

Organosilver Radicals in Gamma-irradiated Ag–NaA Zeolite with Methanol Adsorbate

Tomasz Wasowicz, Janusz Mikosz, Jarosław Sadło and Jacek Michalik*

Department of Radiation Chemistry and Technology, Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland

Hydroxyalkyl silver radicals, $\text{Ag-CH}_2\text{OH}^+$ in γ -irradiated Ag–NaA zeolites with adsorbed methanol have been studied by EPR spectroscopy. These adducts, for silver loadings greater than one Ag^+ per unit cell, are formed directly after irradiation at 77 K. For lower Ag^+ content they appear on annealing above 140 K. It is postulated that the Ag^+ location in the zeolite lattice plays a crucial role in this process, and two different mechanisms of $\text{Ag-CH}_2\text{OH}^+$ formation are discussed depending on Ag^+ location inside or outside a β -cage.

Silver atoms and silver clusters formed in various frozen solutions by ionizing radiation have been extensively studied by EPR spectroscopy.^{1–7} Recently radiation-induced silver agglomeration in zeolites has attracted special interest.^{8–17} Much less is known about the organosilver radicals formed during radiation processes. EPR doublets with relatively low silver isotropic hyperfine couplings were first observed in γ -irradiated frozen methanol solutions: $A_{\text{iso}}(\text{Ag})$ ca. 13.0 mT. A similar doublet was later reported for glassy ethanol samples.¹⁸ Based on detailed analysis of EPR doublets for CD_3OD and $^{13}\text{CH}_3\text{OH}$ samples, Symons¹⁸ assigned them to covalent organosilver radicals, $\text{Ag-CH}_2\text{OH}^+$ and $\text{Ag-CHCH}_3\text{OH}^+$ having a single electron σ^1 bond between silver and carbon. The same author has proposed that they are formed by reaction between Ag^+ cations and matrix-derived radicals, $\dot{\text{C}}\text{H}_2\text{OH}$ or $\text{CH}_3\dot{\text{C}}\text{HOH}$. Besides alcohol glasses Ag doublets with highly reduced A values were only reported for γ -irradiated frozen solutions of $\text{CD}_3\text{CN} + \text{D}_2\text{O}$ mixtures, $A_{\text{iso}}(\text{Ag}) = 17.5$ mT⁴ and in glassy dimethylformamide, $A_{\text{iso}}(\text{Ag}) = 10.0$ mT.⁶

The same type of organosilver radicals have also been generated by matrix isolation techniques but only in exceptional cases. The EPR spectrum of a silver–acetylene adduct prepared by co-condensation of Ag atoms and deuteriated acetylene in an argon matrix reveals a strong doublet with Ag hyperfine splitting of 13.5 mT, but only when Ag and C_2D_2 are allowed to react in the vapour phase before condensation.¹⁹ For C_2H_2 additional splittings of 5.0 and 3.0 mT are recorded indicating an interaction with two non-equivalent protons. As a carrier of that spectrum the Ag–acetylene adduct Ag-CH=CH , having a vinyl structure, has been proposed.

It is noteworthy that monoligand organosilver complexes generated in rare-gas matrices by co-condensation of silver atoms with ethene or higher alkenes are characterized by large silver hyperfine interactions in the range of 54–60 mT.^{20,21}

Recently Mile²² studied reactions of ketene, CH_2CO , with silver atoms in adamantane with the use of a rotating cryostat. At 204 K an almost isotropic doublet was observed with $A_{\text{iso}}(^{107}\text{Ag}^0) = 12.0$ mT, and additional splittings due to interactions with two nonequivalent protons $A(\text{H}_1) = 1.2$ mT, $A(\text{H}_2) = 2.0$ mT. It was assigned to a vinyl structure, namely the β -vinyloxysilver radical $\text{CH}_2=\dot{\text{C}}-\text{OAg}$.

We decided to study the formation of organosilver radicals in γ -irradiated A zeolites at 77 K assuming that the cage structure of zeolite framework would enable us to control that process to some extent and would yield additional information about its mechanism.

