

ESR AND OPTICAL STUDIES OF CATIONIC SILVER CLUSTERS IN ZEOLITE rho

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Nanophase chemistry develops rapidly during last years. The understanding of quantum effects in small dimensions is essential for designing new materials for electronics and optics.

Small metal clusters of a few atoms are thermodynamically unstable and at room temperature they can be only characterized by time-resolved methods [1]. By spectroscopic methods small clusters can be studied only under cryogenic conditions.

Molecular sieves are known as the matrices which are able to stabilize cationic metal clusters at room temperature. In AgNa-A zeolite γ -irradiated at room temperature the ESR spectrum of silver hexamer, Ag_6^{2+} has been observed for several days [2,3]. More recently we found that zeolite AgCs-rho showed unique ability for stabilization of tetrameric silver clusters [4].

The main goal of the studies presented in this article was to correlate the ESR and optical data for small silver clusters in zeolites. To achieve this goal clusters have to be relatively stable at room temperature because diffuse reflectance measurements cannot be carried out at low temperature. For this reason we selected zeolite rho, which in the dehydrated form is able to stabilize Ag_4^{3+} clusters at

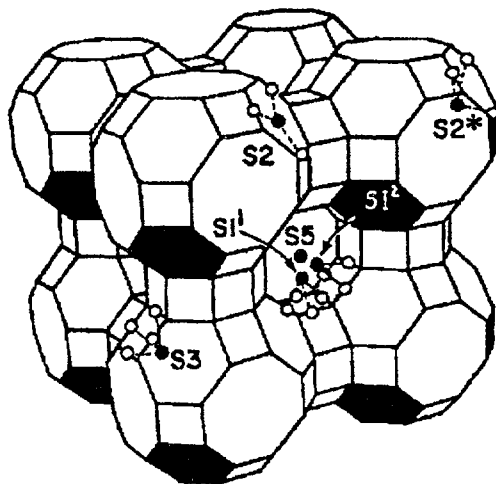


Fig.1. The framework structure of zeolite rho. The preferential locations of exchangeable cations are denoted S.

room temperature for months. The secondary structure of zeolite rho consists of α -cages with a diameter of 1.16 nm joint together through a double eight-member ring (Fig.1). Exchangeable cations preferentially are located inside octagonal prisms and in the vicinity of hexagonal windows.

Silver cations were loaded into NaCs-rho zeolite by cation exchange with AgNO_3 solution at room temperature. After drying zeolite samples were placed into ESR Spectrosil tubings and then attached to a vacuum line. After degassing at room temperature or dehydration at gradually increased temperature till 130°C the samples were sealed off

and irradiated at room temperature for 5 h using an X-ray tube operating at 50 kV and 100 mA. The ESR spectra were measured at room temperature with a Bruker ESP 300 X-band spectrometer. Diffuse reflectance measurements were carried out for the same samples with a home-built optical system using a Spectra Pro-150 monochromator, halogen and deuterium lamps for visible and UV region and a Si photodiode arrayed device.

Synthesis of the zeolite rho requires the presence of Cs^+ in the reaction gel. It was found that bulky Cs^+ cations play an important role in Ag_4^{3+} stabilization by blocking entrances to the octagonal prisms where silver tetramers are located [4]. In Fig.2 the ESR spectra of dehydrated and hydrated AgCs-rho zeolites γ -irradiated at room temperature

