New Silver Clusters in Hydrated Ag–NaA Zeolite

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Two new silver clusters characterized by EPR quartets with hyperfine splittings of about 130×10^{-4} cm^{-1} and distinctly different g values, have been found in hydrated ^{109}Ag–NaA zeolite, X-ray irradiated at 77 K and annealed to 280 K.

The study of small silver clusters contributes to a better understanding of silver agglomeration, which plays a very important role in heterogeneous catalysis and in the photographic process. For small paramagnetic silver clusters EPR spectroscopy is the principal method of characterization. By deposition of silver vapour in organic or inert gas matrices at 77 K neutral trimeric and pentameric clusters are formed.[1,2] Cationic species Ag_2^+, Ag_3^{2+}, Ag_4^{3+} and Ag_5^{4+} were observed in γ-irradiated aqueous and organic glasses at low temperature.[3–5] In γ-irradiated Ag–NaA zeolites bigger cationic clusters have been stabilized such as Ag_6^{n+} and $Ag_6^{n+}\cdot 8Ag^+$.[6,8] Hexameric silver species can also be prepared by hydrogen reduction of Ag–NaA zeolite at a temperature below 25 °C.[9]

Zeolites are especially suitable to stabilize silver clusters with different nuclearity because of geometrical constraints due to their cage and channel-like structure. We showed recently that the presence of water significantly affected the silver agglomeration process in A zeolites.[10] In Ag_6–NaA zeolite dehydrated at 100 °C the well-known Ag_6^{n+} cluster is formed after γ-irradiation at 77 K. It is characterized by an isotropic septet with $g_{iso} = 2.024$ and $A_{iso} = 63.9 \times 10^{-4}$ cm^{-1}.[6,8] If the same zeolite is not dehydrated before irradiation an EPR spectrum is obtained consisting of eight hyperfine lines. This spectrum has been previously ascribed to the species $Ag_3^{2+}\cdots Ag$ with three equivalent Ag nuclei and one Ag nucleus at a greater distance.[10]

In order to substantiate the above assignment, experiments were carried out on Ag_6–NaA zeolite samples containing only one isotope, ^{109}Ag. After annealing the non-dehydrated sample at 280 K the spectrum shown in Fig. 1(*a*) was recorded. In comparison with the spectrum exhibiting the eight lines, additional features are observed, particularly on the four inner lines. Also, it is worth noting that the linewidths are different,

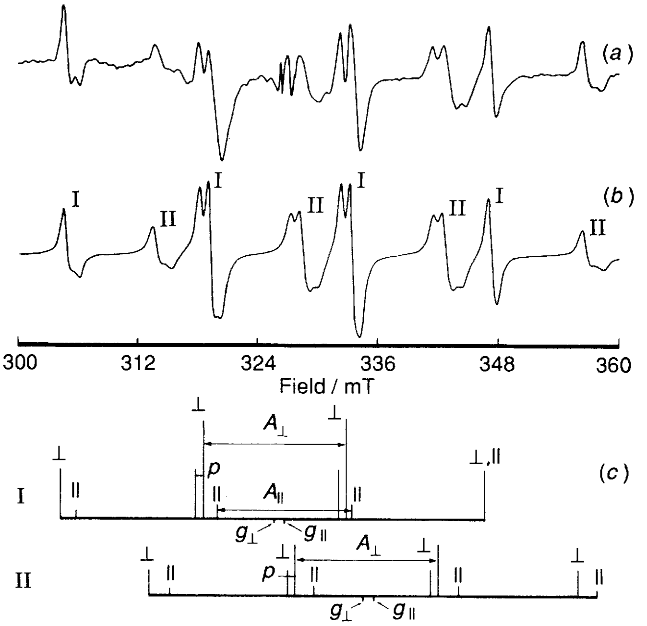

Fig. 1 (*a*) EPR spectrum of hydrated Ag_6–NaA zeolite X-ray irradiated at 77 K and annealed to *ca.* 280 K. At 327 mT ($g = 2$) there are some signals from radicals produced by the X-rays from the matrix. (*b*) Simulated EPR spectrum using parameters given in the text; the labels I and II refer to the two silver clusters. (*c*) Stick diagrams for silver cluster species I and II.

e.g. the derivative linewidth of the first and last line are, respectively, 8 and 12 G. Applying the same experimental procedure on $^{109}Ag_1$–NaA a similar spectrum was observed.