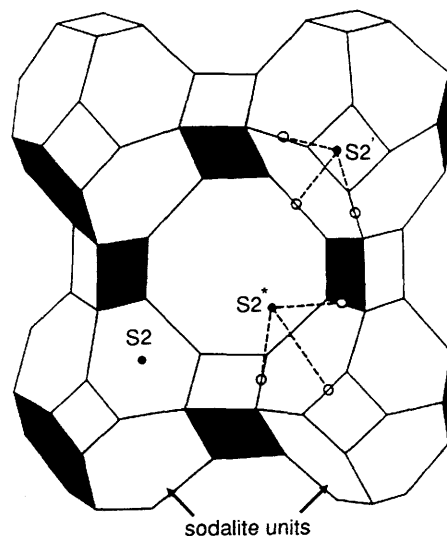


Fig. 1 Schematic diagram of zeolite A structure. Each vertex represents an Al or Si atom and the lines represent O bridges.

In zeolite A alumina and silica tetrahedra are bonded together to form truncated octahedra called β -cages or sodalite units with diameter of 0.66 nm. The sodalite units are coupled on their cubic faces to form larger α -cages with diameter 1.14 nm (Fig. 1) which constitute the channel structure of zeolite A. The entrance to a sodalite unit from an α -cage is only possible through a six-membered ring, called a hexagonal window. Its diameter of 0.23 nm is crucial for our experimental concept. The organic adsorbate molecules are too big to get into sodalite and are localized in α -cages. However, silver cations in A zeolites with low Ag^+ content occupy preferentially S2' sites inside β -cages.^{23,24} For silver concentrations higher than one Ag^+ per unit cell, silver cations can also be located at the centre of the hexagonal window and the S2* site which is slightly displaced into the α -cage (Fig. 1). Thus, in A zeolites with low silver content Ag^+ cations cannot be solvated by organic adsorbates.

In this paper we present the results of an EPR study on organosilver radicals formed in γ -irradiated Ag–NaA zeolites in the presence of adsorbed methanol molecules.

The objective of this work is to elucidate the mechanism of organosilver radical formation by studying the influence of Ag^+ content in zeolite, and annealing temperature, on radical yield. The influence of methanol molecules on silver agglomeration processes in zeolites is also discussed.

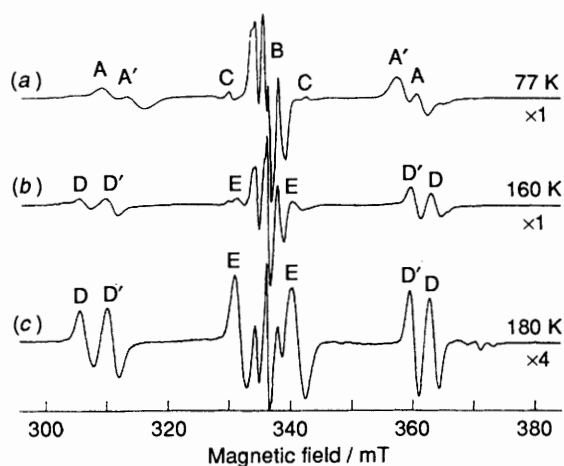


Fig. 2 EPR spectra of $\text{Ag}_1\text{-NaA}$ zeolite with adsorbed CH_3OH irradiated at 77 K and gradually warmed up, showing Ag^0 at sites (A) and (D), CHO radicals (C) and $\text{Ag}\cdot\text{CH}_2\text{OH}$ radicals (E)

