**EPR and ESEEM study of silver clusters in ZK-4 molecular sieves**

**Abstract** Silver clusters generated by γ-irradiation in ZK-4 zeolites – isostructural with Linde type A (LTA) zeolite, have been studied by electron paramagnetic resonance (EPR) spectroscopy. It was shown that even a small decrease of cation capacity resulting from a lower Si/Al ratio in the framework affects distinctly silver agglomeration. In dehydrated ZK-4 with Si/Al = 1.2 and 2.4 only silver dimers are stabilized, whereas in Linde 4A silver hexamers were trapped. In ZK-4 exposed to H₂O and CH₃OH, silver tetramers Ag₄⁺ efficiently are formed. The results of electron spin echo envelope modulation (ESEEM) showed that the adsorbate molecules are in close vicinity to the clusters. It was postulated that in zeolites with low cation capacity the adsorbate molecules make difficult Ag⁺ migration promoting the reactions with Ag⁺ cations located in the same sodalite cage.

**Key words** ZK-4 • EPR • ESEEM • silver clusters

**Introduction**

The size-dependent properties of metal nanoclusters are of considerable interest with respect to fundamental knowledge and possible applications in catalysis and nanotechnology. The unique cluster properties originate from size-dependent distribution of electron energy levels and quantum-size effects. For studying the nuclearity of paramagnetic metal clusters, the electron paramagnetic resonance (EPR) spectroscopy is a major experimental technique.

Silver exchanged Na-A zeolites with high silver loadings reduced chemically or radiolytically, show unique ability to stabilize paramagnetic silver hexamer – Ag₆⁺ where n = 1, 3, 5 for paramagnetic species [2, 11]. It is postulated that hexameric silver clusters are trapped inside sodalite cages of zeolite A. For smaller silver concentration (up to 1Ag⁺ per unit cell), only silver trimers Ag₃⁺ were recorded [14]. Silver hexamers were also recorded in irradiated sodalite, but with significantly different spin Hamiltonian parameters [5]. Based on g value, the assignment of Ag₆⁺ is postulated, whereas the hexamer charge in zeolite A should be smaller (1 or 3). It should be noticed that silver hexamers have been never observed in zeolite X or Y, although faujasite structure is also composed of sodalite cages.
In γ-irradiated AgCs-rho zeolite the subsequent formation of Ag⁺, Ag²⁺, Ag³⁺ and Ag⁴⁺ was observed in thermally annealed samples [7]. Tetrameric cluster is stable above room temperature. After NH₃ adsorption, silver tetramer coordinates six ammonia ligands, two in the first coordination sphere and four in the second one, forming a multicore complex Ag⁴⁺(NH₃)₆(NH₃)₄⁺ [12].

Usually, it is possible from the analysis of EPR spectra to deduce the structure of paramagnetic species. However, the resolution of EPR spectra, in general, is too low to record the spectral features from superhyperfine interactions derived from magnetic nuclei of adsorbate molecules interacting with paramagnetic center. For studying such superhyperfine interaction in polycrystalline media electron spin echo envelope modulation (ESEEM) spectroscopy is best suited. Till now, there are only a few papers available on the interaction of silver clusters with molecular adsorbates in zeolites by the ESEEM method. Based on ESEEM results, it was found that in AgNa-A zeolite silver hexamers, Ag₆⁺ are only stabilized in those sodalite cages which are surrounded by α-cages not containing H₂O molecules. In contrast, Ag₃⁺ can be stabilized in β-cage if H₂O molecules are present in close vicinity. In hydrated AgNa-A zeolite trimeric species directly interact with water molecules trapped in the same β-cage [8].

In aluminasilicophosphate lattice of AgH-SAPO-42, which is isostructural with zeolite A, in dehydrated samples only dimmers Ag⁺ and trimers Ag⁺²⁺ are formed after γ-irradiation. It is due to lower cation capacity in SAPO’s lattice in comparison to zeolite A. In the presence of methanol, silver hydroxydimethyl radicals are the major paramagnetic products of radiolysis in both A and SAPO frameworks. They are stabilized in α-cages by interaction with methanol molecules [10].