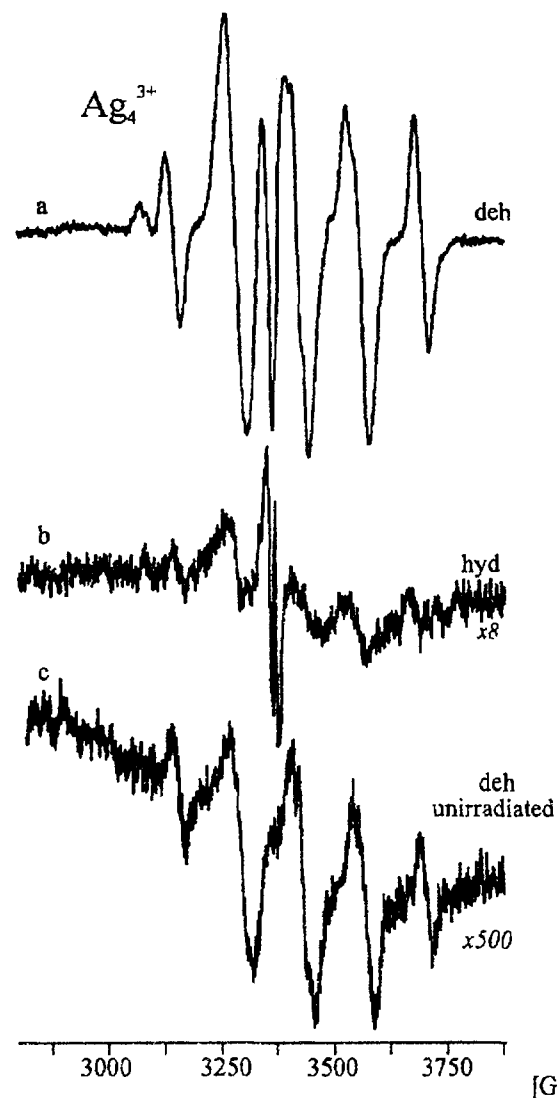


Fig.2. ESR spectra at room temperature of Ag_6Cs -rho zeolite: a) dehydrated form γ -irradiated at room temperature, b) hydrated form γ -irradiated at room temperature, c) dehydrated form non-irradiated.



are shown. The dehydrated sample shows an intense isotropic pentet with hyperfine splitting $A_{iso}=139G$ and $g_{iso}=1.973$ of Ag_4^{3+} clusters and a single narrow line with $g_0=2.010$ assigned to radiation induced paramagnetic centers in the zeolite framework (Fig.2a). In hydrated $AgCs$ -rho the lines of Ag_4^{3+} are barely visible and the dominant ESR signal is a single line representing framework paramagnetic centers (Fig.2b). The results indicate clearly that the silver tetrameric clusters cannot be effectively stabilized at room temperature in $AgCs$ -rho zeolites when water molecules are inside the zeolite cages. In contrast, in the dehydrated samples Ag_4^{3+} signals do not show visible changes for months at room temperature.

In Fig.3 the diffuse reflectance spectra of $AgCs$ -rho samples in dehydrated and hydrated forms are shown. The Kubelka-Munk function was used for the transformation of diffuse reflectivity into absorption coefficient. The spectra are presented in such a way as to make visible the spectral changes arising after γ -irradiation. For dehydrated $AgCs$ -rho zeolite the only radiation effect observed in the diffuse reflectance spectrum is an increase of the intensity of the 282 nm absorption. So, it would seem obvious that the absorption at 282 nm represents the paramagnetic Ag_4^{3+} cluster because the dehydrated sample shows a strong ESR pentet with $A_{iso}=139 G$ at room temperature. Then however,

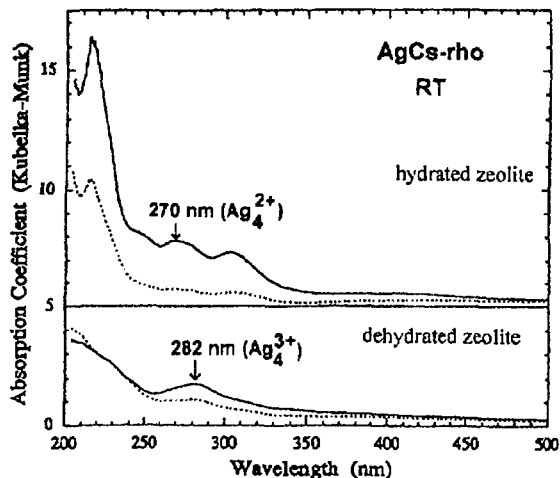


Fig.3. Diffuse reflectance spectra of Ag_6Cs -rho zeolite in a) dehydrated and b) hydrated form. Spectra of non-irradiated samples - dashed lines; spectra of γ -irradiated samples - solid lines.

one could expect, for full correlation between magnetic and optical data, the presence of the ESR pentet also in the unirradiated sample. Till now, ESR was always silent for any type of silver zeolite, in hydrated or dehydrated form, which was not irradiated or not reduced chemically. However, when we very carefully measured the dehydrated $AgCs$ -rho sample by accumulating the ESR spectra for 36 times we were able to record a weak ESR pentet with the hyperfine splitting, the same as for irradiated sample (Fig.2c). According to our best knowledge the spectrum presented in Fig.2c is the first ESR spectrum ever recorded of paramagnetic silver clusters formed during dehydration of zeolite.