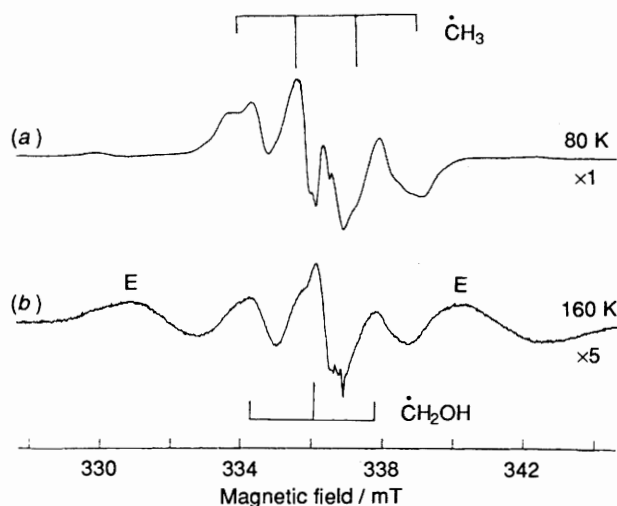


Fig. 3 EPR spectra of $\text{Ag}_{0.3}\text{-NaA}/\text{CH}_3\text{OH}$ zeolite irradiated at 77 K after annealing to 80 K (a) and 160 K (b) showing features assigned to $\dot{\text{C}}\text{H}_3$, $\dot{\text{C}}\text{H}_2\text{OH}$ and $\text{Ag}\cdot\text{CH}_2\text{OH}^+$ (E)

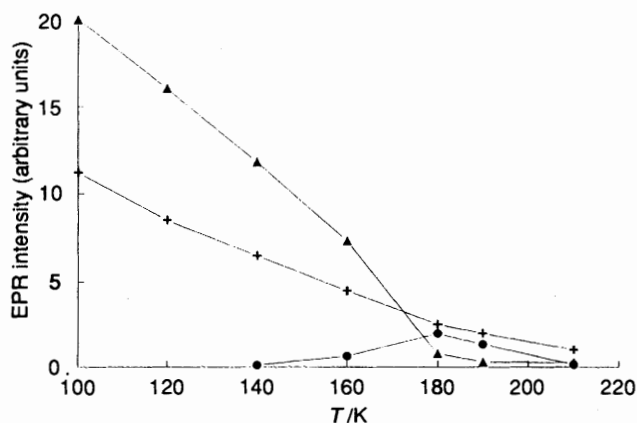


Fig. 4 Plot showing the effect of annealing temperature on the relative yield of radicals in $\text{Ag}_1\text{-NaA}/\text{CH}_3\text{OH}$ zeolite irradiated at 77 K: \blacktriangle , total ($\dot{\text{C}}\text{H}_2\text{OH} + \dot{\text{C}}\text{H}_3$); +, Ag^0 ; \bullet , $\text{Ag}\cdot\text{CH}_2\text{OH}^+$

Experimental

Linde NaA (4 Å) zeolite was washed with 0.1 mol dm^{-3} sodium acetate and then ion-exchanged at room temperature for 24 h with AgNO_3 solutions of various concentrations to prepare Ag-NaA samples with 0.3, 1, 6 and 12 Ag^+ cations per unit cell.

A few samples were exchanged using $^{109}\text{AgNO}_3$ solution (^{109}Ag was purchased from Technobexport, Moscow). Zeolite samples were partially dehydrated in a vacuum line by a slow rise in temperature to 150 °C, or activated at 400 °C in an oxygen flow and then degassed at 150 °C. Methanol was adsorbed on zeolite at room temperature under its vapour pressure before samples were irradiated in a ^{60}Co source at 77 K with a dose of 4 kGy.

The EPR spectra were measured with a Bruker ESP-300 X-band spectrometer in the temperature range 6–290 K using an Oxford Instrument ESR-9 helium flow cryostat.

Results

Organosilver Radicals in Ag-NaA Zeolites Dehydrated at 150 °C.—Directly after the irradiation at 77 K the EPR spectra of zeolite A containing 0.3 and 1 Ag^+ per unit cell show three groups of lines, Fig. 2(a). (i) Four lines spaced closely around $g = 2$ which represent adsorbate radicals, $\dot{\text{C}}\text{H}_2\text{OH}$ and $\dot{\text{C}}\text{H}_3$. (ii) Two doublets with large splittings: $A_{\text{iso}}(\text{A}) = 51.5$ mT and $A_{\text{iso}}(\text{A}') = 44.2$ mT which represent silver atoms, $^{109}\text{Ag}^0$ and $^{107}\text{Ag}^0$ respectively, stabilized at site A in the zeolite lattice. (iii) Low-intensity doublet C with $A_{\text{iso}}(\text{C}) = 12.8$ mT due to CHO radicals.