In hydrated and dehydrated AgH-SAPO-5 and AgH-SAPO-11 molecular sieves, Ag⁶⁺ atoms produced by γ-irradiation do not form stable cationic silver clusters. However, after exposure to methanol prior to irradiation, silver dimers in SAPO-11 and silver dimers and trimers in SAPO-5 are efficiently formed, as was proved by EPR measurements [4]. Ag⁺ dimer is located in a 6-ring channel in both frameworks and is stabilized by the interaction with three methanol molecules. Besides, silver clusters and silver hydroxymethyl radicals are also produced. ESEEM results indicate that these radicals are located in 12-ring (SAPO-5) and 10-ring (SAPO-11) channels and are coordinated by two nonequivalent methanol molecules.

The aluminosilicate framework which is isotypic with Linde type A (LTA) zeolite, but with Si/Al > 1 is called ZK-4. The preliminary EPR results showed that cationic silver clusters are not stabilized in dehydrated ZK-4 zeolites even for the framework with Si/Al = 1.2 so, only slightly higher than 1 [9]. In contrast, ZK-4 samples exposed to water or methanol stabilized efficiently tetrameric silver clusters. It proves that although geometrical constraints play a crucial role with respect to the nuclearity of stabilized clusters, even small changes in the distribution of framework negative charges are able to affect the silver agglomeration process to a great extent.

For better understanding of the role of sodium cations and adsorbate molecules on silver clustering process, we studied ZK-4 zeolites with various Si/Al ratio exposed to water and methanol. The nuclearity of silver clusters have been examined by the EPR method and the interaction of silver clusters with adsorbate molecules by ESEEM technique.

**Experimental**

Na-ZK-4 zeolites with different Si/Al ratios (1.2 and 2.4) were synthesized by a modified Kerr’s method [3]. As the sources of silica and alumina, a colloidal silica sol (Ludox HS40, 40% wt. SiO₂, Dupont) and sodium aluminate (Aldrich) were used, respectively. Tetramethylammonium hydroxide TMAOH (25% TMAOH, Aldrich) was added to the reaction solution as a templating agent. The reaction mixture was placed in a Teflon bottle (or Teflon cap fitted into stainless steel pressure vessel) and heated in an oven at 373 K and autogenous pressure for 2 days. The solid product of synthesis, Na-ZK-4 with TMA template, was filtered and washed with deionized water. After drying at room temperature, it was calcined in O₂ at 813 K for 3 h. The purity and crystallinity of the product were monitored by powder X-ray diffraction (XRD). Si/Al ratios were calculated based on the results of inductive couple plasma (ICP) analysis of calcined samples. Ag⁺ cations were loaded into zeolites by cation exchange with AgNO₃ solution at room temperature. Silver content in Ag⁺ exchanged samples was obtained by ICP as 5Ag⁺ and 4Ag⁺ per unit cell in Na-ZK-4 with Si/Al equal to 1.2 and 2.4, respectively.

After drying, the zeolite samples were loaded into suprasil EPR tubes equipped with stopcocks. Hydrated samples were degassed on a vacuum line at room temperature. Dehydrated samples were heated at 150°C for 2 h and then overnight at 230°C under 600 torr of dry O₂ to reoxidise any reduced silver cations. After removal of oxygen, some samples were exposed to water or methanol vapour at room temperature. Samples selected for ESEEM experiments were exposed to deuterated D₂O or CD₃OH and CH₃OD vapours (Cambridge Isotope Laboratories).

All sample were γ-irradiated at 77 K in a ⁶⁰Co source with a dose of 4 kGy. EPR spectra were recorded with a Bruker ESP-300E X-band spectrometer at various temperatures in the range 110–300 K by using variable-temperature Bruker unit. ESEEM signals were measured with a Bruker ESP-380 FT pulse spectrometer in the temperature range 4.5–6 K using a helium flow cryostat. For three-pulse experiments, a pulse sequence of 90°-τ-90°-τ-90° was employed and τ was swept. Simulations of the experimental data were performed using the analytical expressions derived by Dikanov et al. [1]. The best fits were found by varying the following parameters: (i) the number of interacting nuclei N; (ii) the interaction distance R and (iii) the isotropic hyperfine interaction coupling Aiso, until the sum of squared residuals was minimized.
Results

EPR results

Dehydrated samples of AgNa-ZK-4 zeolites with Si/Al = 1.2 and 2.4 after γ-irradiation at 77 K show the EPR spectra of silver atoms Ag⁰ and divalent silver Ag²⁺. On thermal annealing to room temperature Ag⁰ doublets decay completely in both samples and are replaced by isotropic triplets \( A_{\text{iso}} = 31.6 \text{ mT} \) and \( g_{\text{iso}} = 1.991 \) of Ag²⁺.