This result encouraged us to assign the 282 nm band to the Ag_4^{3+} cluster proving at the same time that Ag_4^{3+} can be produced not only by radiolytic reduction but also by the autoreduction process during zeolite dehydration. It should be noticed however, that concentration of paramagnetic clusters in dehydrated only rho zeolite is much less than in samples exposed to γ -radiation.

In hydrated zeolite two peaks with maxima at 270 and 310 nm appear after irradiation. It was postulated, basing on pulse radiolysis studies of 0.1 $AgNO_3$ water solution, that in a microsecond time scale diamagnetic Ag_4^{2+} clusters, characterized by a strong absorption band with a maximum at 275 nm were formed preferentially [1]. It seems reasonable to assume that also in hydrated zeolites silver cations and atoms are solvated by water molecules in a similar way as in bulk solution, so the agglomeration reactions should proceed similarly in both systems. Thus, we assigned the absorption band at 270 nm to the silver divalent tetramer. The optical spectrum with two maxima 270 and 310 nm corresponds to the ESR spectrum shown in Fig.2b. The ESR pentet is very weak but without any doubts represents Ag_4^{3+} clusters whose concentration is lower by about a factor of 20 than in the irradiated dehydrated zeolite rho, but much higher than in the unirradiated dehydrated sample. The optical band associated with Ag_4^{2+} and Ag_4^{3+} clusters, 270 and 282 nm respectively, are very close, so for low Ag_4^{3+} concentration in hydrated zeolites the 282 nm band is not revealed. The absorption band at 310 nm in hydrated zeolite can also represent only diamagnetic silver cluster. Tentatively we assigned that band to the Ag_3^+ cluster.

Earlier ESR results show that Ag_4^{3+} clusters are formed in both, dehydrated and hydrated zeolite after γ -irradiation at 77 K and subsequent annealing at gradually increased temperature [4]. Present studies reveal that Ag_4^{3+} are stable at room temperature only in dehydrated zeolites whereas in hydrated samples mostly diamagnetic Ag_4^{2+} clusters are trapped at room temperature. The question arises whether the mechanisms of agglomeration are different in two zeolite forms, or the Ag_4^{3+} cluster in hydrated zeolite is transformed into Ag_4^{2+} by the reaction with water molecules. Although the results of combine magnetic and optical studies are unable to answer this question univocally, they suggest that rather the later process is responsible for Ag_4^{2+} formation. It was postulated that Ag_4^{3+} clusters are located inside octagonal prisms of zeolite structure [4,5], where they are easily accessible for water molecules through a wide octagonal window with a diameter of about 0.36 nm. At room temperature when adsorbate molecules become mobile the contact interaction between Ag_4^{3+} and H_2O with subsequent electron transfer seems possible. If our hypothesis is correct then it means that the Ag_2^+ dimerization reaction in which diamagnetic Ag_4^{2+} clusters are formed, as proposed by Ershov et al. [1], does not proceed effectively inside zeolite channels.

References

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ESR STUDY OF SOLID PEPTIDES

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Understanding of the radiation damage of a complex biological system, like protein, requires a detailed knowledge about the final products and radical reaction mechanisms in model compounds in the aqueous liquid phase as well as in the solid state. This is due to the known fact that the state of proteins in vivo lies very often between the solution and the solid state.

The gamma irradiated at 77 K polycrystalline methionine-containing peptides: type X-Met and Met-X (X - aliphatic aminoacid) were evacuated and irradiated with a dose of ~ 5 kGy.

The radicals produced by irradiation were studied over the temperature range 77-293 K by electron spin resonance spectroscopy. The ESR experiments were performed using a Bruker ESP-300 spectrometer with a variable temperature cavity.

The ESR spectra were analysed by a computer simulation (using EPR Software provided by D. Dulling from NIEHS LMB National Institute of Health, USA).