On annealing in the temperature range 100–120 K the radical quartet undergoes a fast transformation to a triplet (Fig. 3). This transformation does not affect the silver atom doublets at all. In our interpretation the primary EPR quartet consists of the quartet assigned to $\dot{\text{C}}\text{H}_3$ radical ($A_{\text{iso}} = 1.7$ mT), which decays at 120 K and the triplet of the much more stable $\dot{\text{C}}\text{H}_2\text{OH}$ radical ($A_{\text{iso}} = 1.8$ mT). At 140 K doublets A and A' disappear completely and a new pair of doublets D ($A_{\text{iso}} = 57.5$ mT) and D' ($A_{\text{iso}} = 49.8$ mT) due to $^{109}\text{Ag}^0$ and $^{107}\text{Ag}^0$ atoms at site D is recorded [Fig. 2(b)]. The transformation of silver centre A to centre D characterized by a greater spin density on the silver atom proves the increase of 'free atom' character of centre D which may be due to the relaxation of the zeolite lattice or to the shift of Ag^0 to a new site.

On warming above 140 K a new doublet E with much smaller splitting appears [Fig. 2(b) and 2(c)]: $A_{\text{iso}}(\text{E}) = 9.3$ mT for $\text{Ag}_{0.3}\text{-NaA}$ and 9.6 mT for $\text{Ag}_1\text{-NaA}$ zeolites. Its intensity increases with annealing temperature up to 180 K, then doublet E grows smaller, decaying completely at ca. 230 K. We assigned doublet E to organosilver radicals $\text{Ag}\cdot\text{CH}_2\text{OH}^+$ although its hfs value is distinctly smaller in comparison to the hfs value (ca. 12.8 mT) of organosilver radicals trapped in methanol glasses.¹⁸ The integral intensity of silver atom lines in $\text{Ag}_1\text{-NaA}$ decreases smoothly over the temperature range 100–210 K (Fig. 4). CHO radicals decay completely below 140 K. In contrast the fast decay of $\dot{\text{C}}\text{H}_2\text{OH}$ radicals in the temperature range 160–180 K correlates well with the growth of $\text{Ag}\cdot\text{CH}_2\text{OH}^+$ radicals. Similar temperature changes of the EPR signal were observed for $\text{Ag}_{0.3}\text{-NaA}$ zeolite.

In zeolites with higher silver content (6 Ag^+ and 12 Ag^+ per unit cell) doublet E is observed directly after irradiation at 77 K with hyperfine splitting of 10.7 mT, slightly bigger than in zeolites with low Ag^+ loadings. For $\text{Ag}_6\text{-NaA}$ the intensity of signal E increases in the temperature range 77–140 K by ca. 50%, whereas for $\text{Ag}_{12}\text{-NaA}$ zeolite signal E starts decaying above 100 K and at 160 K is not seen at all. In neither zeolites do the EPR spectra reveal the doublets due to Ag^0 atoms.

Ag-NaA Zeolites Activated at 400 °C in Oxygen.—Activated zeolites A were loaded with $^{109}\text{Ag}^+$ cations to prepare samples with two silver contents, 1 Ag^+ and 6 Ag^+ per unit cell. In all experiments with zeolites treated at 400 °C deuterated methanol CD_3OD was used as an adsorbate.

