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

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Hydroxyalkyl silver radicals, Ag-CH₂OH⁺ 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 Ag-CH2OH+ 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 yirradiated frozen methanol solutions: A_{iso}(Ag) ca. 13.0 mT. A similar doublet was later reported for glassy ethanol samples.¹⁸ Based on detailed analysis of EPR doublets for CD₃OD and ¹³CH₃OH samples, Symons¹⁸ assigned them to covalent organosilver radicals, Ag-CH₂OH⁺ and Ag-CHCH₃OH⁺ 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, ĊH₂OH or CH₃ĊHOH. Besides alcohol glasses Ag doublets with highly reduced A values were only reported for γ irradiated frozen solutions of $CD_3CN + D_2O$ mixtures, $A_{iso}(Ag) = 17.5 \text{ mT}^4$ and in glassy dimethylformamide, $A_{\rm iso}({\rm Ag}) = 10.0 \,{\rm mT.^6}$

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-condenstion 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 nonequivalent protons. As a carrier of that spectrum the Agacetylene 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, CH₂CO, with silver atoms in adamantane with the use of a rotating cryostat. At 204 K an almost isotropic doublet was observed with A_{iso} $(^{107}Ag^{0}) = 12.0$ mT, and additional splittings due to interactions with two nonequivalent protons $A(H_1) = 1.2 \text{ mT}$, $A(H_2) = 2.0$ mT. It was assigned to a vinyl structure, namely the β -vinyloxysilver radical CH₂=C-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 A1 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 a-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 S2 site 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 y-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 Ag_1 -NaA zeolite with adsorbed CH₃OH irradiated at 77 K and gradually warmed up, showing Ag^0 at sites (A) and (D), CHO radicals (C) and Ag-CH₂OH radicals (E)



Fig. 3 EPR spectra of $Ag_{0,3}$ -NaA/CH₃OH zeolite irradiated at 77 K after annealing to 80 K (*a*) and 160 K (*b*) showing features assigned to CH₃, CH₂OH and Ag-CH₂OH⁺ (E)



Fig. 4 Plot showing the effect of annealing temperature on the relative yield of radicals in Ag_1 -NaA/CH₃OH zeolite irradiated at 77 K: \blacktriangle , total (CH₂OH + CH₃); +, Ag^o; \spadesuit , Ag·CH₂OH⁺

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 AgNO₃ 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 AgNO₃ solution (109 Ag was purchased from Techsnabexport, 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 Xband 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{CH}_2OH and \dot{CH}_3 . (ii) Two doublets with large splittings: $A_{iso}(A) = 51.5$ mT and $A_{iso}(A') = 44.2$ mT which represent silver atoms, $^{109}Ag^{O}$ and $^{107}Ag^{O}$ respectively, stabilized at site A in the zeolite lattice. (iii) Low-intensity doublet C with $A_{iso}(C) = 12.8$ 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 $\dot{C}H_3$ radical ($A_{iso} = 1.7$ mT), which decays at 120 K and the triplet of the much more stable $\dot{C}H_2OH$ radical ($A_{iso} = 1.8$ mT). At 140 K doublets A and A' disappear completely and a new pair of doublets D ($A_{iso} = 57.5$ mT) and D' ($A_{iso} = 49.8$ mT) due to ¹⁰⁹Ag^O and ¹⁰⁷Ag^O 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^O to a new site.

On warming above 140 K a new doublet E with much smaller splitting appears [Fig. 2(b) and 2(c)]: $A_{iso}(E) = 9.3$ mT for $Ag_{0.3}$ -NaA and 9.6 mT for Ag_1 -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 Ag-CH₂OH⁺ 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 Ag₁-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 CH₂OH radicals in the temperature range 160–180 K correlates well with the growth of Ag-CH₂OH⁺ radicals. Similar temperature changes of the EPR signal were observed for Ag_{0.3}-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 Ag₆-NaA the intensity of signal E increases in the temperature range 77-140 K by *ca.* 50%, whereas for Ag₁₂-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^o atoms.

Ag–NaA Zeolites Activated at 400 °C in Oxygen.—Activated zeolites A were loaded with ¹⁰⁹Ag⁺ cations to prepare samples with two silver contents, $1Ag^+$ and $6Ag^+$ per unit cell. In all experiments with zeolites treated at 400 °C deuteriated methanol CD₃OD was used as an adsorbate.