Carbon dioxide analysis was performed by a gas chromatography technique (Perkin Elmer 8700), and analysis of ammonia by using an ion-selective ammonium electrode (Cole-Parmer).

The aim of this study was the identification of various radical intermediates and final products formed on gamma radiolysis of the peptides with varying numbers of methionine residue and their varying location with respect to the terminal functions (Chart 1).

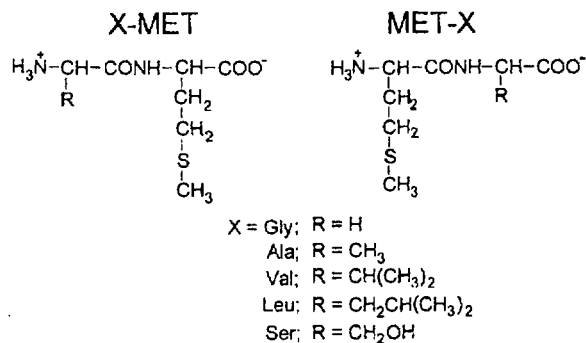


Chart 1.

The major radical observed at 77 K in all peptides is an anion radical formed by the addition of an electron to the carbonyl group of the peptide bond (singlet with $g=2.0068$ and $\Delta H=8G$). Deamination and decarboxylation radicals were detected over the temperature range 150-250 K. H-abstraction radicals in the side chain of methionine residue α (alkylthioalkyl) radicals were observed for

peptides with N-terminal methionine at the same temperature (Figs. 1 and 2), [1-3].

The efficiency of decarboxylation is 2-3 fold higher at X-Met peptides as compared with Met-X

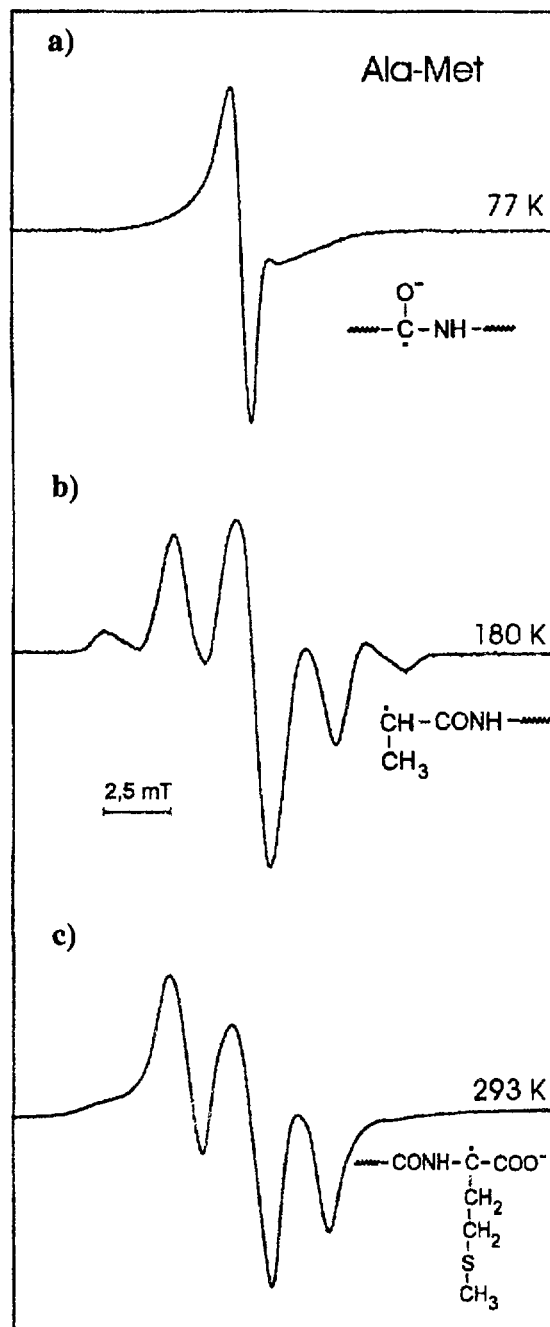


Fig.1. ESR spectra of alanyl-methionine irradiated at 77 K: a) recorded at 77 K - singlet of anion radical; b) 180 K quintet - deamination radical of the alanine residue; c) 293 K triplet - H-abstraction radical of the methionine residue.