allow us to present a very consistent mechanism for silver clustering in A zeolite which is in accordance with earlier conclusions about cluster nuclearities but is more specific about the cluster charges. if $Ag_3{}^0$ is the main product of 77 K γ-irradiation of activated Ag_1–NaA zeolite it seems logical from radiation chemistry concepts that it is formed as a result of electron capture by $Ag_3{}^+$.

$$Ag_3{}^+ + e \rightarrow Ag_3{}^0 \qquad (1)$$

This suggests that the major clustering product in activated Ag_1–NaA could be monovalent silver trimer formed during the autoreduction process. $Ag_3{}^+$ is diamagnetic and undetectable by ESR, but it can have a linear structure and can be located in the sodalite cage as proposed by Gellens,[3] [Ag(S2′)–Ag(S4)–Ag(S2′)]$^+$. We believe that reduction of Ag_1–NaA by H_2 at temperature is also a one-electron transfer process yielding $Ag_3{}^0$. The much lower yield of $Ag_3{}^0$ formation by H_2 reduction can be related to the fact that H_2 at room temperature cannot penetrate the sodalite units through their size-ring opening with a 22-nm diameter since the H_2 kinetic diameter at 273 K is 0.275 nm. The reduction via contact through a six-ring opening would be rather inefficient if the outer Ag in $Ag_3{}^+$ occupied S2′ sites inside a sodalite cage.

The stability of radiation-induced $Ag_3{}^0$ in $Ag_{0.25}$–NaA on thermal annealing in contrast to zeolites with higher silver content provides excellent evidence for silver aggregation in a sodalite cage during activation treatment. In activated $Ag_{0.25}$–NaA one can expect only one $Ag_3{}^+$ cluster per sodalite cage which after γ-irradiation becomes neutral and mobile, but inside the sodalite cage it does not have any partner with which to interact. There are probably two linear Ag_3+ clusters in one sodalite cage for Ag_1–NaA zeolite. We postulate that they are located in two parallel planes because such an arrangement gives the maximum distance between the central nuclei in the $Ag_3{}^+$ trimer, about 0.41–0.42 nm, and because of the repulsion of positive charges should be preferred. For all possible arrangements for two and four linear $Ag_3{}^+$ clusters in a sodalite cage see Figure 2 in ref 14. During γ-irradiation at 77 K one of two $Ag_3{}^+$ is reduced and during thermal annealing at room temperature a neutral $Ag_3{}^0$ can approach a $Ag_3{}^+$ to react to yield $Ag_6{}^+$. If both $Ag_3{}^+$ capture electrons during γ irradiation they can form a neutral hexamer, but $Ag_6{}^0$ being diamagnetic is undetectable by ESR. The geometrical considerations of three or four linear silver clusters located in the same sodalite unit with the silver nuclei occupying S2′–S4–S2′ sites give a very short distance between the central nuclei comparable to the silver–silver bond length in trimeric clusters estimated by Gellens[3] as 0.285–0.300 nm. This leads to the conclusion that if there are more than two $Ag_3{}^+$ clusters in the sodalite cage at least two of them can interact with each other to form diamagnetic $Ag_6{}^{2+}$ which cannot be observed by ESR. $Ag_6{}^{2+}$, by electron capture during γ-irradiation or by one-electron transfer reaction with H_2, yields the $Ag_6{}^+$ cluster represented by ESR signal E. In contrast to Ag_1–NaA, in Ag_5–NaA zeolite both reduction methods give comparable yields of $Ag_6{}^+$. It is likely that in the sodalite cage the silver nuclei of $Ag_6{}^+$ are forced to occupy a more accessible site near the six-ring plane. As a result H_2 in the supercage can more easily interact with silver clusters in the sodalite cage to yield $Ag_6{}^+$ with high efficiency.

Scheme I. The Proposed Silver Clustering Process in Sodalite Cages of Ag–NaA Zeolite with Various Silver Contents



Additional evidence that in activated Ag_5–NaA a six-nucleus cluster is present before γ-irradiation is provided by optical data The absorption band at 510 nm observed in activated Ag_5–NaA disappears after γ-irradiation or H_2 reduction and simultaneously the absorption at 580 nm is observed. The band at 510 nm does not show up in activated Ag_1–NaA zeolite in which, as indicated from ESR data, $Ag_6{}^+$ is formed on thermal annealing by reaction between $Ag_3{}^0$ and $Ag_3{}^+$. Thus we assign the absorption at 580 nm to $Ag_6{}^+$ and that at 510 nm to $Ag_6{}^{2+}$. The assignment of an optical band to $Ag_3{}^0$ species is more ambiguous. The optical spectrum of γ-irradiated $Ag_{0.25}$–NaA in which the $Ag_3{}^0$ cluster is stable shows the largest increase of absorption at 345 nm, but the bands at 240 and 290 nm are also more intense after γ-irradiation. In H_2-reduced Ag_1–NaA in which the ESR quartet ($Ag_3{}^0$) does not transform into a septet but shows rather low intensity, two bands develop in the presence of H_2, one at 400 nm immediately after H_2 admission and another at 360 nm about 1 h later. Subsequent γ-irradiation of the same sample which significantly increases the spin concentration due to efficient formation of $Ag_3{}^0$ only moderately increases the absorption at 360 nm. It is likely that the absorption at 400 nm represents a hydrogen adduct to $Ag_3{}^0$ which later decomposes with $Ag_3{}^0$ formation. In such a case the absorption at 360 nm might be related to neutral silver trimers.