We were able to explain the spectra in terms of two quartets, arising from two different silver clusters (denoted by I and II) present in different amounts and each containing three magnetically equivalent silver nuclei. The spectrum in Fig. 1(*a*) was simulated using the universal spin Hamiltonian programme MAGRES.[11] The best fit to the experimental data was obtained with the following set of parameters (referring to ^{109}Ag): quartet I: $g_\parallel = 2.001$, $g_\perp = 2.008$; $A_\parallel = 129.6 \times 10^{-4}$ cm^{-1}, $A_\perp = 132.3 \times 10^{-4}$ cm^{-1}; quartet II: $g_\parallel = 1.942$, $g_\perp = 1.953$; $A_\parallel = A_\perp = 130 \times 10^{-4}$ cm^{-1}, a linewidth of 7 G (Gaussian line shape) and a ratio between I and II of two.

Fig. 1(*b*) shows the simulated EPR spectrum. The labels I and II on the peaks refer to the two different clusters. The agreement between the experimental spectrum and the simulation is excellent. The inner lines of the quartets show the second-order hyperfine splittings,[12] the outer lines reveal clearly the anisotropies in the *g* tensor (I and II) and in the hyperfine tensor (I). From the values of the magnetic parameters given above one calculates for the second-order splitting of the inner lines a value of about 9 G, which is in perfect agreement with the observed splitting. For the sake of clarity stick diagrams are given for I and II in Fig. 1(*c*). The parallel and perpendicular features are indicated by the usual symbols, the second order hyperfine splitting, equal to $3/2A^2_{iso}/g\beta B_0$, is indicated by *p*. These diagrams illustrate small details in the experimental spectrum, for instance the seventh line in the spectrum belonging to quartet I is very sharp owing to the fact that the anisotropy in the *g* tensor is counterbalanced by the anisotropy in the hyperfine tensor (coincidence of ∥ and ⊥ feature).

From the analysis of the EPR spectrum we conclude that, in hydrated Ag_6–NaA zeolite, upon irradiation two different silver clusters are stabilized to different degrees, having slightly different magnetic parameters. For Ag_1–NaA the same conclusion applies.

The question remains as to what kind of silver structures are responsible for the observed spectra. Two obvious candidates, Ag_3^0 and Ag_3^{2+} can be eliminated on account of their magnetic parameters. Ag_3^0, a Jahn–Teller molecule, has been studied by Howard *et al.*[13] in C_6D_6 and by Kernisant *et al.*,[2] in an N_2 matrix. The EPR spectra observed for Ag_3^0 do not show hyperfine interactions with three equivalent silver nuclei. The ionic trimer Ag_3^{2+} has been observed for the first time by Symons *et al.*[14] and studied recently in detail by us.[15] The structure of Ag_3^{2+} is triangular, the three silver atoms are equivalent and have the following magnetic parameters: $g_\parallel = 1.958$, $g_\perp = 1.981$ and $^{109}A_\parallel = 200 \times 10^{-4}$ cm^{-1}, $^{109}A_\perp = 205 \times 10^{-4}$ cm^{-1}, thus quite different from the magnetic parameters observed for the species I and II.

Subsequently, we may consider higher nuclearity silver clusters, for instance silver clusters of the type Ag_5^{q+} ($q = 0, 2, 4$) for which trigonal bipyramidal structures have been proposed.[1,16,17] The EPR spectrum of Ag_5^0 consists principally of a triplet of multiplets suggesting two equivalent silver nuclei.[1] The cationic cluster Ag_5^{4+} gives an EPR spectrum completely different from what we have observed.[5] Theoretical calculations[16,17] on Ag_5^{q+}, assuming a trigonal bipyramidal structure predict EPR spectra for these pentaatomic species strongly deviating from the spectrum shown in Fig. 1(*a*). Therefore, we conclude that trigonal bipyramidal structures definitely can be ruled out as possible candidates for the silver clusters I and II.

We suggest that the two newly observed silver clusters in hydrated Ag–NaA zeolite are trimeric Ag clusters, but heavily perturbed by interactions with the zeolite lattice, and/or the water molecules.[5] It is known that the *g* values and the spin density distribution of radical ions are strongly affected by neighbouring charges, for instance the EPR spectra of 'free' ions change drastically on association with counter ions.[19] Preliminary electron-spin-echo-envelope-modulation experiments carried out on clusters I and II in samples containing D_2O indicate that there is interaction with the deuterium and the aluminium nuclei.

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