 $^{109}Ag_1$ -NaA zeolite directly after γ -irradiation at 77 K



Fig. 5 EPR spectra of $^{109}Ag_1$ -NaA/CD₃OD 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 $^{109}Ag^0$ sites and doublet E of $^{109}Ag \cdot CD_2OD^+$ adduct



Fig. 6 Plot showing the effect of annealing temperature on the relative yields of ¹⁰⁹Ag⁰ atoms at site G (\bigcirc) and H (\bigcirc) and ¹⁰⁹Ag-CD₂OD⁺ radicals E (\triangle) in ¹⁰⁹Ag₁-NaA zeolite and ¹⁰⁹Ag-CD₂OD⁺ radicals E (+) in ¹⁰⁹Ag₆-NaA zeolite irradiated at 77 K

shows a complex EPR signal with (i) strong singlet at g ca. 2.002 due to \dot{CD}_2OD radical; (ii) four isotropic doublets: F with very narrow line width and $A_{iso}(F) = 74.4$ mT representing free Ag^O atoms and G, H, I with isotropic hfs 46.6, 54.8 and 66.2 mT, respectively, assigned to Ag^O atoms solvated by methanol molecules; and (iii) doublet E ($A_{iso} = 9.7$ mT, $\Delta H_{pp} = 2.6$ mT) of organosilver Ag-CD₂OD⁺ radical (Fig. 5). On temperature annealing doublet G transforms to doublet H in a similar temperature range as Ag^O(A) is transformed to Ag^O(D) in zeolites dehydrated at 150 °C. Silver splittings, $A_{iso}(G) = 52.1$ mT and $A_{iso}(H) = 57.4$ mT do not differ much from hfs values for Ag^O(A) and Ag^O(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 $Ag^{o}(G)$ into $Ag^{o}(H)$, strongly increases on warming above 160 K reaching a maximum at 210 K (Fig. 6). At this temperature the concentration of Ag- CD_2OD^+ 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 $^{109}Ag_6$ -NaA/CD₃OD 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(Ag)/mT	$\Delta H_{pp}/mT$	T/K
Ag ₁ -NaA/150 °C	9.1	1.4	140
	9.6	2.2	180
¹⁰⁹ Ag ₁ -NaA/400 °C	9.7 <i>ª</i>	2.3 <i>ª</i>	100
	10.6 ^{<i>a</i>}	2.3 <i>ª</i>	210
Ag ₆ -NaA/150 °C	10.1	2.2	100
	10.8	2.3	180
$^{109}Ag_{6}$ -NaA/400 °C	$\begin{array}{l} A_{\perp} = 11.6^{a} \\ A_{\parallel} = 7.5^{a} \end{array}$	2.0 <i>ª</i>	100

^a Adsorption of CD₃OD

20% between 210 K and 290 K. The same is true for silver atoms $Ag^{0}(H)$ 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 $^{109}Ag_6$ -NaA zeolite recorded directly after irradiation at 77 K doublet E ($A_{iso} = 9.7 \text{ mT}$) of organosilver radical and the singlet assigned to the radical \dot{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 \dot{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 silvermethanol adducts are formed in zeolites A within a broad range of Ag⁺ content, despite completely different pretreatment conditions before methanol adsorption. In Ag₁-NaA zeolites dehydrated at 150 °C the majority of Ag-CH₂OH⁺ radicals are produced on annealing above 160 K and their formation is much better correlated with fast decay of CH₂OH radicals than with a rather monotonous decay of Ag^o atoms (Fig. 4). In

¹⁰⁹Ag₁-NaA zeolite the concentration of silver atoms does not change at all while the yield of organosilver radical grows rapidly (Fig. 6). This proves directly that CH₂OH radicals are active species which by reaction with Ag⁺ form silver-methanol adducts. It is not clear, however, how contact reaction is possible because the CH₂OH radical is too big to pass through the hexagonal window into the sodalite cage, where Ag⁺ cations are located. To explain this we have to assume that the Ag⁺ cation moves from the S2' to the S2 site in the hexagonal window during annealing of irradiated zeolites, probably because of a new charge distribution in the zeolite framework caused by irradiation. Ag⁺ ions at S2 are accessible for radicals in zeolite α -cages and can react with CH_2OH radicals at a temperature which enables molecular motion or radical mobility. It is concluded that in A zeolites with low silver loadings the formation of organosilver radicals is controlled by diffusion of Ag⁺ cations to S2 sites. Although such a mechanism can also explain the increase of Ag·CH₂OH⁺ concentration on annealing of zeolites with higher Ag⁺ content (6Ag⁺ and 12Ag⁺ per unit cell) it cannot apply to the formation of silvermethanol adducts at 77 K. Before irradiation Ag⁺ cations occupying S2 and S2* sites in the α -cage are solvated by methanol molecules. So, it seems unquestionable that silver paramagnetic adducts are formed by reaction between Ag⁺ and CH_2OH radicals located in the same α -cage. The reactions leading to their formation can be summarized in Scheme 1 which is based on radiation processes in methanol glass.²⁵