A strong, separate absorption band observed in all activated Ag–NaA samples in the range 440–460 nm with intensity decreasing significantly after H_2 reduction and only moderately after γ-irradiation could be assigned to the $Ag_3{}^+$ cluster as a precursor of $Ag_3{}^0$. However, the poor correlation between ESR and optical data for γ-irradiated and H_2-reduced samples makes this assignment rather ambiguous. γ-Irradiation which efficiently produces $Ag_3{}^0$ or $Ag_6{}^+$ in Ag_1–NaA only weakly decreases the absorption at 440–460 nm in contrast to H_2 reduction which causes significant decay of the same band with a low yield or $Ag_3{}^0$. The proposed clustering mechanism for Ag–NaA zeolites with various silver contents is summarized in Scheme I.

The $Ag_3{}^0$ and $Ag_6{}^+$ clusters show different stability in the presence of air at room temperature. Whereas the ESR quartet decreases significantly during 10 min the septet changes its intensity only a little during 2 h. The absorption bands assigned to $Ag_3{}^0$ (360 nm) and $Ag_6{}^+$ (580 nm) show similar kinetics on air admission. It seems probable that the faster decay of $Ag_3{}^0$

is related to its greater mobility which makes it easier to contact oxygen or water vapor.

Ag–NaA zeolites reduced by H_2 above 473 K do not show the ESR spectra of silver clusters but only a broad singlet C due to the magnetic resonance of conduction electrons in small silver crystallites.[6] Signal C does not appear in γ-irradiated Ag–NaA samples even after 3 days of annealing at room temperature.

It was reported earlier in hydrated $Ag_{0.7}$–NaA zeolite exposed to X-irradiation at 77 K that silver atoms were stabilized at 77 K.[7] Our present ESR study on hydrated Ag_5–NaA γ-irradiated at 77 K does not reveal the ESR spectrum of Ag^0 atoms in this matrix. The complex ESR spectrum presented in Figure 6 is probably a superposition of two or more spectra of silver clusters. This implies the migration of Ag^0 inside the zeolite lattice even at 77 K. In zeolites with higher silver content there is high probability that a Ag^0 atom can meet a Ag^+ cation before it becomes immobilized in a lattice trap. Further ESR studies of hydrated and partially dehydrated Ag–NaA with high silver content using γ-irradiation at 77 K would be useful to clarify the silver clustering process during activation treatment.

Conclusions

The γ-irradiation of activated zeolites appears to be a very useful technique to efficiently produce paramagnetic silver clusters in Ag–NaA zeolite. Depending on the silver content, in Ag–NaA an isotropic quartet with $g = 2.043$ and $A = 102$ G or an isotropic septet with $g = 2.046$ and $A = 67.6$ G is observed by ESR after γ-irradiation at 77 K. The quartet was assigned to a neutral linear silver cluster Ag_3^0 and the septet to a Ag_6^+ species The same clusters are formed in activated Ag–NaA after hydrogen reduction at room temperature. The efficiency of Ag_6^+ formation in Ag_5–NaA is the same for H_2 reduction and γ-irradiation. However, in Ag_1–NaA hydrogen reduction is much less efficient and the yield of Ag_3^0 is about one order of magnitude lower than after γ-irradiation at 77 K. This strongly suggests that silver nuclei of linear Ag_3^0 occupy relatively inaccessible sites to hydrogen inside the sodalite cage.

Besides the formation of Ag_3^0 in Ag_1–NaA zeolite exposed to H_2 before γ-irradiation at 77 K, divalent silver trimeric clusters Ag_3^{2+} with the ESR parameters $g = 1.972$ and $A = 208$ G are also formed with much lower yield.

It is concluded that the predominant silver clusters in activated Ag–NaA with various silver contents are not paramagnetic which agrees with very recent magnetic susceptibility measurements.[27] It is proposed that autoreduction of silver in Ag–NaA leads to diamagnetic Ag_3^+ clusters with a characteristic optical absorption maximum at 440–460 nm. If there is only one Ag_3^+ per sodalite cage the neutral Ag_3^0 cluster formed after electron capture during radiolysis is the final radiation product. We were unable to assign unambiguously an absorption band to Ag_3^0, but there is some evidence that the absorption at 360 nm is related to Ag_3^0.

The γ-irradiation at 77 K of Ag–NaA with two Ag_3^+ clusters per sodalite cage initially leads to the formation of Ag_3^0 which on thermal annealing reacts with Ag_3^+ in the vicinity yield Ag_6^+. The formation of Ag_3^+ is associated with the appearance of an absorption at 580 nm.

In zeolites with high silver content activation treatment can lead to aggregation of 9 or even 12 silver nuclei per sodalite cage arranged as linear trimers.[14] We point out that if there are more than two Ag_3^+ linear clusters per sodalite cage at least two of them must interact to form diamagnetic Ag_6^{2+} with a characteristic absorption at 510 nm. This band disappears after γ-irradiation and a new absorption at 580 nm appears simultaneously with the formation of paramagnetic Ag_6^+ clusters as a result of electron capture by Ag_6^{2+}.

The absence of silver dimers, tetramers, and pentamers in activated and γ-irradiated Ag–NaA suggests that the structure of zeolite A facilitates the formation of trimers or multiplets of trimers.

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Registry No. Ag, 7440-22-4; Ag_3^0, 12595-26-5; Ag_6^+, 73145-14-9; H_2, 1333-74-0.

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