Both Ag²⁺ and Ag⁰ species are also the main paramagnetic products of radiolysis at 77 K of AgNa-ZK-4 zeolites exposed to water vapour. However, in this case, thermal treatment leads to the formation of silver tetramers Ag⁴⁺ (\( A_{\text{iso}} = 13.9 \text{ mT} \) and \( g_{\text{iso}} = 1.970 \)) for both Si/Al ratios (Fig. 1). It is worthy of noticing that the temperature of Ag⁴⁺ formation depends on the Si/Al ratio. In zeolite with Si/Al = 2.4 the Ag⁴⁺ pentet is easily observed below 135 K, but it decays completely above 230 K. In zeolite with Si/Al = 1.2 the Ag⁴⁺ signal appears only above 140 K and starts decaying above 250 K.

In Ag-ZK-4 samples with methanol vapour adsorbed prior to irradiation, two doublets representing paramagnetic silver species are recorded at low temperature (Fig. 2). The first one with large hyperfine splitting is due to Ag⁰ atoms. The EPR parameters depend only slightly on the Si/Al ratio and for zeolites with Si/Al = 1.2 and 1.4 are \( A_{\text{iso}} = 54.6 \text{ mT} \), \( g_{\text{iso}} = 1.989 \) and \( A_{\text{iso}} = 57.0 \text{ mT} \), \( g_{\text{iso}} = 1.987 \), respectively. The splittings of the second doublet are much smaller: \( A_{\text{iso}} = 12.2 \text{ mT} \) with \( g_{\text{iso}} = 2.003 \) and \( A_{\text{iso}} = 14.8 \text{ mT} \) with \( g_{\text{iso}} = 2.003 \) for Si/Al = 1.2 and 2.4, respectively. Similar signals were observed earlier in different molecular sieves and were assigned to silver hydroxymethyl radicals Ag –CH₂OH⁺ having a single \( \sigma \) bond between silver and carbon [6, 13, 15]. The experiments with protonated and deuterated samples proved that spin density is nearly in 100% located on silver and carbon nuclei.

In both types of Ag-ZK-4 zeolites, the signal of silver hydroxymethyl radicals starts decaying above 180 K and at 210 K is not observed at all. In the same temperature range, a new signal \( Q \) of five lines is gaining its intensity. It was assigned to Ag⁴⁺ cluster with EPR parameters \( A_{\text{iso}} = 12.2 \text{ mT} \) with \( g_{\text{iso}} = 1.976 \) and \( A_{\text{iso}} = 13.5 \text{ mT} \) with \( g_{\text{iso}} = 1.976 \) for Si/Al = 1.2 and 2.4, respectively, slightly smaller than in the Ag-ZK-4/H₂O samples. Ag⁴⁺ signals disappear quickly at room temperature in both types of zeolite samples.

Fig. 1. EPR spectra of AgNa-ZK-4 zeolites with Si/Al = 1.2 and 2.4 exposed to D₂O.

Fig. 2. EPR spectra of AgNa-ZK-4 zeolites with Si/Al = 1.2 and 2.4 exposed to CD₃OH.
ESEEM results

For ESEEM study, we used the samples of Ag-ZK-4 exposed to deuterated adsorbates, D$_2$O and methanol with deuterated methyl group CD$_3$OH, and hydroxyl group CH$_3$OD. The pulse experiments were carried out after sample annealing at 200 K, setting magnetic field at the fourth line of Ag$_4^{3+}$ quintet. Figure 3 shows the deuterium modulation due to the interaction between Ag$_4^{3+}$ cluster and D$_2$O in Ag-ZK-4/D$_2$O zeolite. The dashed lines represent the best simulation of ESEEM spectra. The best fits to experimental modulation patterns were obtained assuming the interaction with two deuterons at a distance of 0.265 nm for zeolite with Si/Al = 1.2 and with four more distant deuterons for zeolite with Si/Al = 2.4.

Similar results were obtained for Ag-ZK-4 zeolites with adsorbed methanol (Fig. 4). For the framework with Si/Al = 1.2, Ag$_4^{3+}$ interacts with one methanol molecule and with two methanol molecules in zeolite with Si/Al = 2.4. The parameters of the best simulations for the interaction of Ag$_4^{3+}$ with D$_2$O and methanol deuterated in methyl and hydroxyl groups are collected in Table 1. A comparison of interaction distances for CD$_3$OH and CH$_3$OD clearly indicates that methanol molecules are pointed towards Ag$_4^{3+}$ with their molecular dipoles.