$^{109}\text{Ag}_1\text{-NaA}$ zeolite directly after γ -irradiation at 77 K

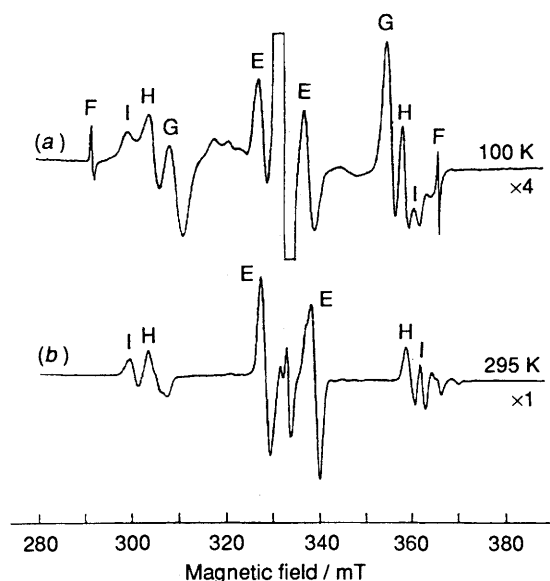


Fig. 5 EPR spectra of $^{109}\text{Ag}_1\text{-NaA/CD}_3\text{OD}$ zeolite irradiated at 77 K after annealing to 100 K (a) and 295 K (b) showing features F, G, H and I assigned to various $^{109}\text{Ag}^0$ sites and doublet E of $^{109}\text{Ag-CD}_2\text{OD}^+$ adduct

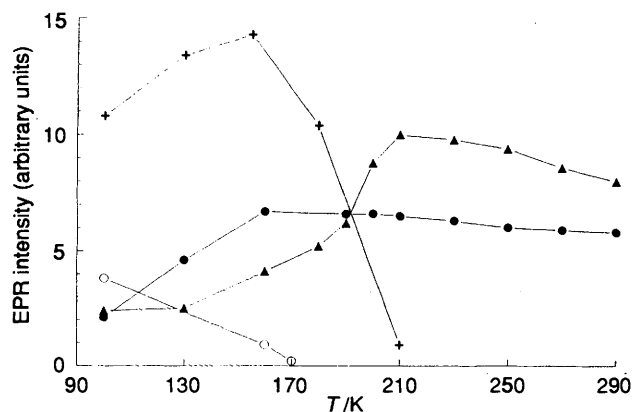


Fig. 6 Plot showing the effect of annealing temperature on the relative yields of $^{109}\text{Ag}^0$ atoms at site G (○) and H (●) and $^{109}\text{Ag-CD}_2\text{OD}^+$ radicals E (▲) in $^{109}\text{Ag}_1\text{-NaA}$ zeolite and $^{109}\text{Ag-CD}_2\text{OD}^+$ radicals E (+) in $^{109}\text{Ag}_6\text{-NaA}$ zeolite irradiated at 77 K

shows a complex EPR signal with (i) strong singlet at g ca. 2.002 due to CD_2OD radical; (ii) four isotropic doublets: F with very narrow line width and $A_{\text{iso}}(\text{F}) = 74.4$ mT representing free Ag^0 atoms and G, H, I with isotropic hfs 46.6, 54.8 and 66.2 mT, respectively, assigned to Ag^0 atoms solvated by methanol molecules; and (iii) doublet E ($A_{\text{iso}} = 9.7$ mT, $\Delta H_{\text{pp}} = 2.6$ mT) of organosilver $\text{Ag-CD}_2\text{OD}^+$ radical (Fig. 5). On temperature annealing doublet G transforms to doublet H in a similar temperature range as $\text{Ag}^0(\text{A})$ is transformed to $\text{Ag}^0(\text{D})$ in zeolites dehydrated at 150 °C. Silver splittings, $A_{\text{iso}}(\text{G}) = 52.1$ mT and $A_{\text{iso}}(\text{H}) = 57.4$ mT do not differ much from hfs values for $\text{Ag}^0(\text{A})$ and $\text{Ag}^0(\text{D})$, respectively. This leads to the conclusion that the locations of silver atoms in zeolites dehydrated at 150 °C and those activated at 400 °C are rather similar.