Because of the size of the α -cage the local environment of the Ag⁺ cation, especially at S2^{*}, after CH₃OH adsorption can resemble, to some degree, the solvation structure of Ag⁺ cations in methanol glass. So, one can expect the formation of hydroxyalkylsilver radical in both systems at the same temperature. However, in methanol glass these species are not observed below 120 K¹⁸ in contrast to zeolites. This might be due to a greater degree of molecular mobility at 77 K in zeolite cages. As an alternative explanation one can assume that because of geometrical size constraints, in the zeolite cage the Ag⁺ solvation structure is slightly distorted which can be favourable for the formation of organosilver radical at lower temperature. Lower hfs values for Ag•CH₂OH⁺ radicals in A zeolite (A_{iso} ca. 10 mT) than in methanol glass (A_{iso} ca. 12.8 mT¹⁸) indicating lower spin density on silver and a slightly different radical structure support the latter concept.

The Ag-CH₂OH⁺ adduct represents an interesting class of organometallic radicals with one-electron silver-carbon bonds which are also relevant to organometallic syntheses or transition-metal catalysis. We believe that we will be able to stabilize, in zeolite cages, other radicals of this type, also. Recently we reported the formation of Ag-ND2+ radical characterized by an EPR quartet with hfs of 145 mT^{26} which is another example of a silver species with a one-electron bond.

The presence of methanol molecules in α -cages affects distinctly the radiation-induced reactions of silver in zeolite. In contrast to dehydrated Ag-NaA zeolites, divalent Ag²⁺ cations are not stabilized at all in such systems. This might be due to the formation of hydrogen atoms in reaction (1) proposed by

$$e^- + CH_3OH(ad) \longrightarrow CH_3O^- + H$$
 (1)

Nakazato²⁷ for the radiolysis of methanol adsorbed on zeolite. H atoms produced by this mechanism can easily penetrate the sodalite unit through the hexagonal window and reduce Ag²⁺ located inside.

Silver tetramers Ag_3^{2+} and silver hexamers Ag_6^{n+} , which are the most stable radiation products in dehydrated Ag_1-NaA^{16} and Ag₆-NaA¹⁵ zeolites are not formed in the presence of CH₃OH molecules, although both clusters are trapped inside the β -cage. It proves that migration of Ag^o atoms from α - to β -cage plays an important role in silver agglomeration. This process is blocked or greatly inhibited by formation of silvermethanol adducts.

Greater stability of Ag-CH₂OH⁺ radicals in zeolites activated at 400 °C might be due to the conversion of zeolite lattice sites at elevated temperature. However, more complete studies are needed to prove this hypothesis, which may throw some more light on the mechanism of heterogenous transitionmetal catalysis.

Conclusion

Silver atoms, methanol radicals and organosilver adducts stabilized at low temperature in Ag-NaA zeolites have been studied by EPR spectroscopy. It was proved that Ag CH₂OH⁺ adducts are formed by reaction of Ag⁺ ions with CH₂OH radicals. In zeolites with high silver content the reaction occurs in α -cages at 77 K and involves the reorganization of an Ag⁺ $-(CH_3OH)_n$ complex as a consequence of proton transfer. For low silver loadings Ag-CH₂OH⁺ radicals are produced at higher temperature (above 140 K) because reactants are separated and the formation of a reactive complex requires a diffusion of Ag^+ cations and some mobility of CH_2OH radicals.

The presence of methanol in zeolite cages strongly affects silver agglomeration processes as the result of competition between CH₂OH radicals and Ag^o atoms for reaction with Ag⁺ cations.

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