Table 1. The parameters of the best simulations for the interaction of Ag$_4^{3+}$ with D$_2$O and methanol deuterated in methyl and hydroxyl group

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<tr>
<td>D$_2$O</td>
<td>Si/Al = 1.2</td>
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<td></td>
<td>Si/Al = 1.4</td>
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<td>Si/Al = 1.4</td>
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Discussion

ZK-4 zeolite belongs to the $Pm-3m$ space group with $a = b = c = 1.1919$ nm. Alumina and silica tetrahedra are bonded together to form truncated octahedra called sodalite units or $\beta$-cages, with a diameter of 0.66 nm. Four rings of the neighbouring sodalite units are connected by oxygen bridges forming bigger units of...
under such circumstances, the smaller be due to the larger void space in the lattices with larger molecular sieves with similar Ag+ loading. This might fully developed at 140 K. At that temperature, long-distance change of cation positions in order to balance atoms, does not seem to be possible. However, a short-distance change of cation positions in order to balance more efficiently lattice negative charge in the vicinity of Ag0 atom formed radiolytically seems quite probable. So, we postulate that Ag4+ clusters in hydrated ZK-4 zeolites with Si/Al = 1.2 and 2.4 are formed in the β-cages originally loading with four Ag+. When one Ag+ is reduced by radiolysis at 77 K the short-distance rearrangement of three remaining cations leads to the formation of Ag3+ cluster. It seems that silver coalescence process is preferential when the zeolite cages are loaded with Na+ cations or H2O molecules. If the hexagonal windows connecting β- and α-cages are not blocked, then silver atoms are able to escape to bigger cages and Ag4+ clusters are not formed.

ESEEM results show clearly that water molecules are in close vicinity of radiolytically formed silver tetramers indicating that they play an important role in cluster formation. In ZK-4 zeolite with higher cation capacity (Si/Al = 1.2), silver tetramer interacts with one water molecule. The distance between unpaired electron and deuterium nuclei suggests that Ag3+ cluster and water molecule are located in the same cage. Possibly, deuterons are placed in the hexagonal window plane with oxygen inside β-cage pointed into tetramer. Other hexagonal windows can be blocked by more distant D2O molecules non-interacting with Ag4+. At 250 K, the trapping site of Ag3+ becomes ineffective because thermal energy facilitates the molecular movements and Ag4+ decays.

In contrast, silver tetramers in ZK-4 with Si/Al = 2.4 interact with two water molecules. The interacting distances indicate that water molecules are more distant, possibly with oxygen in the hexagonal window and deuterons in α-cage. We speculate that the interaction with second water molecule is due to the smaller amount of Na+ cations in sodalite cages. Then, more water ligands are coordinated by cationic silver species. Thereby, other water ligands are less coordinated and the coordination sphere is expanded. On the other hand, a lower amount of cations makes the cages more open what facilitates Ag4+ migration. Ag4+ clusters are more stable and start decay at lower temperature in ZK-4 with Si/Al = 2.4.

Silver tetramers are also stabilized in ZK-4 zeolites exposed to methanol vapour. However, they are formed at much higher annealing temperature. At low temperatures Ag-CH3OH+ radicals are efficiently formed reducing substantially the amount of silver species that can participate in silver agglomeration. Ag3+ pentet is appearing in the EPR spectrum only above 200 K. The build-up of pentet is correlated with the decay of Ag-CH3OH+ doublyt clearly indicating that agglomeration can proceed only if silver is released from silver hydroxymethyl radicals.

The ESEEM results show that Ag4+ in the zeolite with Si/Al = 1.2 interacts with one methanol molecule while with two molecules for Si/Al = 2.4. The interacting distances to hydroxyl deuterons of CH3OD are longer than distances for D2O molecules. Based on that, we postulate that Ag3+ cluster trapped in β-cage interacts with one or two methanol molecules located in α-cage and directed with the molecular dipoles into the silver tetramer through the hexagonal window. In the presence of methanol, Ag4+ clusters are more stable and start decaying only above 280 K. It might be due to the more efficient blocking of lattice windows by more spacious methanol molecules.

Fig. 5. The framework of Linde type A and ZK-4 zeolites. 26-hedra composed of eight, six and four rings, called α-cages or supercages with a diameter of 1.14 nm. The communication between α- and β-cages is possible only through hexagonal windows with a diameter of 0.23 nm (Fig. 5). The supercages are connected by octagonal windows with a diameter of 0.41 nm.