The intensity of doublet E, which stays nearly unchanged during transformation of $\text{Ag}^0(\text{G})$ into $\text{Ag}^0(\text{H})$, strongly increases on warming above 160 K reaching a maximum at 210 K (Fig. 6). At this temperature the concentration of $\text{Ag-CD}_2\text{OD}^+$ radicals is higher by a factor of ca. 4 in comparison to the concentration at 77 K. Remarkably, it does not change much on annealing at higher temperature, decreasing by only

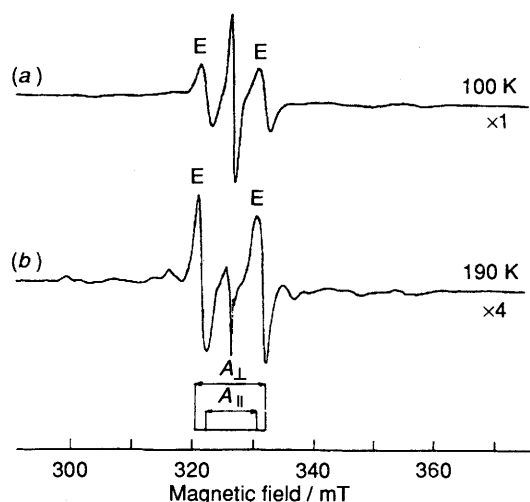


Fig. 7 EPR spectra of $^{109}\text{Ag}_6\text{-NaA/CD}_3\text{OD}$ zeolite irradiated at 77 K and annealed at 100 K (a) and 190 K (b)

Table 1 EPR parameters of silver-methanol adducts stabilized in Ag-NaA zeolites

Zeolite	$A(\text{Ag})/\text{mT}$	$\Delta H_{\text{pp}}/\text{mT}$	T/K
$\text{Ag}_1\text{-NaA}/150\text{ °C}$	9.1	1.4	140
	9.6	2.2	180
$^{109}\text{Ag}_1\text{-NaA}/400\text{ °C}$	9.7 ^a	2.3 ^a	100
	10.6 ^a	2.3 ^a	210
$\text{Ag}_6\text{-NaA}/150\text{ °C}$	10.1	2.2	100
	10.8	2.3	180
$^{109}\text{Ag}_6\text{-NaA}/400\text{ °C}$	$A_{\perp} = 11.6^a$	2.0 ^a	100
	$A_{\parallel} = 7.5^a$		

^a Adsorption of CD_3OD

20% between 210 K and 290 K. The same is true for silver atoms $\text{Ag}^0(\text{H})$ whose concentration is nearly unchanged until 290 K. Even at 295 K both species are still observed for a few minutes. The temperature dependence of EPR signal intensities of silver atoms at different sites and of organosilver radicals in zeolites activated at 400 °C are shown in Fig. 6.

In the EPR spectrum of $^{109}\text{Ag}_6\text{-NaA}$ zeolite recorded directly after irradiation at 77 K doublet E ($A_{\text{iso}} = 9.7$ mT) of organosilver radical and the singlet assigned to the radical CD_2OD are dominant [Fig. 7(a)]. Low-intensity features spreading over the range of 60.0 mT are due to silver clusters of unknown nuclearity. The EPR lines representing silver atoms are not observed at all. The intensity of doublet E increases with temperature up to 150 K and then decays rapidly at higher temperatures. At 190 K CD_2OD radicals disappear completely and the anisotropy of both lines of doublet E is clearly seen [Fig. 7(b)]. At the temperature above 210 K doublet E of organosilver radicals disappears completely. The EPR parameters for the silver-methanol adducts in various Ag-NaA zeolites are presented in Table 1.

Discussion

The EPR results described above clearly indicate that silver-methanol adducts are formed in zeolites A within a broad range of Ag^+ content, despite completely different pretreatment conditions before methanol adsorption. In $\text{Ag}_1\text{-NaA}$ zeolites dehydrated at 150 °C the majority of $\text{Ag-CH}_2\text{OH}^+$ radicals are produced on annealing above 160 K and their formation is much better correlated with fast decay of CH_2OH radicals than with a rather monotonous decay of Ag^0 atoms (Fig. 4). In

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