The cation exchange capacity of zeolite directly depends on the Si/Al ratio. In the LTA zeolite with Si/Al = 1, 12 monovalent cations balance framework negative charges in unit cell. In dehydrated samples of AgNa-LTA zeolite, Ag6+ clusters are formed in a very broad range of silver loadings, from 2Ag+ to 12Ag+ cations per unit cell [11].

The ICP data show that in Ag-ZK-4 fully exchanged with Ag+ the silver loading is 5Ag+ and 4Ag+ per unit cell for the samples with Si/Al = 1.2 and 2.4, respectively. Despite of that, in dehydrated AgNa-ZK-4 silver hexamers have never been observed for any Ag+ loadings. In dehydrated samples with Si/Al = 1.2 silver trimers and tetramers appear, while for the framework with Si/Al = 2.4 only dimers are recorded. The above clearly shows that even a small decrease of zeolite cation capacity strongly affects silver clustering in isosstructural molecular sieves with similar Ag+ loading. This might be due to the larger void space in the lattices with larger Si/Al ratio. Under such circumstances, the smaller amount of sodium cocations blocking windows connecting cages and channels makes easier the migration of Ag÷ out of sodalite cages to α-cages or to the surface of crystallites where metallic particles silent for EPR are formed [10].

This conclusion is consistent with the observation of cationic silver clusters of higher nuclearity in hydrated ZK-4 zeolites. For both Si/Al ratios, the intense quintets of Ag5+ clusters were recorded (Fig. 1). Like Na+ cocations water molecules facilitate the agglomeration process of silver species located in the same cage by blocking windows of cages. The EPR lines of Ag5+ are fully developed at 140 K. At that temperature, long-distance migration of silver species, even neutral Ag0 atoms, does not seem to be possible. However, a short-distance change of cation positions in order to balance more efficiently lattice negative charge in the vicinity of Ag0 atom formed radiolytically seems quite probable. So, we postulate that Ag4+ clusters in hydrated ZK-4 zeolites with Si/Al = 1.2 and 2.4 are formed in the β-cages originally loading with four Ag+. When one Ag+ is reduced by radiolysis at 77 K the short-distance rearrangement of three remaining cations leads to the formation of Ag3+ cluster. It seems that silver coalescence process is preferential when the zeolite cages are loaded with Na+ cations or H2O molecules. If the hexagonal windows connecting β- and α-cages are not blocked, then silver atoms are able to escape to bigger cages and Ag4+ clusters are not formed.
The hyperfine splittings of Ag$^{3+}$ in ZK-4/CH$_3$OH differ slightly for samples with different Si/Al ratio. However, additional experiments are necessary to speculate on the effect of cocation loadings on the cluster structure which determines the hyperfine parameters.

That effect was clearly seen for silver hydroxymethyl radicals stabilized in isostructural zeolites with different cation capacity. For example, $A_{CH_2OH}^{\text{iso}}$(Ag) for Ag•CH$_2$OH$^+$ in zeolite 4A (Si/Al = 1) is 10.6 mT [6, 13, 15] whereas in isostructural SAPO-42 molecular sieve (Si/Al = 5) increases to 13.1 mT. This suggests that sterical constrains can affect the radical structure and subsequently the spin density on silver nucleus which is reflected by the value of hyperfine splitting. To prove that assumption we plan to calculate hyperfine splittings for Ag$^{3+}$ cluster and Ag•CH$_2$OH$^+$ radical stabilized in the traps of different dimensions using density-functional theory (DFT).

Conclusions

In contrast to LTA zeolite, which preferentially stabilizes silver hexamers in sodalite cages, the isostructural zeolites ZK-4 with lower cation loadings (Si/Al = 1.2 and 2.4) trapped only clusters with lower nuclearity – dimers in dehydrated samples and tetramers in samples exposed to water and methanol. Those results clearly show that for effective trapping of silver clusters the presence of suitable framework cages is not sufficient. The crucial role plays also total cation capacity and presence of adsorbates which are able to control migration of Ag$^0$ atoms out of sodalite cages. The ESEEM results proved that water and methanol molecules are in close vicinity of silver clusters in ZK-4 zeolites blocking the migration routes. It was also found that hyperfine splittings of silver clusters depend on total cation capacity. It was speculated that small changes of cluster structure constrained by zeolite lattice and neighbouring cocations might affect the distribution of spin density.

References